

Rapid Synthesis of Cellulose Esters by Transesterification of Cellulose with Vinyl Esters under the Catalysis of NaOH or KOH in DMSO

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S Supporting Information

ABSTRACT: Traditionally, a long reaction time was required in the synthesis of cellulose esters (CEs). In this work, dimethyl sulfoxide (DMSO)/aqueous NaOH or KOH was introduced as an efficient reaction system for rapidly synthesizing CEs by transesterification. Surprisingly, cellulose could react with vinyl acetate, vinyl propionate, and vinyl butyrate and synthesized cellulose acetate, cellulose propionate, and cellulose butyrate with a high degree of substitution (2.14–2.34) in 5 min, which was in sharp contrast to hours of existing methods. The effects of solvents, catalysts, and esterifying agents on the synthesis of CEs were comparatively investigated to better understand this method. The structure and thermal properties of obtained CEs were characterized by Fourier transform infrared (FTIR) and ¹H and ¹³C nuclear magnetic resonance (NMR) spectroscopies and differential scanning calorimetry. Results from these spectra confirmed the successful synthesis of these CEs. Furthermore, these CEs showed similar thermal properties compared to products obtained from other methods.

KEYWORDS: Cellulose, vinyl esters, transesterification

INTRODUCTION

Cellulose, the most abundant, renewable, and biodegradable natural polymer in the world, is considered as an important alternative resource to replace petrochemical resources for obtaining biofuels, chemicals, and materials.¹ Materials from cellulose and cellulose derivatives are being developed over a broad range of applications for their environmental benefits and good biocompatibility.^{2,3} Because cellulose does not melt and dissolve in common solvents, the processing of cellulose is difficult, and thus, the development and practical applications of cellulose are subjected to severe limitations. However, cellulose derivatives with tailored properties can be obtained by introducing different substituent groups. Chemical modification, especially esterification, provides an important way for the wide use of cellulose.

Thus far, varieties of cellulose esters (CEs), such as inorganic CEs, organic CEs, and cellulose mixed esters, have been successfully synthesized.⁴ Besides cellulose nitrate and cellulose xanthate, CEs, such as cellulose acetate (CA), cellulose acetate propionate (CAP), and cellulose acetate butyrate (CAB), are the most commonly used cellulose derivatives and have been put into commercial process for decades. These CEs have been extensively used in membranes, fibers, plastics, and filters and possess a crucial position in photosensitive film, separation membrane, cigarette filter, and coating industry.⁵

CEs are usually synthesized by the esterification of cellulose with corresponding acids, acid anhydrides, or acyl chloride under the aid of a catalyst.⁴ During the practical production, CEs are usually synthesized under heterogeneous conditions using sulfuric acid as a catalyst.⁶ Because the glycosidic oxygen bond is subject to acidic hydrolysis during the production of CEs, the degradation of cellulose is always severe and only cotton fibers

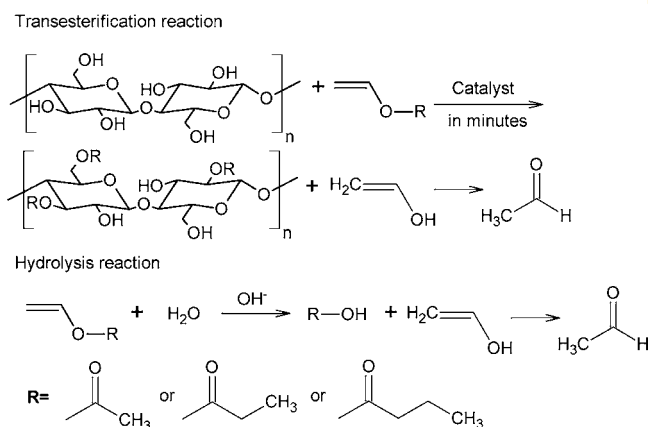


Figure 1. Transesterification and hydrolysis reaction of vinyl esters under the catalysis of NaOH or KOH in DMSO.

and high-purity dissolving pulp can be used in the manufacture of CEs. Furthermore, because of the high crystalline structure and low reactivity of cellulose, the preparation of CEs is time-consuming and laborious.

Transesterification is an important method for producing polyethylene terephthalate and biodiesel.^{7,8} It was reported that, during the production of biodiesel, an approximate conversion of 80% could be achieved within 1 min.⁹ Transesterification is also

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used in the synthesis of polysaccharide esters. Rooney reported that starch could react with methyl palmitate to produce starch palmitate using potassium methoxide as a catalyst in dimethyl sulfoxide (DMSO) for 6 h.¹⁰ Protease and lipase were also used to catalyze polysaccharide hydroxyl groups reacting with vinyl esters to synthesize polysaccharide acrylate in *N,N*-dimethylformamide (DMF) or DMSO, and a regioselective acylation was observed.^{11,12} Some salts also showed catalytic ability in the synthesis of starch esters.¹³ Heinze et al. reported that cellulose could dissolve in DMSO/tetrabutylammonium fluoride (TBAF) and reacted with vinyl esters.¹⁴ However, hours to days were required for most of the above-mentioned reactions, or the reaction mainly occurred on the surface of polysaccharides. The degree of substitution (DS) of most polysaccharide derivatives was relatively low (<2.0).^{10,13,15,16}

In this work, we developed a new reaction system composed of DMSO, aqueous NaOH or KOH, and vinyl esters to rapidly

synthesize CEs. Aqueous NaOH or KOH was used to catalyze the transesterification reaction of cellulose with vinyl esters. It was surprising to find that CEs with relatively high DS (>2.0) could be synthesized within 5 min, which was in sharp contrast with hours to days for synthesizing CEs using traditional methods. Furthermore, these CEs synthesized by transesterification were characterized by Fourier transform infrared (FTIR) and ¹H, and ¹³C nuclear magnetic resonance (NMR). The thermal properties were studied by differential scanning calorimetry (DSC) analysis.

MATERIALS AND METHODS

Materials. Microcrystalline cellulose (MCC) was purchased from Sinopharm Chemical Reagent Company (China), and its degree of polymerization was 286 according to the method by ISO/FDIS 5351:2009. The DS was determined by ¹H NMR. Vinyl acetate, vinyl

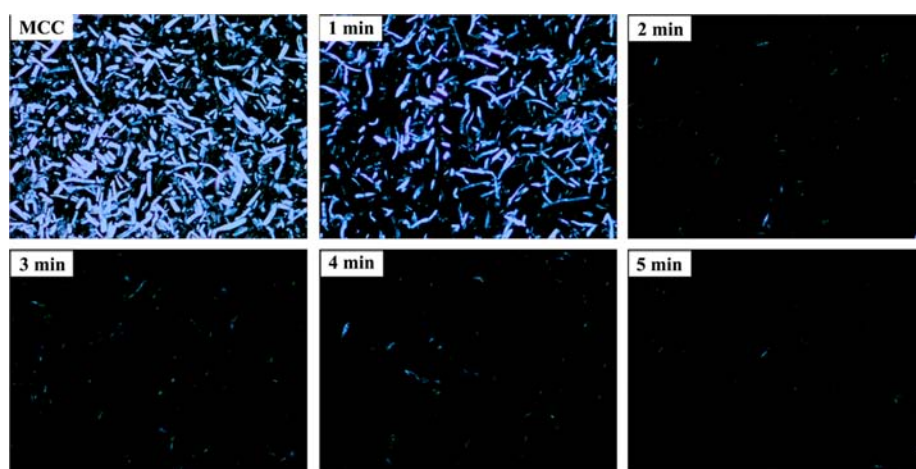


Figure 2. Polarizing images of the reaction mixture at different times (DMSO, NaOH, 6:1 molar ratio of vinyl acetate/anhydroglucose unit, and 100 °C).

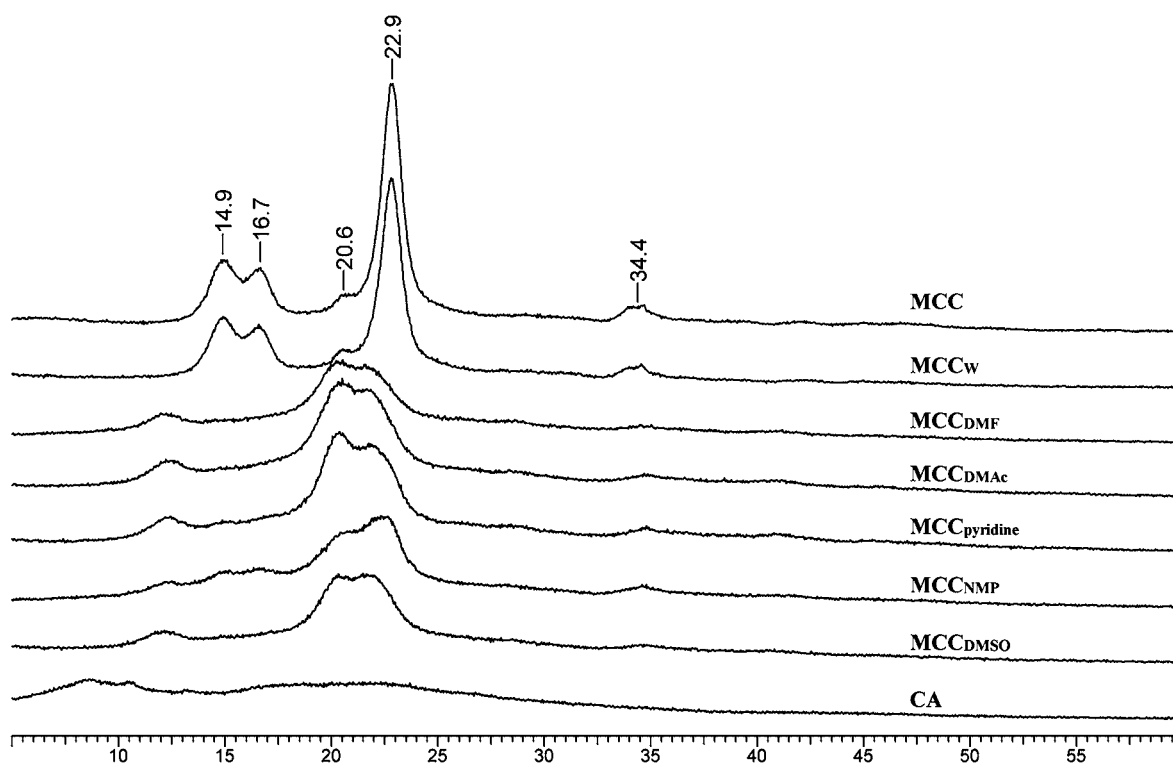


Figure 3. XRD patterns of MCC, MCC treated with 20 g/L aqueous NaOH (MCC_w), MCC treated with NaOH in various organic solvents, and produced CA.

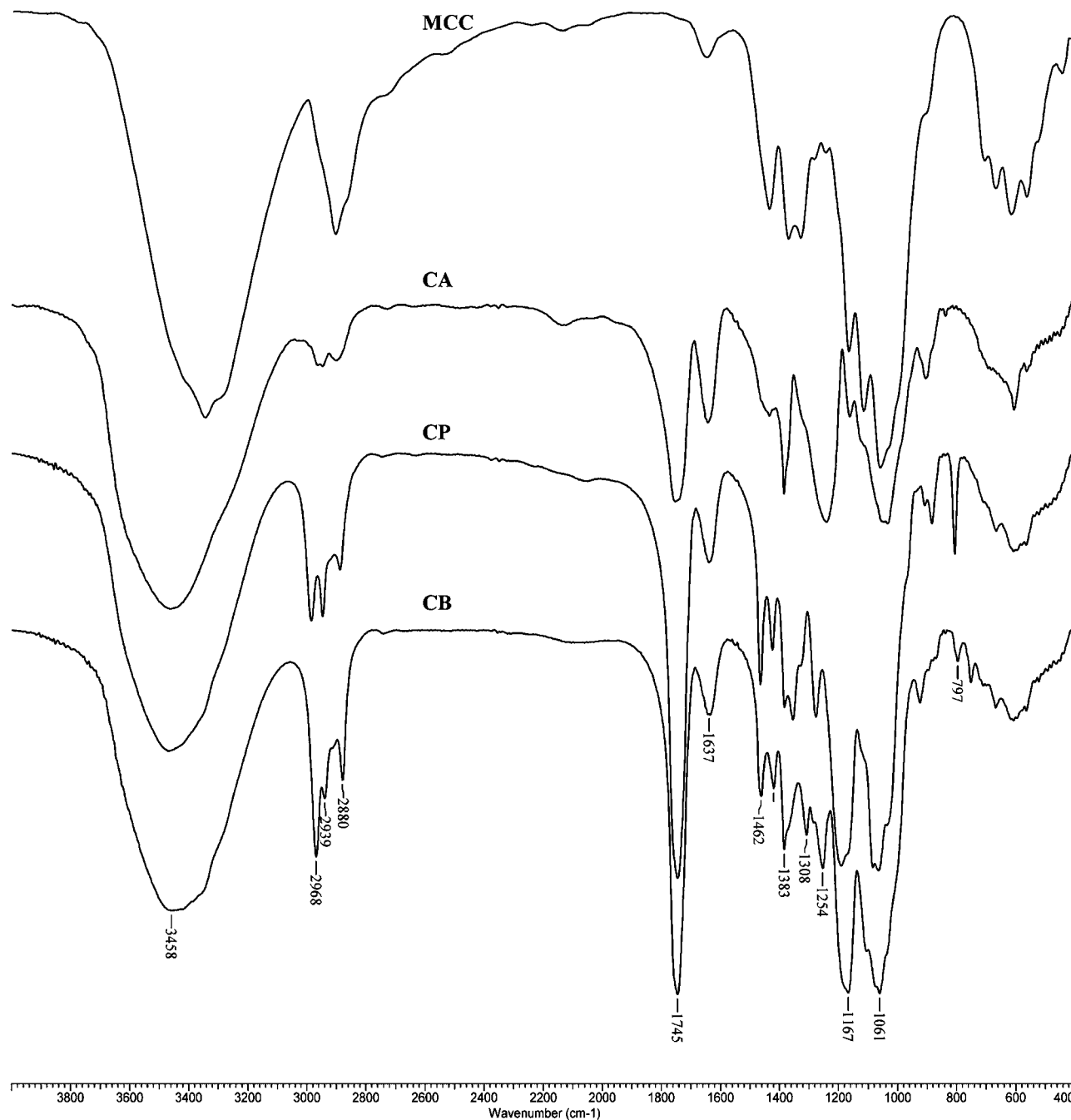


Figure 4. FTIR spectra of CA, CP, and CB.

propionate, and vinyl butyrate stabilized with 4-methoxyphenol were purchased from Tokyo Chemical Industry Co., Ltd. Other chemicals were all analytical-grade reagents and used as received without further purification.

Synthesis of Cellulose Esters. In a three-neck flask equipped with a magnetic stirrer and a condenser, 0.81 g of MCC (0.005 mol anhydroglucose units), 20 mL of DMSO, and 2 mL of aqueous sodium hydrate solution (200 g/L) were added. The mixture was stirred at room temperature for 5 min to swell the cellulose fibers and activate hydroxyl groups. Then, the flask was transferred into an oil bath (100 °C) and stirred for another 2 min. Thereafter, 0.03 mol of vinyl ester was immediately poured into the mixture and ran for 5 min. Upon the completion of the reaction, plenty of water was poured into the mixture. The product was filtered and washed with water and ethanol and then dried in a vacuum oven at 60 °C.

Characterizations. The FTIR spectra of MCC, cellulose acetate (CA), cellulose propionate (CP), and cellulose butyrate (CB) were recorded on a Bruker spectrophotometer in the range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1} . A KBr disc containing 1% finely ground sample was used for measurement. ^1H and ^{13}C NMR spectra were obtained on a Bruker AVIII 400 MHz spectrometer in $\text{DMSO-}d_6$. The solvent signals were used as internal standards for both ^1H and ^{13}C NMR. X-ray diffraction (XRD) of MCC, MCC treated with alkali in different solvents, and CA were performed on a D8 Advance instrument (Bruker AXS, Germany) with Ni-filtered $\text{Cu K}\alpha$ radiation (wavelength = 0.154 nm) in the range of $2\theta = 5\text{--}60^\circ$. Differential scanning calorimetry (DSC) analysis was performed on a TG-Q200 (TA Instrument, New Castle, DE) under a nitrogen atmosphere at a heating rate of 10 $^\circ\text{C min}^{-1}$ from 0 to 300 $^\circ\text{C}$.

RESULTS AND DISCUSSION

Reaction Mechanism and Effect of Reaction Conditions.

The transesterification reaction is a reversible reaction, and the reaction equilibrium is closely related to the alcohol in reactants and products.¹⁷ Figure 1 shows the transesterification reaction and hydrolysis reaction of vinyl esters under the catalysis of NaOH or KOH. During this reaction, the product vinyl alcohol is less stable and can be converted into acetaldehyde immediately, which can effectively prevent the occurrence of the reverse reaction and, thus, promote the formation of CEs. Therefore, as shown in Figure 2, despite the reaction being performed in heterogeneous conditions, the reaction was extremely fast and the produced CEs could dissolve into the solvent and, thus, form a homogeneous phase within minutes. Hydrolysis of vinyl esters is a side reaction in this process, which consumes vinyl esters and results in the excessive use of vinyl esters.

Because the transesterification is synchronized with the dissolving CEs, the selection of the reaction solvent is very important for successful preparation of CEs. The solvent must meet the following principles at least: (1) the prepared CEs must dissolve in the solvent; (2) the solvent must not react with the vinyl esters; and (3) because of the high reaction temperature, the solvent must have a high boiling point or the reaction has to operate under pressure. In this study, we used DMF, *N,N*-dimethyl acetamide (DMAC), pyridine, DMSO, and *N*-methylpyrrolidone (NMP) as solvents, LiOH, NaOH, and KOH as catalysts, and methyl acetate, ethyl acetate, vinyl acetate, vinyl propionate, and vinyl butyrate as esterifying agents to synthesize CEs. It should be noted that LiOH, NaOH, or KOH is insoluble in the above-mentioned solvents, and thus, aqueous LiOH (5 M), NaOH (5 M), or KOH (5 M) solution was used in this study. Results from polarizing microscopy show that almost all crystals disappeared using DMSO as the solvent, while lots of crystals still can be observed in DMF, DMAC, pyridine, and NMP (as shown in Figure S1 of the Supporting Information). Therefore, DMSO is a highly suitable solvent for this reaction. The reaction rate is closely related to the catalyst used. As mentioned above, a long reaction time was required in the synthesis of polysaccharide esters using other catalysts.^{11–14} However, NaOH or KOH shows high catalytic activity in this transesterification reaction, and the crystals almost disappear within 5 min, while LiOH does not (as shown in Figure S2 of the Supporting Information). The type of esterifying agent also shows great influence on the synthesis of CEs, and vinyl esters are the most commonly used esters in the synthesis of CEs by transesterification.¹⁸ It can be found that most crystals disappeared or became much smaller using vinyl esters as esterifying agents, while plenty of fibrous crystals could be found using methyl acetate and ethyl acetate as esterifying agents (as shown in Figure S3 of the Supporting Information). Therefore, vinyl esters are the ideal esterifying agents for this transesterification reaction. Transesterification and hydrolysis of vinyl esters are competitive to one another, and any factors in favor of hydrolysis of vinyl esters might lead to the extensive consumption of vinyl esters or the catalyst and then disfavor the synthesis of cellulose esters. The probable reasons are proposed as follows: the use of DMSO, NaOH, KOH, and vinyl esters probably makes the transesterification reaction the dominant reaction, and thus, the hydrolysis reaction is restrained, while other solvents, catalysts, and esterifying agents are likely to accelerate the hydrolysis of esterifying agents or the consumption of catalysts. Therefore, DMSO, NaOH or KOH, and vinyl esters are suitable for the synthesis of CEs in this study.

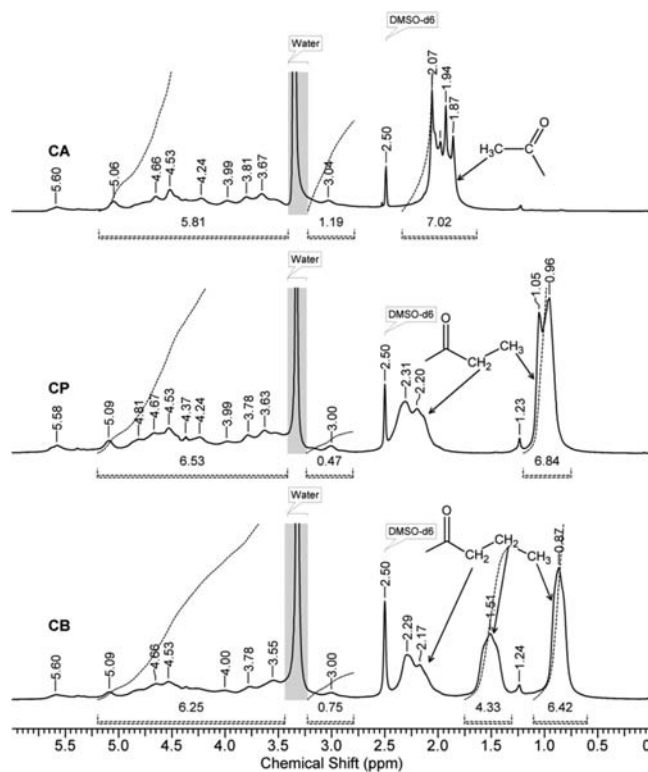


Figure 5. ¹H NMR spectra of CA, CP, and CB.

XRD Analysis. XRD was used to monitor the crystalline structure change of MCC during the transesterification process, as illustrated in Figure 3. Eight XRD patterns from top to bottom are originated from MCC, MCC treated with 20 g/L aqueous sodium hydrate (MCC_w), MCC treated with DMF, DMAC, pyridine, NMP, and DMSO containing aqueous sodium hydrate (labeled as MCC_{DMF}, MCC_{DMAC}, MCC_{pyridine}, MCC_{NMP}, and MCC_{DMSO}, respectively), and CA product. In all of these cases, except MCC, the same amount of NaOH was used to pretreat MCC for 5 min at room temperature as the method described in the section of synthesis of cellulose esters, and the transesterification was carried out at 100 °C for another 5 min.

As seen, MCC and MCC_w both show a sharp peak at $2\theta = 22.9^\circ$ and three relatively weak diffraction peaks at $2\theta = 14.9^\circ$, 16.7° , and 34.4° , which are a characteristic structure of cellulose I. It means that pretreatment with 20 g/L NaOH cannot change the crystalline structure of cellulose I. Liu and Hu reported that, only when the alkaline concentration is high enough (>12 wt %), cellulose I can be converted into cellulose II.¹⁹ After treatment with aqueous NaOH in organic solvents, however, the diffraction patterns of MCC change evidently. Three peaks at $2\theta = 12.2^\circ$, 20.5° , and 21.8° indicate a typical diffraction pattern of cellulose II. Because NaOH was insoluble in these organic solvents, when the aqueous NaOH was poured into the mixture of organic solvents and MCC, most aqueous NaOH would adhere to the hydrophilic surface of cellulose fibers and then organic solvents would wrest water from aqueous NaOH gradually and drive NaOH penetrate into the interior of cellulose fibers, resulting in the crystalline structure transformation and activation of cellulose hydroxyl groups. When vinyl esters were added, cellulose-active hydroxyl groups could react with the vinyl esters violently under the catalysis of NaOH embedded in cellulose fibers.

However, despite cellulose I converting into cellulose II in all of these organic solvents, large amounts of crystals can be

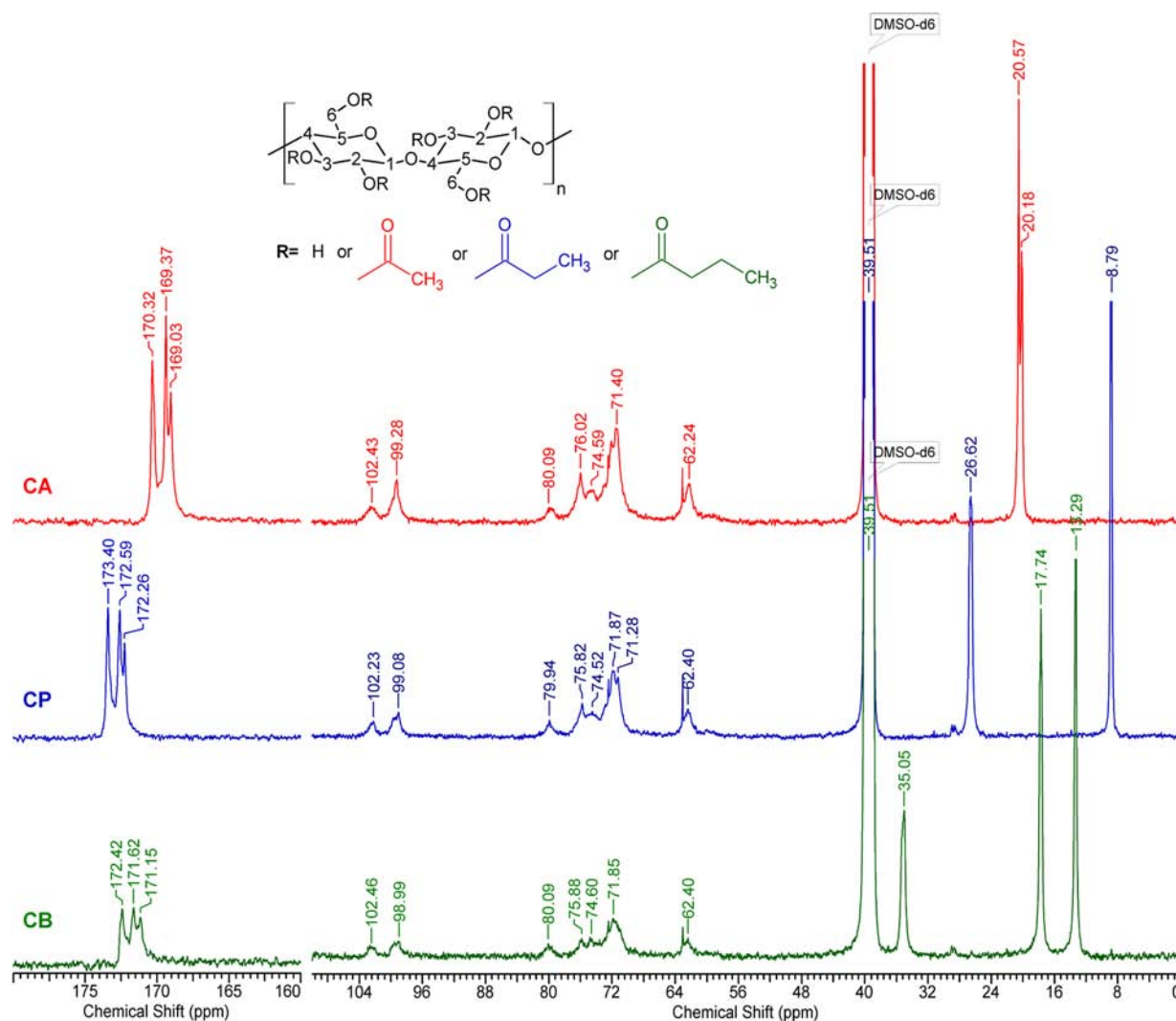


Figure 6. ^{13}C NMR spectra of CA, CP, and CB.

observed in these mixtures, except DMSO, after the addition of vinyl acetate for 5 min (as shown in Figure S1 of the Supporting Information). It probably could be explained by the fact that the synthesized cellulose acetate could not dissolve into these solvents as quickly as in DMSO and most of the vinyl acetate was hydrolyzed after the esterification of the surface of cellulose fibers. It indicates that DMF, DMAc, pyridine, and NMP are not suitable solvents for synthesizing CA under the given conditions. In addition, no obvious crystalline peaks can be observed in the XRD pattern of CA synthesized in DMSO, indicating that the transesterification reaction happened in not only the amorphous region but also the crystalline region. It is in line with the results observed from polarizing microscopy that almost all of the crystals disappeared within 2 min (as shown in Figure 2).

FTIR Analysis. The FTIR spectra of MCC and the synthesized CA, CP, and CB were measured and illustrated in Figure 4. The sharp peaks at 2968, 2939, 2880, and 1420 cm^{-1} are assigned to the asymmetric stretching of α -saturated methyl groups, CH_2 asymmetric and CH_2 symmetric stretching, and CH_2 scissoring, respectively.²⁰ The strong signals around 1745 and 1163 cm^{-1} are due to $\text{C}=\text{O}$ and $\text{C}-\text{C}-\text{O}$ stretching absorption of saturated carboxylic esters.²¹ These results confirmed the successful synthesis of CA, CP, and CB by transesterification preliminarily.

NMR Analysis. The ^1H and ^{13}C NMR spectra of CA, CP, and CB were detected on a Bruker AV-III 400 M spectrometer and illustrated in Figures 5 and 6, respectively. The DS was determined by ^1H NMR. Integrals between 2.80 and 5.20 ppm (except the dark signals from residue water) assigned to the seven protons of the anhydroglucose unit were used as a reference. Integrals from methyl protons of CA, CP, and CB were used to calculate the DS. The DS of CA, CP, and CB calculated by ^1H NMR is 2.34, 2.28, and 2.14, respectively. The assignments of these spectra were illustrated below, and these data confirmed the successful synthesis of CA, CP, and CB. ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$, δ): CA 20.2 and 20.6 (CH_3), 62.2–102.4 (carbons of the anhydroglucose ring), 170.3, 169.4, and 169.0 ($\text{C}=\text{O}$ at C6, C3, and C2 positions, respectively); CP 8.8 (CH_3), 26.6 (CH_2), 62.4–102.2 (carbons of the anhydroglucose ring), 173.4, 172.6, and 172.3 ($\text{C}=\text{O}$ at C6, C3, and C2 positions, respectively); and CB 13.3 (CH_3), 17.7, and 35.0 (CH_2), 62.4–102.5 (carbons of the anhydroglucose ring), 172.4, 171.6, and 171.2 ($\text{C}=\text{O}$ at C6, C3, and C2 positions, respectively).

DSC Analysis. To investigate the thermal properties of CEs synthesized by transesterification, the DSC curves of CA, CP, and CB were determined and shown in Figure 7. No melt temperature (T_m) was found in the DSC curve of CA, because of the decomposition temperature, and the T_m of CA was extremely

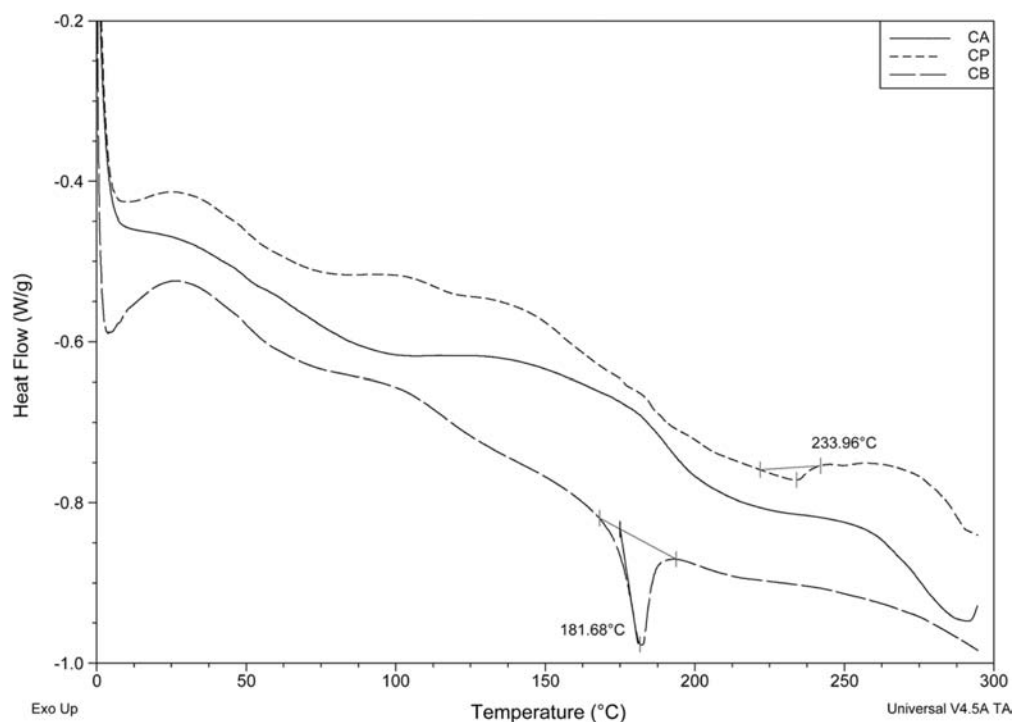


Figure 7. DSC curves of CA, CP, and CB.

close. However, T_m could be observed in both the curves of CP (234 °C) and CB (182 °C), which were highly consistent with the results of the previous work.²² These results indicated that CA, CP, and CB synthesized in this work had similar properties to the products from other methods.

To conclude, DMSO/aqueous NaOH (or KOH) is a highly suitable system for the production of CEs. The little time required for the synthesis of cellulose acetate, cellulose propionate, and cellulose butyrate via the transesterification reaction places the solvent system described here beyond the state-of-art. The findings of this study have very important implications in the preparation of CEs and may open up new windows for synthesizing CEs and other cellulose derivatives.

■ ASSOCIATED CONTENT

Supporting Information

Crystal change of MCC under different reaction conditions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ REFERENCES

- Demirbaş, A. Biomass resource facilities and biomass conversion processing for fuels and chemicals. *Energy Convers. Manage.* **2001**, *42*, 1357–1378.
- Klemm, D.; Heublein, B.; Fink, H.-P.; Bohn, A. Cellulose: Fascinating biopolymer and sustainable raw material. *Angew. Chem., Int. Ed.* **2005**, *44*, 3358–3393.
- Chang, C.; Zhang, L. Cellulose-based hydrogels: Present status and application prospects. *Carbohydr. Polym.* **2011**, *84*, 40–53.
- Balsler, K.; Hoppe, L.; Eicher, T.; Wandel, M.; Astheimer, H. J.; Steinmeier, H.; Allen, J. M. Cellulose esters. *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH Verlag GmbH and Co. KGaA: Weinheim, Germany, 2000.
- Glasser, W. G. 6. Prospects for future applications of cellulose acetate. *Macromol. Symp.* **2004**, *208*, 371–394.
- Hummel, A. 3.2 Industrial processes. *Macromol. Symp.* **2004**, *208*, 61–80.
- Santacesaria, E.; Trulli, F.; Minervini, L.; Di, S. M.; Tesser, R.; Contessa, S. Kinetic and catalytic aspects in melt transesterification of dimethyl terephthalate with ethylene glycol. *J. Appl. Polym. Sci.* **1994**, *54*, 1371–1384.
- Kim, H. J.; Kang, B. S.; Kim, M. J.; Park, Y. M.; Kim, D. K.; Lee, J. S.; Lee, K.-Y. Transesterification of vegetable oil to biodiesel using heterogeneous base catalyst. *Catal. Today* **2004**, *93–95*, 315–320.
- Ma, F.; Hanna, M. A. Biodiesel production: A review. *Bioresour. Technol.* **1999**, *70*, 1–15.
- Rooney, M. L. Interesterification of starch with methyl palmitate. *Polymer* **1976**, *17*, 555–558.
- Ferreira, L.; Gil, M. H.; Dordick, J. S. Enzymatic synthesis of dextran-containing hydrogels. *Biomaterials* **2002**, *23*, 3957–3967.
- Ferreira, L.; Carvalho, R.; Gil, M. H.; Dordick, J. S. Enzymatic synthesis of inulin-containing hydrogels. *Biomacromolecules* **2002**, *3*, 333–341.
- Dicke, R. A straight way to regioselectively functionalized polysaccharide esters. *Cellulose* **2004**, *11*, 255–263.
- Heinze, T.; Dicke, R.; Koschella, A.; Kull, A. H.; Klotz, E. A.; Koch, W. Effective preparation of cellulose derivatives in a new simple cellulose solvent. *Macromol. Chem. Phys.* **2000**, *201*, 627–631.

- (15) Xie, J.; Hsieh, Y.-L. Enzyme-catalyzed transesterification of vinyl esters on cellulose solids. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 1931–1939.
- (16) Çetin, N. S.; Tingaut, P.; Özmen, N.; Henry, N.; Harper, D.; Dadmun, M.; Sèbe, G. Acetylation of cellulose nanowhiskers with vinyl acetate under moderate conditions. *Macromol. Biosci.* **2009**, *9*, 997–1003.
- (17) Meher, L. C.; Vidya Sagar, D.; Naik, S. N. Technical aspects of biodiesel production by transesterification—A review. *Renewable Sustainable Energy Rev.* **2006**, *10*, 248–268.
- (18) Adachi, S.; Kobayashi, T. Synthesis of esters by immobilized lipase catalyzed condensation reaction of sugars and fatty acids in water-miscible organic solvent. *J. Biosci. Bioeng.* **2005**, *99*, 87–94.
- (19) Liu, Y.; Hu, H. X-ray diffraction study of bamboo fibers treated with NaOH. *Fibers Polym.* **2008**, *9*, 735–739.
- (20) Jandura, P.; Kokta, B. V.; Riedl, B. Fibrous long-chain organic acid cellulose esters and their characterization by diffuse reflectance FTIR spectroscopy, solid-state CP/MAS ¹³C-NMR, and X-ray diffraction. *J. Appl. Polym. Sci.* **2000**, *78*, 1354–1365.
- (21) Schilling, M.; Bouchard, M.; Khanjian, H.; Learner, T.; Phenix, A.; Rivenc, R. Application of chemical and thermal analysis methods for studying cellulose ester plastics. *Acc. Chem. Res.* **2010**, *43*, 888–896.
- (22) Maim, C. J.; Mench, J. W.; Kendall, D. L.; Hiatt, G. D. Aliphatic acid esters of cellulose: Properties. *Ind. Eng. Chem.* **1951**, *43*, 688–691.