Acetylation of Cellulose Using Recyclable Polymeric Catalysts

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ABSTRACT: The esterification of cellulose with acetyl chloride in *N*-methyl-2-pyrrolidinone proceeded smoothly using crosslinked polyvinylpyridine (C-PVP) as catalysts. The structures of the cellulose acetates were confirmed by FTIR, ^{1}H-NMR, and ^{13}C-NMR analyses. The molecular weights were determined by GPC, and the thermal properties were characterized with DSC and TGA. The effects of reaction conditions on yields and degree of substitutions were evaluated in detail. C-PVP was recycled by a simple alkali treatment, and the recycled C-PVP could be readily reused as catalysts in cellulose acetylations without adverse effects on the reactions. The influences of C-PVP on the structures of cellulose acetate samples were further discussed. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 3288–3296, 2006

Key words: cellulose; acetylation; cellulose acetate; synthesis; polyvinylpyridine; recyclable polymeric catalysts

INTRODUCTION

Cellulose is the most abundant natural polymer on earth with outstanding properties and a wide variety of applications. However, cellulose is not easy to process because it is neither meltable nor soluble in most conventional solvents, limiting its greater uses. On the other hand, many cellulose derivatives can be dissolved in common organic solvents and/or melted at relatively low temperatures, making them attractive materials in a broad range of fields.[1–2] Among these derivatives, cellulose acetate (CA) is the most commercially significant product. CA was first reported in 1865 and commercialized in 1905,[2] which has been extensively used in coatings, textile fibers, consumer products, optical films, filtration membranes, composites, laminates, and medical applications.[1–5]

Despite the long history and wide availability of CA, its synthesis approaches still warrant further investigations. Today, the industrial manufacturing of CA relies heavily on the so-called "acetic acid process," which involves the activation of cellulose by swelling in acetic acid, followed by acetylation with acetic anhydride in the presence of sulfuric acid or perchloric acid as catalysts. Depending on the final uses, a hydrolysis step may be added to produce secondary cellulose acetate.[6–8] This process offers the advantages of low cost and high productivity, producing CA with reliable quality for many industrial applications. However, due to the harsh conditions employed in the reactions, the acetic acid process is accompanied by serious degradation of the cellulose polymer chains.

Consequently, much effort has been devoted to develop new preparation pathways of cellulose esters. To date, the synthesis of CA and other cellulose derivatives in *N,N*-dimethylacetamide (DMAC)/LiCl, dimethyl sulfoxide (DMSO)/tetrabutyl ammonium fluoride trihydrate, dimethyl formamide(DMF)/chloral/pyridine, NaOH/urea aqueous solutions, molten inorganic salts, ionic liquids, etc., have been reported; some of these investigations have achieved very promising results.[9–16] It is believed that continuous advances in this area may lead to new breakthroughs in cellulose functionalizations.

Although unconventional methods such as *in situ* activation and/or "catalyst-free" syntheses have been developed for cellulose esterifications,[11,17–20] many preparation approaches still use acid chlorides as esterification agents,[3,11,17] and acid scavengers such as pyridine or triethylamine (TEA) as catalysts to facilitate the reactions. However, both pyridine and TEA are toxic and odorous, and they can adversely affect the yield and quality of the final products.[17]

In response to these challenges, we investigated the synthesis of CA in *N*-methyl-2-pyrrolidinone (NMP) using acetyl chloride as acetylation agent, and a polymeric acid scavenger, crosslinked polyvinylpyridine (C-PVP), as catalysts. We chose NMP because it is widely available at low cost and with low toxicity;[21] it

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is a good cellulose-swelling agent; and it is a highly polar aprotic solvent, which can promote the nucleophilic substitution of esterification reactions.[22] C-PVP was selected as catalyst because it is odorless, nontoxic, insoluble, and easy to recycle, making it an attractive candidate as reusable, environmentally friendly acid scavenger. The effectiveness of C-PVP as catalysts in cellulose esterification has been confirmed in the DMAC/LiCl solvent system,[19] but the reusability of C-PVP and the effects of recycled C-PVP on cellulose esterification reactions have never been reported. We found that in the NMP/C-PVP system, cellulose acetate could be synthesized with high yields under mild conditions. The structures of the products were characterized with FTIR, ^{1}H-NMR, ^{13}C-NMR, GPC, DSC, and TGA studies. The new reaction system showed interesting selectivity on the three hydroxyl groups of the anhydroglucose unit (AGU). Furthermore, C-PVP could be recycled by a simple alkali treatment, and the recycled C-PVP could be readily reused in cellulose acetylations.

EXPERIMENTAL

Materials

Cellulose microcrystalline (Baker, Phillipsburg, NJ), NMP (Aldrich, Milwaukee, WI), acetyl chloride (Acros, Fairlawn, NJ), and C-PVP (crosslinked with 2% divinyl benzene, 60-mesh powders, Acros) were used as received. Other chemicals were regent grade and purchased from Fisher Scientific (Fairlawn, NJ).

Instruments

FTIR spectra were recorded on a Thermo Nicolet AVATAR 370 FTIR spectrometer. ^{1}H-NMR and ^{13}C-NMR studies were carried out using a Bruker Advance DRX-400 spectrometer operating at 400 MHz (100 MHz for ^{13}C-NMR spectra). The molecular weights of the samples were measured by gel permeation chromatography (GPC) in DMF, which contained a Waters SEC equipped with two 300-mm Waters Styrgel columns and a Waters 2414 refractive index detector. A series of poly(ethylene glycol) (PEG) samples with molecular weights ranging from 970 to 5.7×10^5 were employed as standards. The thermal analysis of the samples was performed using a differential scanning calorimeter (Shimadzu DSC-60) and a thermal gravimetric analyzer (Shimadzu TGA-50) at a heating rate of 10°C/min under N_2 atmosphere.

Acetylation of cellulose

In acetylation, each experiment was conducted three times. The average values of yield and degree of substitution were reported, and the variation from batch to batch was within 10%. For a typical preparation process of cellulose acetate, 0.5 g cellulose (0.01 mol of hydroxyl functionality[9]) was added into 6.0 mL NMP containing different amounts of C-PVP under constant stirring. A certain amount of acetyl chloride was dropped into the mixture at room temperature in 30 min. The mixtures were stirred at a predetermined temperature for a certain period of time. At the end of the reaction, the mixture was filtered to remove C-PVP, and the filtrates were precipitated into 50 mL ethanol. The precipitates were filtered and dried at 50°C. For further purification, the precipitates were dissolved in 30 mL of NMP, filtered, and the solution was poured into 100 mL of distilled water. The precipitated CA samples were collected, washed with distilled water, and dried at 50°C under reduced pressure. The yield was determined according to eq. (1):

$$\text{Yield } \% = W_1/W_2 \times 100 \quad (1)$$

where W_1 represented the weight of CA obtained from the acetylation reactions (g), and W_2 was the theoretical weight of CA (g) if all the hydroxyl groups of the AGU were substituted.

To determine the degree of substitution (DS) of the samples, approximately 0.2 g dry cellulose acetate was swollen in a flask containing 8 mL of 75% ethanol at 60°C for 30 min. 8 mL of 0.5*N* NaOH ethanol solutions were added. The mixtures were kept at 60°C for 15 min, and then at room temperature for 72 h under constant stirring. Three flasks were used as blanks (same condition, but no CA samples). The excess alkali was titrated with 0.5*N* HCl aqueous solutions to a phenolphthalein end point. Then, 1 mL of 0.5*N* HCl was added, which was back-titrated with 0.5*N* NaOH after standing at room temperature for 24 h. Each sample was titrated three times, and the average was reported. DS was calculated according to the following equations:[23]

$$\% \text{ acetyl} = [(A - B) - (C - D)] \times 2.15/W \quad (2)$$

$$\text{DS} = (3.86 \times \% \text{ acetyl})/(102.4 - \% \text{ acetyl}) \quad (3)$$

where A was the volume of NaOH solutions (mL) added to the sample, B was the volume of NaOH solutions (mL) added to the blank, C was the volume of HCl solutions (mL) added to the sample, D was the volume of HCl solutions (mL) added to the blank, and W was the weight of the CA sample (g).

Recycling of C-PVP

After acetylation, C-PVP was isolated from the reaction media by filtration and neutralized with 10% NaOH aqueous solutions at room temperature for 24 h

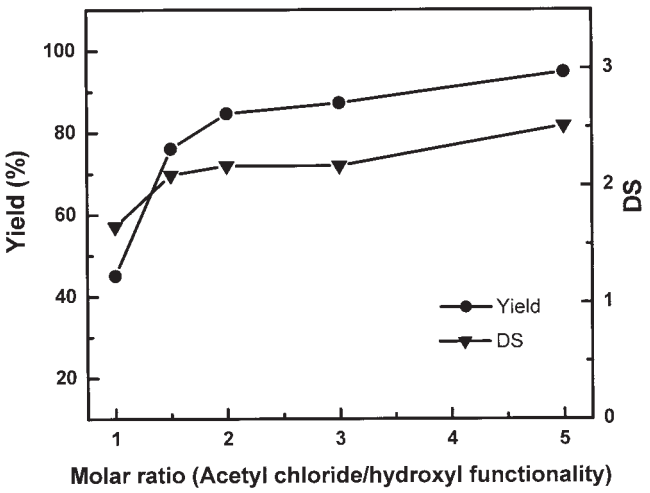


Figure 1 Effects of acetyl chloride/hydroxyl functionality molar ratio on the yield and DS of cellulose acetate (reaction temperature: 80°C; reaction time: 6 h).

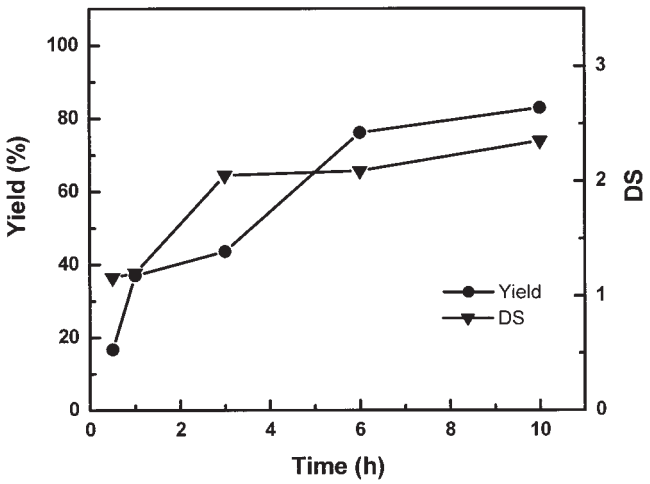


Figure 3 Effects of reaction time on the yield and DS of cellulose acetate (molar ratio: acetyl chloride/hydroxyl functionality = 1.5/1; temperature: 80°C).

(bath ratio: 10/1). After washed thoroughly with distilled water (the washing solution was tested with pH strips to ensure that all the sodium hydroxide was removed), the samples were dried at 100°C to constant weight and reused in cellulose acetylations.

RESULTS AND DISCUSSION

Synthesizing CA in the NMP/C-PVP system

In our screening studies, different solvents including dichloromethane, chloroform, acetone, ethyl acetate, DMF, DMAC, and NMP were employed as solvents in the acetylation of cellulose using C-PVP as catalysts. CA could only be synthesized in the latter three highly polar aprotic solvents. These findings could be related to two factors. First, DMF, DMAC, and NMP could partially break the inter- and intramolecular hydrogen bonds to swell the cellulose molecules. Thus, acetyl chloride could react with hydroxyl groups to synthesize CA. In the meantime, the formed CA dissolved progressively into the solutions as the reaction advanced, so the "hidden" hydroxyl groups became accessible as a result of the "peeling" of cellulose.[24,25] Second, CA was formed through the nucleophilic attack of hydroxyl groups at the partially positively charged carbonyl carbon atoms of acetyl chlorides. According to the reaction mechanism, the more polar the solvent, the faster the reactions because in polar solvents, there was a greater charge in the transition state than in the starting compounds, and the energy of the ionic transition state was reduced by the sol-

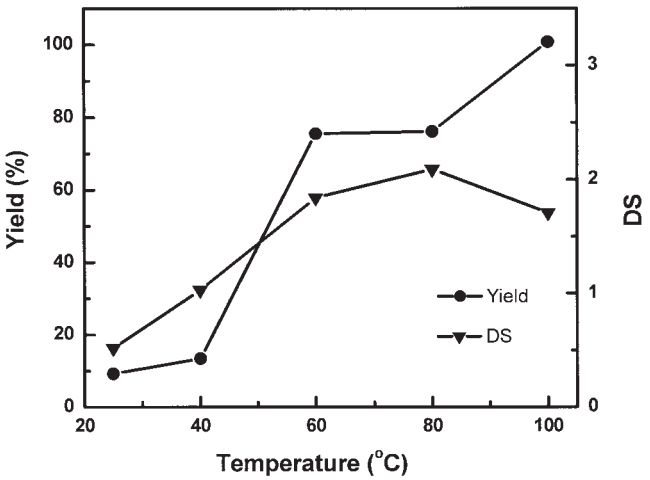


Figure 2 Effects of temperature on the yield and DS of cellulose acetate (molar ratio: acetyl chloride/hydroxyl functionality = 1.5/1; time: 6 h).

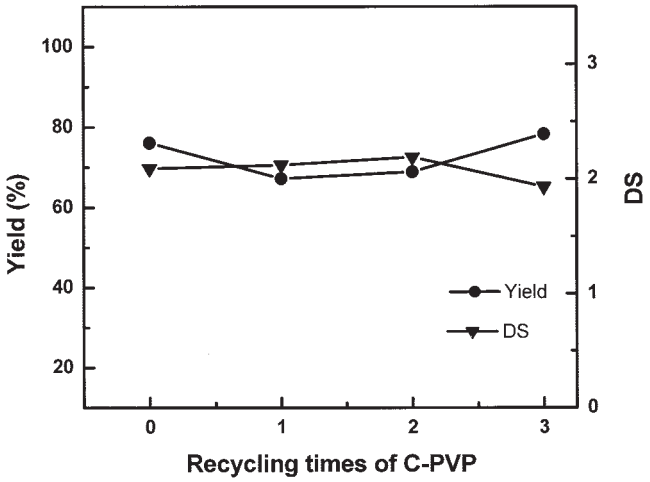


Figure 4 Effects of recycled C-PVP on the yield and DS of cellulose acetate (molar ratio: acetyl chloride/hydroxyl functionality = 1.5/1; temperature: 80°C; time: 6 h).

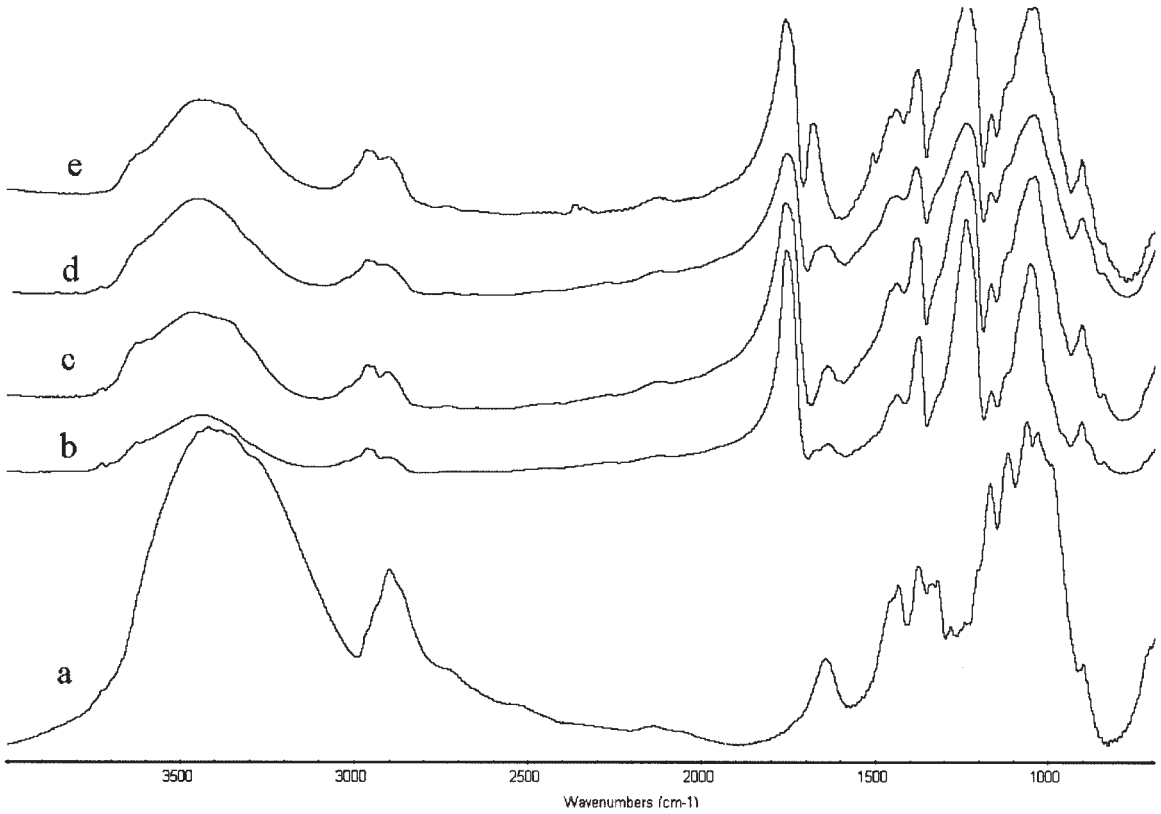


Figure 5 FTIR spectra of (a) pure cellulose, (b) CA synthesized with unrecycled C-PVP, (c) CA synthesized with C-PVP that was recycled once; (d) CA synthesized with C-PVP that was recycled twice; and (e) CA synthesized with C-PVP that was recycled for three times (molar ratio: acetyl chloride/hydroxyl functionality = 1.5/1; temperature: 80°C; time: 6 h).

vents.[22] DMF, DMAC, and NMP had higher polarity than other solvents employed in the studies. As a result, acetylation reactions could be smoothly carried out in these media.

It should be noted that although all the three aprotic solvents could be successfully used in acetylation reactions, their toxicity and safety differ significantly. Among them, NMP had the lowest toxicity.[21] Therefore, NMP was selected as the solvent for our further studies.

The effects of reaction conditions on yield and DS were investigated by varying the molar ratios of acetyl chloride/hydroxyl functionality (the molar ratio of acetyl chloride/C-PVP was kept at 1/1 throughout this study). As shown in Figure 1, if the molar ratio equaled to 1, the yield and DS were rather low, which could be caused by the heterogeneous reaction conditions. Consequently, excess amounts of acetyl chloride and C-PVP were employed to promote the reactions. With the increase of acetyl chloride/hydroxyl functionality molar ratios, the yield and DS values increased rapidly. At a molar ratio of 1.5 : 1, the yield was about 80% and the DS increased to 2.1. After that, both data gradually increased to constant values. When the molar ratio was further increased to 5 : 1, a yield of 95% and a DS of 2.5 could be obtained.

The influences of reaction temperature on cellulose acetylation are presented in Figure 2. In the range of 20–80°C, increasing temperatures significantly increased the yield and DS values. It is believed that at higher temperatures, the swellability of cellulose and the diffusion rate of acetyl chloride increased significantly. Both factors promoted the acetylation reactions. However, at even higher temperatures, although the yield continued to increase (more CA was obtained), the DS began to decrease, which could be caused by the hydrolysis of the ester groups and/or the decomposition of cellulose backbones.

To provide more information about the acetylation reactions, Figure 3 shows the effects of reaction time on the yield and DS values. It can be seen clearly that both of them gradually increased with the increase of reaction time. After 6 h, the data began to level off.

Effects of recycled C-PVP

After acetylation, C-PVP was recycled with a simple alkali treatment. To evaluate the effects of recycled C-PVP on acetylation reactions, Figure 4 shows the relationship between recycling times and the yield and DS values. Keeping other conditions constant, after three times of recycling, the yield and DS values

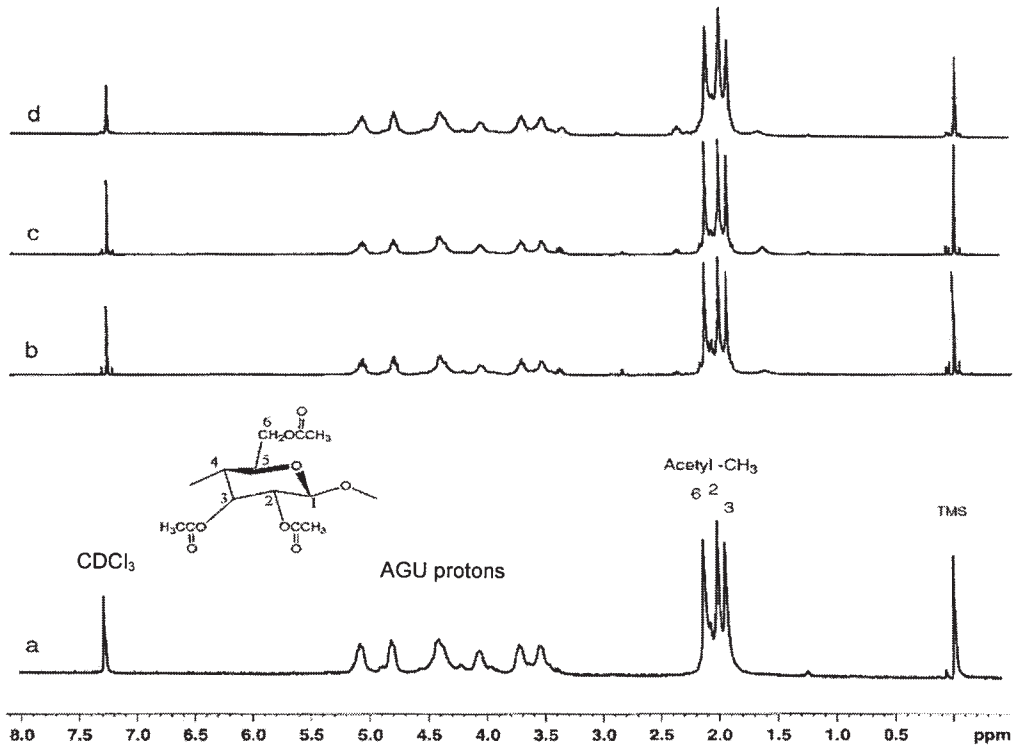


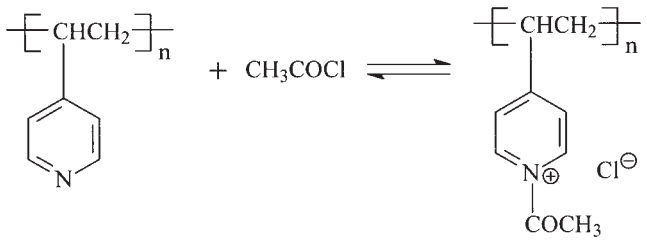
Figure 6 ^{1}H-NMR spectra of CA samples synthesized with (a) unrecycled C-PVP; (b) C-PVP that was recycled once; (c) C-PVP that was recycled twice; and (d) C-PVP that was recycled for three times (molar ratio: acetyl chloride/hydroxyl functionality = 1.5/1; temperature: 80°C; time: 6 h).

were essentially unchanged, suggesting that C-PVP could be a promising recyclable and reusable catalyst for cellulose esterifications.

To examine the effects of recycled C-PVP on the chemical structures of the samples, Figure 5 shows the FTIR spectra of cellulose and CA samples synthesized in the presence of C-PVP with different recycling times. In the spectrum of pure cellulose [Fig. 5(a)], the broad peak centered at 3450 cm^{-1} was related to hydroxyl groups, and the 1635 cm^{-1} band was attributable to the water of hydration.[26] In the IR spectra of the CA samples [Figs. 5(b–e)], the intensity of the 3450 cm^{-1} band markedly decreased. Moreover, a sharp peak at 1755 cm^{-1} could be observed, which must be caused by the stretching vibrations of the carbonyl groups.

The FTIR results were confirmed by ^{1}H-NMR studies. All the CA samples displayed similar proton signals, as shown in Figure 6. Among these signals, the multiple bands in the region of 3.4–5.3 ppm were attributed to the AGU protons, and the peaks in the range of 1.8–2.2 ppm were correspondent to the methyl protons of the acetyl groups.[25] It should be noted that early studies have shown that the NMR spectra of partially substituted cellulose esters were complicated, and it was difficult to assign the acetyl proton signals.[25,27–30] This was largely caused by the irregular distribution of the acetyl groups. In each AGU, three hydroxyl groups were available for esterification reactions. Before a total substitution was achieved (DS = 3), cellulose acetate samples could have seven differently acetylated AGUs, and these could have a total of 12 magnetically different acetyl groups, which significantly complicated the NMR spectra of the samples.[30] Therefore, a perdeuterioacetylation technique was recommended to simplify the NMR analysis, which involved the conversion of the residual hydroxyl groups into deuterated acetyl groups through reaction with acetyl chloride-d_3.[25,29,30] After perdeuterioacetylation, the proton signals corresponding to the 2-, 3-, and 6- acetyl groups in the glucose residues could be distinguished.

However, our study showed that without perdeuterioacetylation, all the partially substituted CA sam-



Scheme 1 Intermediate formation between C-PVP and acetyl chloride.

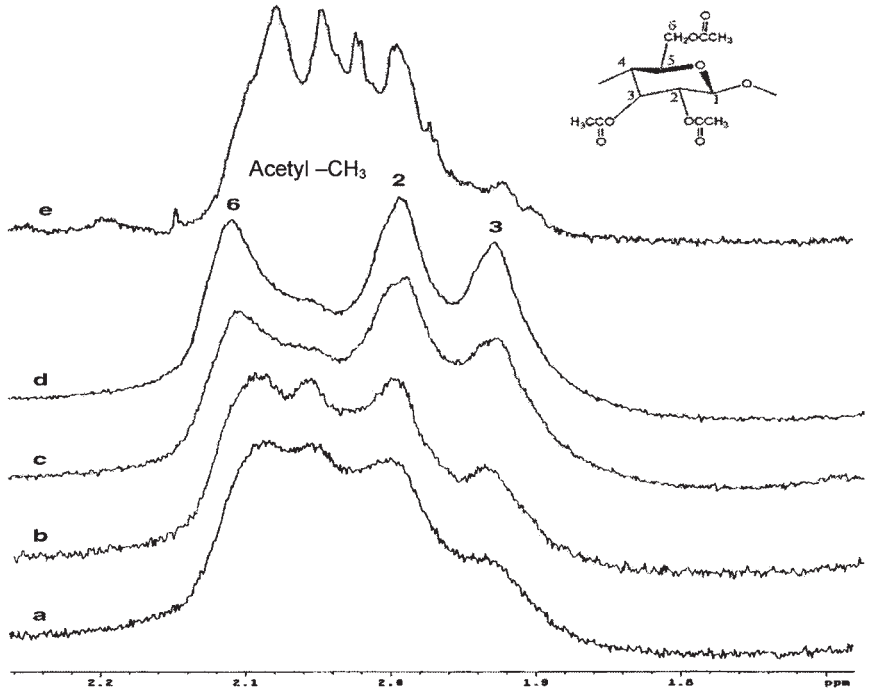


Figure 7 ^{1}H-NMR spectra of CA samples synthesized with unrecycled C-PVP after (a) 30 min; (b) 1 h; (c) 3 h; and (d) 6 h of reactions; and (e) CA samples synthesized using un-crosslinked and unrecycled PVP after 6 h of reactions (molar ratio: acetyl chloride/hydroxyl functionality = 1.5/1; temperature: 80°C).

ples (DS ~ 2.0. See Fig. 4 for details) showed three clearly distinguishable peaks at 1.95, 2.01, and 2.13 ppm, which were assigned to the methyl protons of the acetyl groups substituted at positions 3, 2, and 6 of the repeating units, respectively.[25] A possible reason for this phenomenon might be related to C-PVP. In this system, acetyl chloride could form highly reactive intermediates with C-PVP, as shown in Scheme 1.[31–33] At the beginning of the reactions, these intermediates might only play a minor role because both cellulose and the intermediates were insoluble in NMP. With the increase of reaction time, however, some partially substituted cellulose acetates were formed through the reaction of cellulose with acetyl chloride, which were soluble in NMP. These CA samples could react with the intermediates at the surfaces of C-PVP. The intermediates had much higher reactivity than acetyl chloride, but their mobility was lower. Therefore, the contact of the hydroxyl groups with the intermediates might be the rate-determining step. Thus, CA samples with high DS values might have lower chance for the reaction, and those with low DS values could react faster because they had more "free" hydroxyl groups. Consequently, the intermediates might "level off" the DS values, and relatively even distributions of the acetyl groups could be obtained.

This hypothesis was supported by the following observations: (1) As shown in Figure 7, at the beginning of the reactions, the acetyl proton signals of CA samples showed complicated patterns in ^{1}H-NMR studies, but with the increase of reaction time, three distinguishable peaks could be observed [Fig. 7(a–d)]; and(2) keeping other conditions constant, if uncrosslinked PVP was used as catalysts, the acetyl protons exhibited multiple peaks in the NMR spectrum (see particularly the difference between spectrum (d) and spectrum (e) of Fig. 7). It is also interesting to note that Heinze's group used C-PVP to synthesize cellulose acetates in DMAC/LiCl using acetyl chloride as acetylation agent.[19] They found that if a large excess of C-PVP was used, the resultant CA formed strong interactions with C-PVP, which could not be separated

TABLE I
Distribution of Acetyl Groups at Positions 2-, 3-, and 6- of the AGU Using C-PVP as Catalysts in the Acetylation Reactions

C-PVP recycling times[a]	DS[b]	Percentage of acetyl group at different positions (%)[c]		
		Position 3	Position 2	Position 6
0	2.09	27.8	35.9	36.3
1	2.12	27.3	35.7	37.0
2	2.19	27.6	36.1	36.3
3	1.93	26.3	37.0	36.6

[a] Number of times that C-PVP was recycled before it was used in the acetylation reactions.
[b] Degree of substitution obtained from titration (see the Experimental section).
[c] Calculated based on ^{1}H-NMR signals (see the text for details).

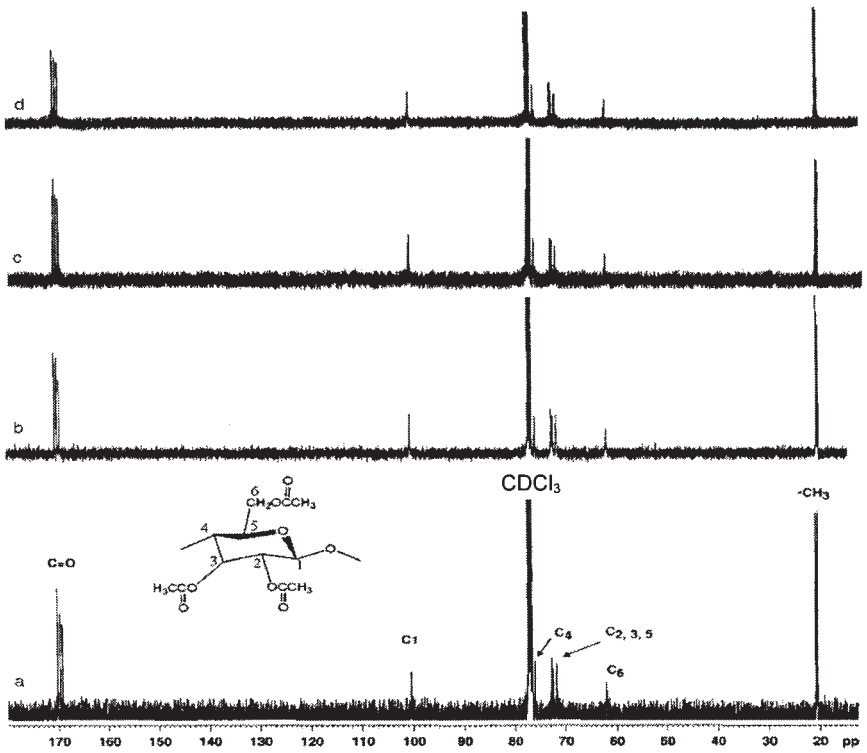


Figure 8 ^{13}C-NMR spectra of CA samples synthesized with (a) unrecycled C-PVP; (b) C-PVP that was recycled once; (c) C-PVP that was recycled twice; and (d) C-PVP that was recycled for three times (molar ratio: acetyl chloride/hydroxyl functionality = 1.5/1; temperature: 80°C; time: 6 h).

by solvent extraction. If un-crosslinked PVP was used, this phenomenon could not be detected. These findings might imply that in the presence of C-PVP, acetylation reactions could occur on the surfaces of C-PVP.

The clearly distinguishable methyl proton signals in the ^{1}H-NMR spectra offer the possibility to estimate the reactivity of the three AGU hydroxyl groups. For example, when unrecycled C-PVP was used in the

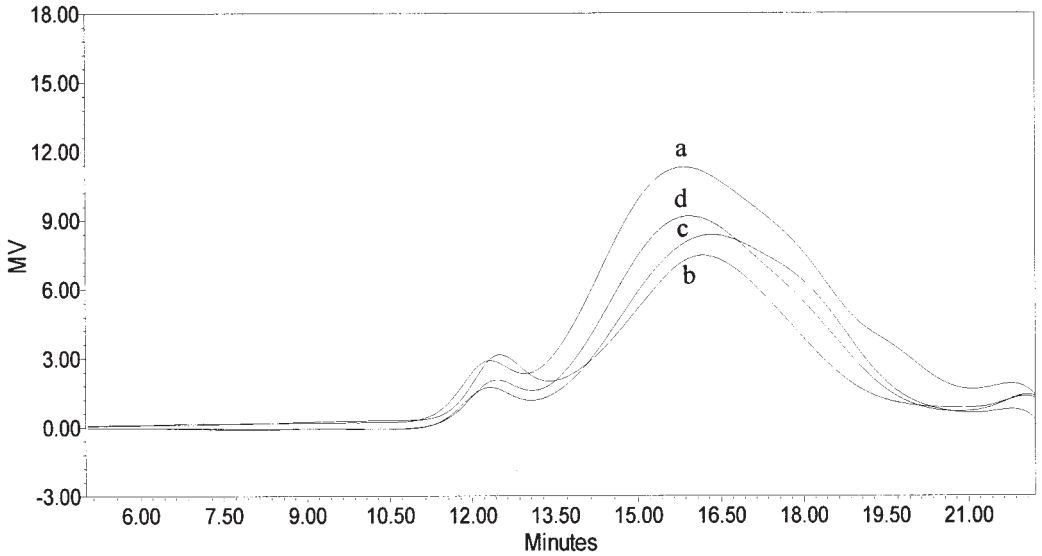


Figure 9 GPC curves of CA samples synthesized with (a) unrecycled C-PVP; (b) C-PVP that was recycled once; (c) C-PVP that was recycled twice; and (d) C-PVP that was recycled for three times (molar ratio: acetyl chloride/hydroxyl functionality = 1.5/1; temperature: 80°C; time: 6 h).

synthesis, the DS value of the corresponding CA sample was 2.1, and the integration ratio of the 1.95, 2.01, and 2.13 ppm peaks was 2.25/2.91/2.94, indicating that among the substituted acetyl groups, about 27.8% of them attached to position-3, about 35.9% connected to position-2, and approximately 36.3% substituted at position-6. Similarly, acetyl distributions in other CA samples were calculated, as summarized in Table I. The general trend was that the primary hydroxyl group (position-6) showed similar reactivity as the hydroxyl group at position-2, and both of them were slightly more reactive than the hydroxyl group at position-3. Again, these findings suggest that C-PVP might have "leveling off" effects on the acetylation reactions.

To provide further information regarding the effects of recycled C-PVP on CA structures, Figure 8 shows the ^{13}C-NMR spectra of the samples. As expected, all the samples exhibited very similar carbon signals. In these spectra, the signals corresponding to the AGU carbons located in the region of 60–105 ppm. The methyl carbons exhibited three lines around 20 ppm, and the carbonyl carbons showed signals around 170 ppm. All these observations were in good agreement with the literature data.[25]

The effects of recycled C-PVP on the molecular weights of CA samples were investigated using GPC. As shown in Figure 9, all the samples displayed two humps in the elution chromatograms. The small prehump around 12.5 min could be caused by microgels,[25] and the main humps in the range of 13.7–20.0 min were corresponding to cellulose acetates. The broadness of the CA humps suggested that the samples had relatively wide molecular weight distributions. From the calibration curve generated from PEG standards, the molecular weights and molecular weight distributions of the samples were obtained; the data was listed in Table II. The number average molecular weights (M_n) of the samples were in the range of 1.3×10^4–2.1×10^4 Da, and the weight average molecular weights (M_w) were around 4.0×10^4–4.7×10^4 Da (PEG equivalent), which were comparable to the molecular weight of the original cellulose sample (4.2×10^4 Da based on viscosity measurements[3,4]).

TABLE II
Molecular Weight and Molecular Weight Distribution of CA Samples Synthesized Using C-PVP as Catalysts

C-PVP recycling times[a]	M_n	M_w	Polydispersity[b]
0	13617	45237	3.32
1	21008	45362	2.16
2	13746	40272	2.93
3	18018	47055	2.61

[a] Number of times that C-PVP was recycled before it was used in the acetylation reactions.
[b] Polydispersity = M_w/M_n.

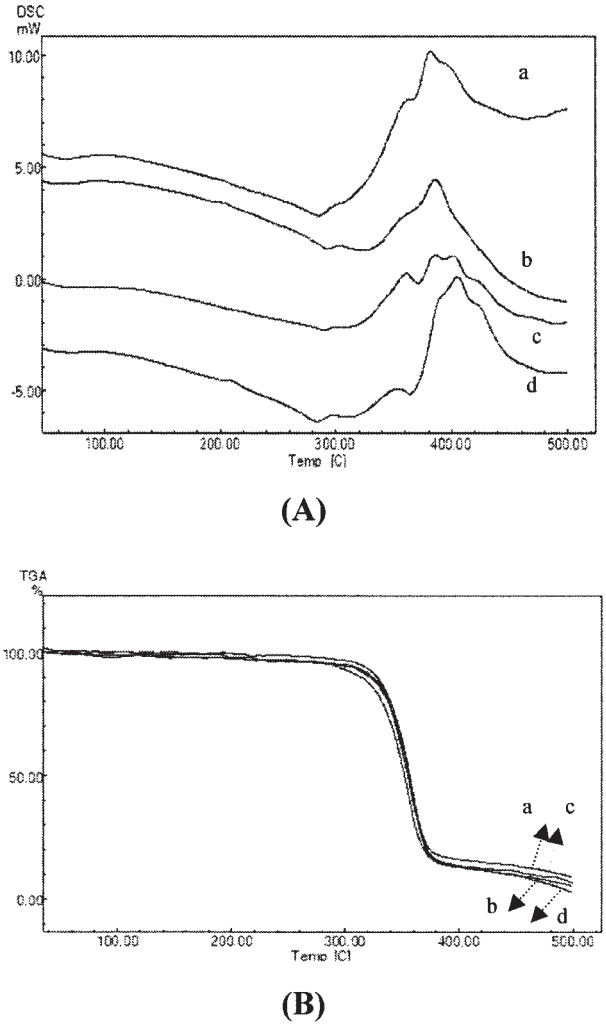


Figure 10 (A) DSC curves of CA samples; and (B) TGA curves of CA samples. The samples were synthesized with (a) unrecycled C-PVP; (b) C-PVP that was recycled once; (c) C-PVP that was recycled twice; and (d) C-PVP that was recycled for three times (molar ratio: acetyl chloride/hydroxyl functionality = 1.5/1; temperature: 80°C; time: 6 h).

The use of recycled C-PVP did not seem to affect the molecular weights and the molecular weight distributions of the products.

The thermal properties of CA samples were examined in DSC and TGA studies, as shown in Figure 10. In the DSC curves [Fig. 10(A)], CA samples showed weak melting peaks in the range of 280–290°C.[34] The strong exothermal peaks at higher temperatures could be caused by decomposition, which was confirmed in TGA studies by the fast weight loss of the samples [Fig. 10(B)]. All the samples displayed similar DSC and TGA curves, further suggesting that recycled C-PVP could be readily reused in acetylation reactions.

CONCLUSIONS

C-PVP was used as catalyst in the acetylation of cellulose with acetyl chloride in NMP. The effects of

reaction conditions on cellulose esterifications were established. The samples were characterized with FTIR, ^{1}H-NMR, ^{13}C-NMR, GPC, DSC, and TGA analysis. Cellulose acetate with a DS up to 2.5 could be smoothly prepared using the new approach. C-PVP showed a unique "leveling off" effect on the substitution reactions. Upon a simple alkali treatment, C-PVP could be recycled and readily reused in further acetylations, which showed little effect on the reactions and the structures of the CA samples.

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