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Inverse Temperature-Dependent Pathway of Cellulose Decrystallization in Trifluoroacetic Acid

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An unusual inverse temperature-dependent pathway was observed during cellulose decrystallization in trifluoroacetic acid (TFA). Decreasing the TFA treatment temperature accelerated the cellulose decrystallization process. It took only 100 min to completely decrystallize cellulose at 0 °C in TFA, a result not achieved in 48 h at 25 °C in the same medium. There was neither cellulose esterification nor a change of cellulose macrofibril morphology by TFA treatment at 0 °C. Our IR data suggest that TFA molecules are present as cyclic dimers when they penetrate into crystalline cellulose regions, transforming crystalline cellulose to amorphous cellulose. On the other hand, the rate of TFA penetration into the cellulose matrix was greatly retarded at higher temperatures where monomeric TFA prevails. At elevated temperatures, esterification of TFA monomers on the external surface of crystalline cellulose, agglomeration of cellulose macrofibrils, as well as water released from the esterification reaction, inhibit the diffusion rate of TFA into the cellulose crystalline region and decrease the TFA swelling capability.

1. Introduction

Cellulose is the most abundant renewable material in the biosphere. It exists in a variety of crystalline and amorphous topologies. The main building blocks are linear polymeric D-glucose units, cross-linked by β-1,4-glucoside bonds. Hydrogen bonding between polymer chains is the main binding mode, stabilizing molecular crystals in cellulose but limiting its solubility in most common solvents.

Decrystallizing cellulose opens a potentially efficient pathway for its utilization in the production of fuels and industrial chemicals. According to the conventional wisdom, strong mineral acids and certain polar solvents, capable of disrupting the hydrogen-bonding network between cellulose polymer chains, are effective for cellulose decrystallization.

Cellulose can be mechanically decrystallized,[1] but the energy cost is rather high. An alternate approach is to use swelling agents that are capable of decrystallizing cellulose. Liquid ammonia is a widely used swelling agent, albeit at a rather low temperature (below −30 °C). It can penetrate into the cellulose crystalline region by breaking O···H—O bonds and forming N···H—O bonds.[2] Generally, cellulose decrystallization or dissolution processes require a strong electron donor−acceptor interaction (hydrogen bonding) as the driving force, which has been reported for many nonderivatizing organic solvents.[3−6]

When a volatile swelling agent or solvent is used to decrystallize cellulose, the separation of the swelling agent from decrystallized cellulose is relatively simple. Trifluoroacetic acid (TFA), as a volatile liquid between −15 and 78 °C, is one possible nonaqueous solvent for cellulose swelling.[7] TFA offers a more convenient operating temperature window than liquid ammonia. Cellulose is dissolved in TFA at room temperature when exposed for extended periods.[7] The dissolution of cellulose in TFA was complete after 25 days, and the dissolution products had DS (degree of substitution) values of 1.21−1.34.[8] A ^{13}C NMR spectroscopic study by Nehls et al. suggests that most of the C_6−OH groups in cellulose are trifluoroacetylated (a result of esterification) after 10 h while the C_2−OH groups start to be trifluoroacetylated after 2 days with TFA at room temperature.[8] Hasegawa et al.[9] studied the dissolving state of cellulose in TFA by Fourier transfer infrared spectroscopy (FTIR) and ^{13}C NMR spectroscopy. They noted that C_6–OH groups were trifluoroacetylated, but interestingly, acetal linkages were not broken. Esterification is a highly temperature-dependent process and could be dramatically reduced or eliminated at low temperature.

When cellulose is dissolved in a solvent, its supramolecular structure is destroyed and cellulose loses its crystallinity. The complete disappearance of cellulose crystallinity in a swelling process usually indicates the completion of the dissolution process. In this paper, we reveal a new route to rapidly decrystallize cellulose without esterification or morphology change on the macrofiber. Decrystallization without esterification not only eliminates TFA consumption but also preserves uncontaminated cellulose polymer chains in readily useful amorphous states. We also elucidate a striking observation of TFA dimer induced cellulose decrystallization.

2. Materials and Methods

2.1. Sample Preparation. Cellulose (cotton linters, product no. C6663) and trifluoroacetic acid (99%) were purchased from Sigma-Aldrich. Cellulose and trifluoroacetic acid (1:15 mass ratio) were mixed at different temperatures for different times in sealed flasks. Unless otherwise stated, after treatment, samples were exposed to a vacuum (30 mTorr) at specified temperatures for 2 days. For samples that were evacuated at 105 °C for 2 days, a vacuum oven at approximately 200 Torr was used, following 30 mTorr evacuation for 2 h at 25 °C.

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2.2. X-ray Diffraction Method (XRD). XRD measurements were performed on a Philips PW3040/00 X'Pert MPD system. The diffracted intensity of Cu Kα radiation (wavelength of 0.1542 nm, under a condition of 50 kV and 40 mA) was measured in a 2θ range between 10° and 50°.

2.3. CP/MAS ^{13}C Solid-state NMR. Cross-polarization/magic angle spinning (CP/MAS) ^{13}C solid-state NMR experiments were performed on a Chemagnetics CMX100 spectrometer operating under a static field strength of 2.3 T (100 mHZ ^{1}H) at 25 °C. The contact time for CP was 1 ms with a proton pulse of 5.5 μs and decoupling power of 45 kHz. The MAS speed was 3 kHz. The delay time after the acquisition of the FID signal was 2 s. The chemical shifts were calibrated by using the hexamethylbenzene methyl resonance at 17.3 ppm. Cellulose crystallinity index (I_{Cr}) was determined from the peak areas assigned to C_4 crystalline (86−92 ppm) and C_4 noncrystalline (79−86 ppm) material.

2.4. ^{13}C liquid NMR. ^{13}C liquid NMR was taken on a Varian Infinity CMX 500-MHz NMR spectrometer. Spectra were accumulated using a 5 μs pulse width at 300 K. The chemical shifts were measured on the δ scale (ppm) relative to tetramethylsilane in DMSO-d_6. The NMR spectra of methyl β-D-glucopyranoside TFA solution was taken without locking to deuterium.

2.5. Fourier Transform Infrared Spectroscopy (FTIR). KBr pellets of samples were prepared by mixing 2−4 mg of cellulose sample with 200−250 mg of KBr (spectroscopic grade) with an alumina mortar. The 13 mm diameter pellets were prepared in a standard tool under a pressure of 1360 atm. IR spectra were recorded using a Nicolet 740 FTIR spectrometer with a DTGS detector at 4 cm^{-1} resolution. N_2 gas flow was used as background for each spectrum, and 64 scans were taken per sample.

2.6. Scanning Electron Microscopy (SEM). Zeiss-LEO 982 Scanning Electron Microscopy operated at 2 keV was used to image cellulose samples after hydrolysis. Samples were coated with carbon using a vacuum sputter-coater to improve the conductivity of the samples and thus the quality of the SEM images.

2.7. Degree of Polymerization Measurement. The degree of polymerization (DP) was calculated by dividing the total glucosyl monomer concentration by the reducing-end concentration following the procedure of Zhang and Lynd.[10] The method was based on UV analysis. Each sample was tested in triplicate. Calibration standards and cellulose samples were analyzed the same day.

3. Results

Figure 1 shows cellulose XRD patterns for an untreated sample and samples treated by TFA for 3 h at 0, 25, 45, and 65 °C. The strongest peak, at $2\theta = 22.6°$, originates from the cellulose crystalline plane [002].[11,12] The intensity of this peak was dependent on the temperature at which crystalline cellulose was treated by TFA. Surprisingly, decreasing TFA treatment temperature accelerates the disappearance of this crystalline peak. After cellulose was treated at 0 °C for 3 h, this crystalline peak had essentially disappeared. The area of the [002] peak was normalized to that of untreated cellulose and was used to define the relative crystallinity of cellulose samples. The results are shown in the insert of Figure 1. An inverse temperature effect on cellulose decrystallization in TFA is clearly revealed in Figure 1. The same effect was also observed for other crystalline cellulose peaks. TFA treatment at low temperature reduces the long-range order in crystalline cellulose at a rate that accelerates with decreasing TFA treatment temperature.

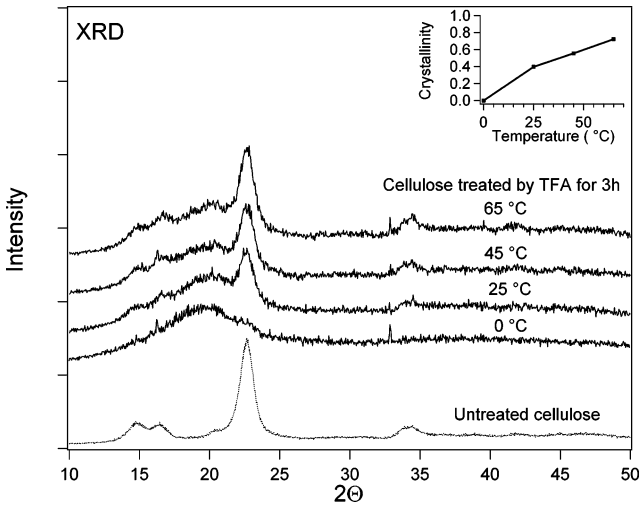

Figure 1. XRD patterns of as-received cellulose and that treated by TFA for 3 h at 0, 25, 45, and 65 °C. The insert shows the relationship between the relative crystallinity of cellulose samples and TFA treating temperature.

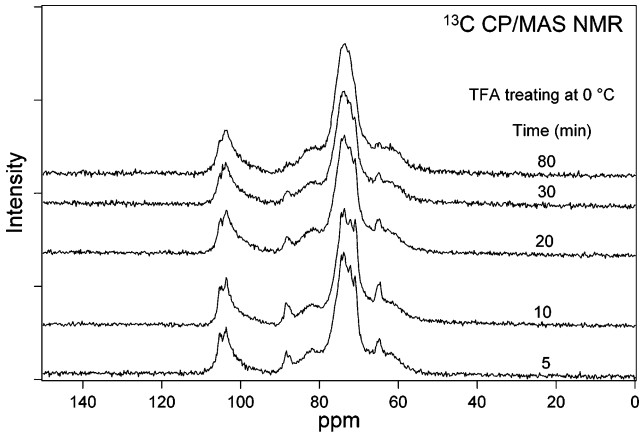

Figure 2. ^{13}C CP/MAS NMR of cellulose treated in TFA at 0 °C for 5, 10, 20, 30, and 80 min.

We followed cellulose decrystallization in TFA at 0 °C by ^{13}C CP/MAS NMR and by XRD. The ^{13}C CP/MAS NMR spectra for cellulose samples treated at 0 °C in TFA for 5, 10, 20, 30, and 80 min are shown in Figure 2. Crystalline cellulose has a fairly sharp peak for C_4 at 86−92 ppm. This peak, already small at 5 min, continues to decrease over time. The C_4 resonance for disorded (noncrystalline) cellulose is broad and located at 79−86 ppm. Similarly, the C_6 peak for crystalline cellulose at 63−67 ppm is reduced over time. The C_6 resonance associated with amorphous cellulose is the broad peak between 56 and 63 ppm.[1,12,13] The ^{13}C CP/MAS data is in agreement with XRD data.

Figure 3 is a plot of the rate of cellulose decrystallization in TFA at 0 °C by following the intensity of the [002] XRD peak after treatment for 10, 30, 80, and 100 min. Most of the cellulose decrystallization occurred in the first 30 min, and the crystalline peak disappeared in 100 min. In contrast, crystalline peaks could still be detected by XRD when cellulose was treated by TFA at 25 °C even after 48 h. Decreasing the TFA treatment temperature dramatically shortens the time required to decrystallize cellulose.

Figure 4 shows the SEM images of cellulose after TFA treatment. These samples were treated for 3 h at 0 °C (Figure 4A), 25 °C (Figure 4B), and 65 °C (Figure 4C) and

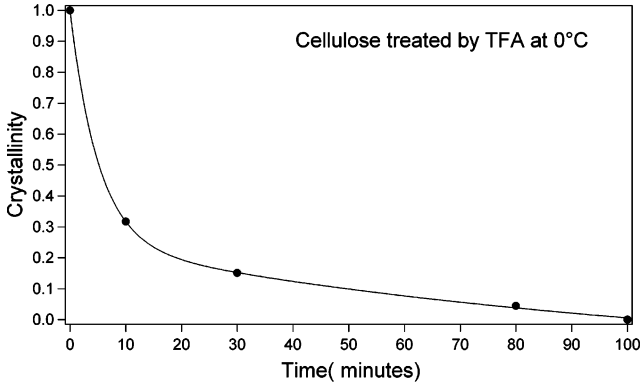

Figure 3. Rate of cellulose decrystallization in TFA at 0 °C for 10, 30, 80, and 100 min measured by XRD.

then under vacuum as described in the Materials and Methods section. Although crystalline cellulose was transformed to amorphous cellulose, after TFA treatment for 3 h at 0 °C, the macrofibril structure of cellulose was not altered as compared with the untreated cellulose (not shown).[14] The macrofibrils of cellulose treated at 25 °C were shortened, and some agglomeration was noted. The sample treated at 65 °C showed agglomeration of macrofibrils to a more severe extent. The agglomeration of macrofibrils at higher temperature was attributed to the intermolecular dehydration between macrofibrils[14] since TFA is a strong acid that is known to be capable of catalyzing the dehydration.[15,16]

We measured the DP value for the untreated crystalline cellulose and cellulose decrystallized at 0 °C. These two samples were similar in morphology. The untreated cellulose in this study had a DP of 317.7 and that for the TFA-treated material at 0 °C had a DP of 112.9. We did not examine the DP for cellulose treated at higher temperatures, which resulted in severe agglomeration and esterification which would cause uncertainty in our DP measurement.

We examined the effect that temperature has during the removal of TFA under vacuum. In this post treatment (PT) study, cellulose and TFA were mixed at 0 °C for 3 h. A portion of the mixture was exposed to vacuum (30 mTorr) for 2 h at 0 °C (PT_0). A second portion was exposed to vacuum (30 mTorr) for 2 h at 25 °C (PT_{25}). A third portion was exposed to vacuum (30 mTorr) for 2 h at 25 °C and transferred to a vacuum oven for 2 days at 105 °C (PT_{105}). In Figure 5, FTIR of these samples are shown along with the FTIR of untreated cellulose. The vibration peak at 1785 cm^{-1} in Figure 5 corresponds to that of the carbonyl group in liquid TFA (1783 cm^{-1}),[17] which exists predominantly as a cyclic dimer. The vibration peak for sample PT_{105} was shifted to 1792 cm^{-1}. We attribute this shift to the formation of cellulose trifluoroacetate at the higher temperature.[9,18] However, the resolution of the IR peaks is insufficient for this to be conclusive. To better understand the competition between esterification, which occurs at higher temperatures, and decrystallization *without* esterification, which we claim occurs at lower temperatures, we used a model compound, methyl β-D-glucopyranoside.

Methyl β-D-glucopyranoside has a similar structure to the glucan unit on cellulose. Figure 6 shows ^{13}C NMR spectra for methyl β-D-glucopyranoside treated in TFA at 0, 25, and 50 °C. Upon dissolution in TFA at 0 °C for 3 h, there was no trifluoroacetylation observed by NMR on the treated cellulose. When the temperature was raised to 25 °C for 1 h, new NMR peaks were observed due to esterification. The NMR results offer strong support that the OH groups on the glucan unit of cellulose do not react with TFA at 0 °C.

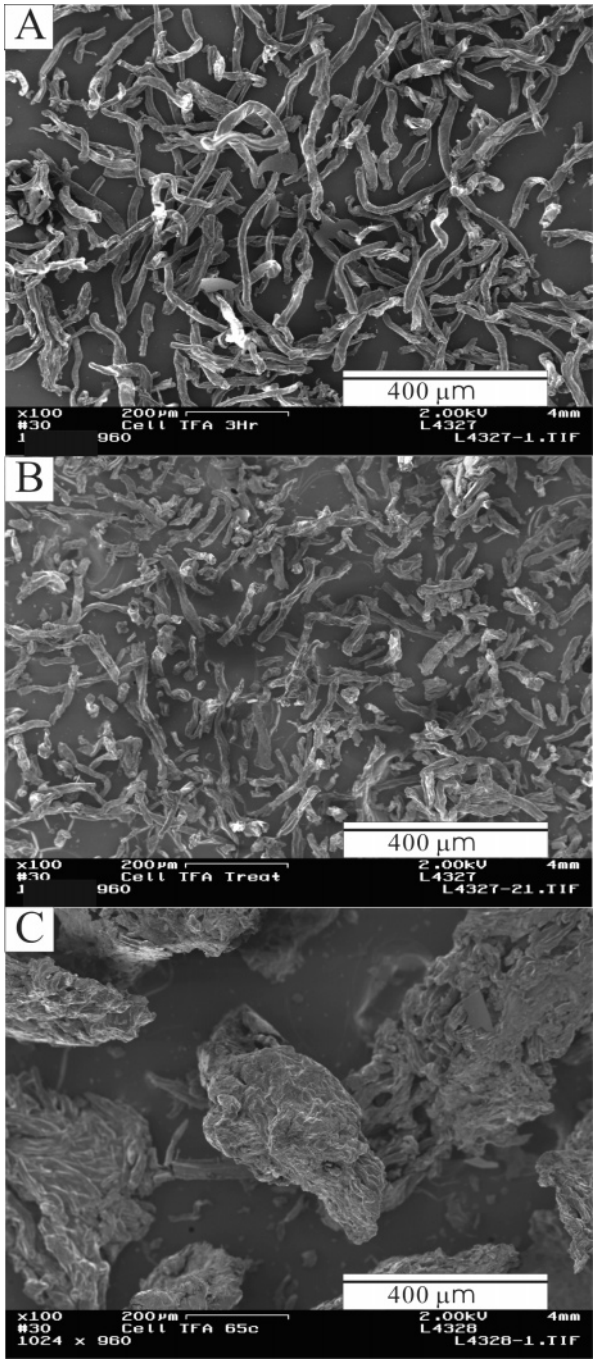

Figure 4. Scanning electron micrographs of cellulose samples after TFA treatment for 3 h at three temperatures (Following treatment, TFA was removed in vacuo for 2 h at 25 °C at 30 mTorr followed by 2 days at 105 °C in a vacuum oven): (A) treated at 0 °C; (B) treated at 25 °C; (C) treated at 65 °C.

Dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF) are two common solvents for cellulose esters, and the solubility of cellulose esters is highly related to the degree of substitution (DS). Samples PT_0, PT_{25}, and PT_{105}, showed a significant difference in their solubility. In DMSO, only PT_{105} was soluble. This suggests that, when exposed to higher temperatures, cellulose initially treated at 0 °C can esterify. To determine the degree of trifluoroacetylation that occurred under vacuum at 105 °C, PT_{105} was dissolved in DMSO-d_6 and analyzed by ^{13}C NMR. The result is shown in Figure 7. The peak at 60.3 ppm was assigned to C_6 of cellulose and the peak at 67.1 ppm was assigned to C_6 of trifluoroacetylated cellulose.[9] Trifluoroacetylation of C_6-OH also causes some shifts in the C_4, C_5, and C_1

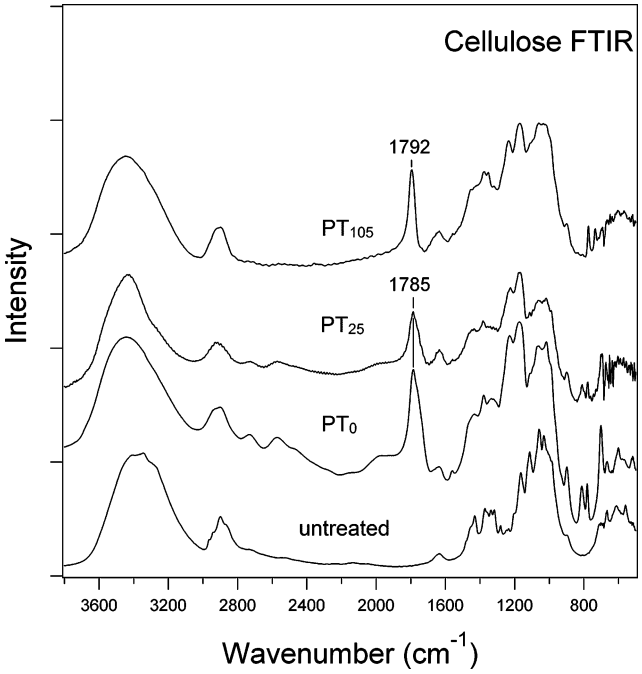

Figure 5. FTIR spectra of as-received cellulose and that treated by TFA for 3 h at 0 °C: PT_0, TFA removed under vacuum for 3 h at 0 °C; PT_{25}, TFA removed under vacuum for 3 h at 25 °C; PT_{105}, TFA removed under vacuum for 2 h at 25 °C and 2 days at 105 °C in a vacuum oven; as-received cellulose.

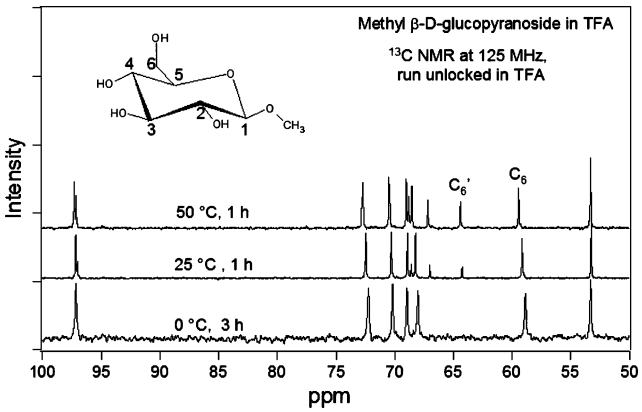

Figure 6. ^{13}C NMR spectrum of methyl β-D-glucopyranoside TFA solution at different temperatures (the solution was pretreated at that temperature for the time indicated). The sample was run unlocked in TFA.

resonances. The large downfield shift of 6.8 ppm observed for C_6 after trifluoroacetylation was not observed for C_2 or C_3. The NMR spectrum suggests that the trifluoroacetylation only occurred on the C_6–OH of cellulose but not on the C_2−OH and C_3–OH. On the basis of the peak areas of C_6 (60.3 ppm) and C'_6 (67.1 ppm), we estimate that only 25% of cellulose C_6–OH groups were trifluoroacetylated. The solubility of cellulose ester in DMF highly depends on the degree of trifluoroacetylation, and it was found that a degree of trifluoroacetylation of 1.4 or greater is required.[18] PT_{105} is not soluble in DMF consistent with our finding of a degree of trifluoroacetylation of 0.25. The molar ratio between TFA and C_6–OH in PT_{105} is 1:2.9 (the mass difference between the vacuum treated sample and the original cellulose is 20 wt %). This molar ratio is consistent with the relative size of the C_6–OH and trifluoroacetylated C_6–OH peaks in the ^{13}C NMR. Thus, it appears that all residual TFA in the sample is in the ester form with C_6−OH groups on cellulose.

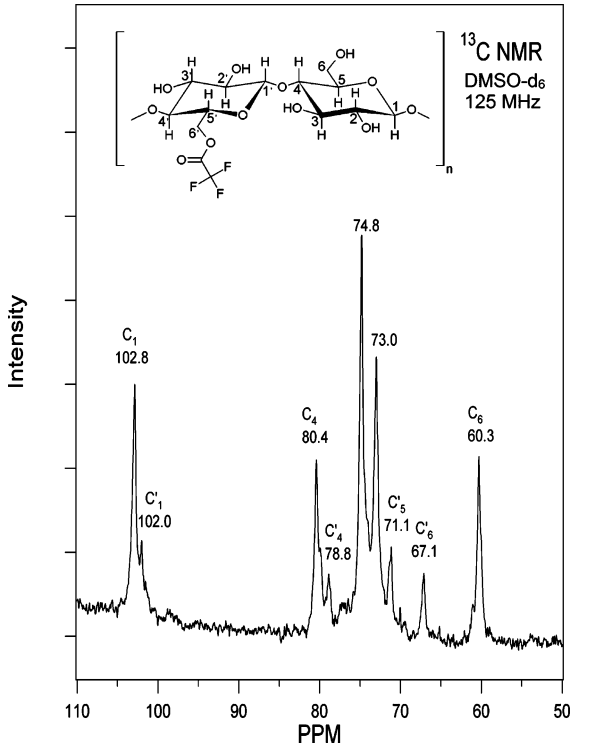

Figure 7. ^{13}C NMR spectrum of cellulose sample PT_{105}. Cellulose sample was treated by TFA for 3 h at 0 °C; TFA was removed under vacuum for 3 h at 25 °C and 2 days at 105 °C in a vacuum oven and then dissolved in DMSO-d_6.

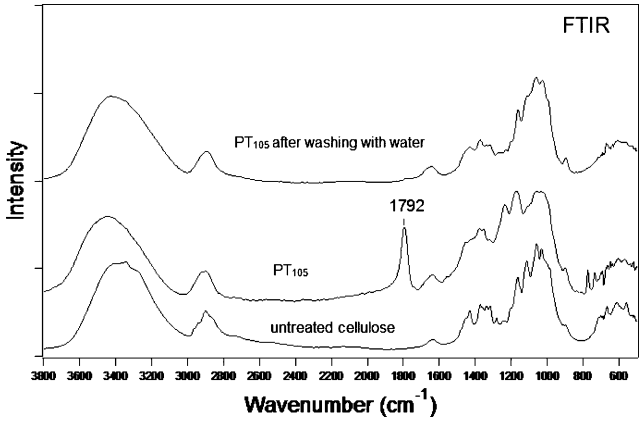

Figure 8. FTIR spectra of untreated cellulose, PT_{105} treated cellulose containing residual TFA in the form of cellulose trifluoroacetate, and PT_{105} cellulose washed with water to remove TFA.

All the PT samples contained residual TFA. We demonstrated that the residual TFA can be removed by water washing. Figure 8 shows FTIR, of untreated cellulose, PT_{105}, and PT_{105} after water washing. In this example, even the esterified TFA is hydrolyzed and removed by washing with water, as evidenced by the disappearance of the absorption at 1795 cm^{-1}.

We did a final set of experiments to further examine the ability of TFA to decrystallize cellulose at low temperatures. In one study, we compared cellulose that was treated with TFA at 65 °C for 3 h, labeled T_{65}, to cellulose treated with TFA at 65 °C for 3 h followed by 0 °C for 10 min. This second sample was labeled T_{65-0}. Cellulose in a third sample was treated only at 0 °C for 10 min. This sample was labeled T_0. Cellulose in a fourth sample was treated at −10 °C for 10 min. The fourth sample was labeled T_{-10}. Each of the four samples was exposed to a vacuum (30 mTorr) for 2 h at room temperature and transferred to a vacuum oven for 2 days at 105 °C (∼200 Torr)

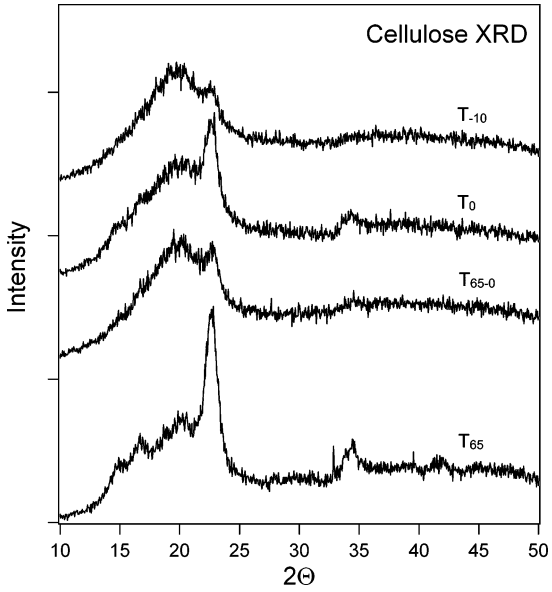

Figure 9. Cellulose treated by TFA as indicated followed by vacuum for 2 h at 25 °C at 30 mTorr and 2 days at 105 °C in a vacuum oven: T_{65}, treated at 65 °C for 3 h; T_{65-0}, treated at 65 °C for 3 h and 0 °C for 10 min; T_0, treated at 0 °C for 10 min; T_{-10}, treated at −10 °C for 10 min.

after TFA treatment following which XRD diffractograms were taken. The results are shown in Figure 9.

The data shown in Figure 9 demonstrate that low-temperature TFA treatment can still decrystallize cellulose at 0 °C even after strong agglomeration of the macrofibrils (Figure 4) and esterification, which results from treatment of TFA at 65 °C. In fact, the degree of crystallinity was lower in sample T_{65-0} than in sample T_0. Even more interesting, however, is the sample treated only at −10 °C for 10 min, with no other treatment. T_{-10} showed the lowest degree of crystallinity of all the samples in the study and a strong manifestation of the inverse temperature effect.

4. Discussion

The purpose of this paper is to present the unusual inverse temperature effect on cellulose decrystallization discovered when treating with TFA. It took only 100 min to decrystallize cellulose at 0 °C in TFA, a result not achieved in 48 h at 25 °C in the same medium. The striking observation of the inverse temperature effect was further verified by the experimental result at −10 °C in which the decrystallization rate was even faster than that at 0 °C. The degree of polymerization was moderately decreased through TFA treatment at 0 °C. The untreated crystalline cellulose had a DP value of 317.7, which was decreased to 112.9 after TFA treatment. Therefore, the conversion of crystalline cellulose to amorphous cellulose from low-temperature TFA treatment can be mainly ascribed to decrystallization, rather than full depolymerization.

At low temperature, decrystallization is fast, whereas ester formation with trifluoroacetic acid is negligible, as follows from NMR analysis of methyl β-D-glucopyranoside in TFA. Esterification occurs only after the temperature of methyl β-D-glucopyranoside TFA solution is raised to 25 °C. Raising TFA treatment temperature further leads to a higher level of esterification. In contrast to the literature report that deep esterification occurred during cellulose dissolution in TFA,[8] our results indicate that esterification can be prevented at low temperature. This new observation has an important practical implication: TFA is not consumed in the cellulose decrystallization process and hence can potentially be fully recycled. Even when the sample experienced a small degree of esterification through vacuum treatment at elevated temperatures, the TFA ester was hydrolyzed and TFA removed by treating with water.

Although treatment at low temperature affects the crystallinity, it does not appear to impact the morphology of cellulose macrofibrils. However, treatment at higher temperature results in cellulose macrofibril agglomeration. TFA is still capable of effectively decrystallizing the remaining crystalline region of the agglomerated cellulose when the temperature is lowered to 0 °C. The results obtained at higher temperature, consistent with the published work,[8] suggest that cellulose dissolution at higher temperature is a slow reaction zone migration process. Complete decrystallization of cellulose at higher temperature does occur, but at a much reduced rate, accompanied by esterification.

In the paragraphs that follow we propose an explanation for the unusual phenomenon of the inverse temperature effect. TFA has a chemical equilibrium between monomer and dimer.[19] The concentration of TFA dimer is particularly favored at low temperatures. For example, in CCl_4, the dimerization equilibrium constant was 58 mol^{-1} at 40 °C. With a small decrease in temperature, the constant largely increased to 128 mol^{-1} at 25 °C and to 205 mol^{-1} at 15 °C.[19] Even though the constant is not available for 0 °C, these reported dimerization equilibrium constant values indicate that TFA dimer formation is very sensitive to temperature in the temperature range of our study. The carbonyl group of the TFA monomer has a vibration frequency at 1830 cm^{-1}.[20] The proton of the TFA molecule is more acidic and a better electron acceptor than that on the OH groups of cellulose. The carbonyl group vibration frequency decreases from 1830 cm^{-1} for a monomer to 1785 cm^{-1} for a dimer when two TFA molecules form a cyclic dimer, the result of strong hydrogen bonding between carboxylic acid groups.[21] Our FTIR data show that the carbonyl group vibration frequency (1783 cm^{-1}) of TFA molecules in cellulose matrix is consistent with the TFA cyclic dimer.[21] The IR absorption spectra of TFA monomer, cyclic dimer, and linear dimer in supercritical CO_2 have been well characterized.[21] Interestingly, the IR absorption frequency of TFA in cellulose is at the same position as that reported in supercritical CO_2 for the cyclic dimer.[21] The monomeric TFA has an IR absorption band at 1812 cm^{-1} under supercritical CO_2, reflecting an interaction of TFA monomer with CO_2.[21] At a lower temperature, the OH groups in cellulose are not expected to favorably break stronger hydrogen bonding in the dimer, as the proton on the OH groups of cellulose can only form a weaker hydrogen bond with the carbonyl group of the TFA monomer molecule.

TFA molecules are able to penetrate into the cellulose crystalline region in their cyclic dimer form. The percentage of TFA cyclic dimer in TFA liquid is increased by decreasing temperature. We propose this is a predominant cause of the inverse temperature effect on cellulose decrystallization. Increasing temperature leads to more available TFA monomers. At higher temperature, TFA monomers form hydrogen bonds and TFA further reacts with cellulose to form esters. Both result in a retarding penetration rate of TFA monomer through the crystalline cellulose. In addition, water released during esterification further decreases the amount of TFA cyclic dimer. Separate experiments, not shown, indicate that a small amount of water can dramatically decrease the TFA swelling capability.

Nonderivatizing solvents for cellulose usually penetrate into the cellulose crystal region by an electron donor−acceptor interaction.[22] Organic solvents with N → O and C═O dipoles form strong intermolecular interaction between these bonds and cellulose.[22] Our FTIR data suggest that the TFA cyclic dimer

remains intact when it penetrates into the cellulose crystalline region. Therefore, we infer a weak interaction between the −C═O on the TFA cyclic dimer and cellulose OH groups during the cellulose decrystallization process in TFA at 0 °C, however, this interaction was sufficient to disrupt the hydrogen bonding in crystalline cellulose. The mechanism of cellulose decrystallization in TFA at 0 °C or below is therefore different from the mechanism of cellulose decrystallization in traditional nonderivatizing solvents.

5. Conclusions

Cellulose was completely decrystallized in 100 min at 0 °C by TFA treatment. A similar degree of decrystallization was not achieved in 48 h at 25 °C. An inverse temperature effect was observed in the temperature range of −10 to 65 °C. Treating cellulose with TFA at 0 °C or below did not cause an esterification reaction and morphology change on cellulose macrofibrils. Importantly, cellulose decrystallization at 0 °C does not consume TFA molecules. Attempts to remove residual TFA molecules at a higher temperature caused partial esterification of C_6OH.

We interpret the findings as TFA molecules penetrating into the cellulose crystalline region in a cyclic dimer form at 0 °C or below. No strong interaction between TFA cyclic dimer molecules and cellulose was suggested by FTIR results. At higher temperatures, the rate of cellulose decrystallization by TFA monomers is limited by a slow reactive zone migration from the external surface of the macrofibril toward the interior. Water released in the esterification reaction also contributes to a dramatically decreased TFA penetration rate.

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