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A novel transesterification system to rapidly synthesize cellulose aliphatic esters

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Abstract Cellulose aliphatic esters (CEs) are important cellulose derivatives that have been widely used in many fields such as plastics, textiles, membranes, etc. However, in traditional methods, long pretreatment and reaction times limit the manufacture of CEs and their widespread application. Herein, a very efficient method for the preparation of CEs in a heterogeneous system was developed. This method involved the transesterification of cellulose with vinyl esters (from C4 to C14) in dimethylsulfoxide under the catalysis of aqueous NaOH. For better understanding of this new reaction system, factors such as the water content, amount of catalyst, reaction temperature and molar ratio of vinyl acetate to the anhydroglucose unit were explored. Results obtained from FT-IR, ^{1}H and ^{13}C NMR spectroscopies confirmed that CEs could be synthesized at 100 °C within 5 min. High water content or excessive amounts of NaOH were detrimental to the synthesis of CEs. Results from small-angle X-ray diffraction showed that the interplanar spacings of these CEs showed an increasing trend with the length of the aliphatic chain. Thermogravimetric analysis and derivative thermogravimetric analysis showed that CEs had higher thermal stability than cellulose. This work provides a new and highly efficient method to synthesize various CEs.

Introduction

Lignocellulosic biomass, mainly containing cellulose, hemicelluloses and lignin, shows promising potential application in various areas and has been considered an ideal alternative to obtain energy, chemicals and materials from petroleum resources (Balat and Balat 2009; Dodds and Gross 2007; Gandini 2008). Cellulose is one of the most abundant, renewable and biodegradable lignocellulosic resources; the development and application of cellulose-based functional polymers and materials have attracted widespread attention (Heinze et al. 2007; Zhou et al. 1995).

Cellulose aliphatic esters (CEs) are one kind of the most important cellulose derivatives and have been applied in membranes, fibers, plastics and filters for decades; they play important roles in various aspects of our daily lives and industry (Rustemeyer 2004; Edgar et al. 2001; Shibata 2004; Sata et al. 2004). By now, most CEs are synthesized by esterification of cellulose with the corresponding acids, acid

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anhydrides or acyl chlorides in heterogeneous or homogeneous systems (Balser et al. 2000). Many reports showed that cellulose could react with fatty acids, acid anhydrides or acyl chlorides in DMAc/LiCl (Satge et al. 2002; Vaca-Garcia et al. 1998), ionic liquids (Liu et al. 2007; Wu et al. 2004) and DMSO/TBAF (Ass et al. 2004) to homogeneously synthesize CEs. Among these solvent systems, ionic liquids are found to be powerful solvents for cellulose dissolving and have been widely used in cellulose modification. Because of the dissolving of cellulose, the hydroxyl groups of cellulose could react with esterifying agents readily and homogeneously (Liu et al. 2007; Wu et al. 2004). However, the expensive solvents and the time-consuming process of cellulose dissolution limit their industrial application. Therefore, the manufacture of CEs is always carried out under heterogeneous conditions (Hummel 2004). For example, cellulose can react with acetic anhydride in acetic acid in the presence of sulfuric acid as a catalyst and produce CA (Saka 2004). However, because the glycosidic oxygen bond of cellulose is subject to acidic hydrolysis, the degradation of cellulose is always severe during the pretreatment and acetylation process (Hummel 2004). Furthermore, there are strict requirements to the cellulosic materials used in the manufacture of CA, and long pretreatment and reaction times are also indispensable. Therefore, these deficiencies limit the manufacture of CEs and their widespread application.

Transesterification is an important method used in numerous applications in the food, cosmetic and pharmaceutical sectors (Vicente et al. 2004), and it has shown promising application in producing polyethylene terephthalate and biodiesel (Kim et al. 2004; Santacesaria et al. 1994). Synthesis of polysaccharide esters by transesterification was also reported. Rooney (1976) studied the transesterification of starch with methyl esters of palmitic, lauric and actanoic acids in DMSO using potassium methoxide as catalyst, and a series of starch esters were synthesized heterogeneously. Heinze et al. (2000) reported that cellulose could react with various vinyl esters homogeneously in a DMSO/TBAF system with or without catalyst. Ferreira et al. used enzymes to catalyze the transesterification of inulin and dextran with vinyl acrylate in DMF or DMSO and prepared polysaccharide-containing hydrogels (Ferreira et al. 2002a, b; Wu et al. 2004). In addition, regioselective esters of starch, cyclodextrines and similar polysaccharides were synthesized

via transesterification with vinyl acetate in DMSO using Na_2HPO_4 as catalyst (Dicke 2004). Çetin et al. reported that cellulose nanowhiskers could react with vinyl acetate in DMF under the catalysis of K_2CO_3, producing acetylated cellulose nonowhiskers (Çetin et al. 2009). In all of these cases, however, long pretreatment and/or reaction times (from hours to days) were required, and for many of them the reactions could only occur on the surface of cellulose materials (Çetin et al. 2009; Ferreira et al. 2002b; Heinze et al. 2000; Rooney 1976; Xie and Hsieh 2001).

In this work, a new and highly efficient reaction system containing dimethyl sulfoxide, aqueous NaOH and vinyl esters was developed to rapidly synthesize a series of CEs by transesterification within 5 min. The structures of these CEs were comparatively studied by Fourier transform infrared (FTIR) spectroscopy, wide-angle and small-angle X-ray diffraction patterns (WAXD and SAXD), and ^1H NMR, and ^{13}C NMR spectroscopies. In addition, their thermal behaviors were also analyzed using thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG). This work supplies a simple and rapid method to prepare various CEs.

Experimental section

Materials

Microcrystalline cellulose (MCC) was purchased from Sinopharm Chemical Reagent Co., which was dried in an oven at 105 °C for 12 h before utilization. According to the method of ISO/FDIS 5351:2009, the degree of polymerization (DP) of MCC was 211. Vinyl acetate, vinyl propionate, vinyl butyrate, vinyl hexanoate, vinyl octanoate, vinyl dexanoate and vinyl laurate stabilized with 4-methoxyphenol were purchased from Tokyo Chemical Industry Co. Other chemicals, like NaOH and anhydrous ethanol, were all analytical reagents and used as received.

Preparation of cellulose acetate under different conditions

The synthesis of cellulose acetate (CA) was carried out in a 25-ml three-neck flask equipped with a magnetic stirrer and a condenser; 2.5 mmol (anhydroglucose

units, 162 g/mol) of dried MCC was added to the flask containing DMSO. The required amount of NaOH solution was added at room temperature and stirred for 5 min to activate the cellulose hydroxyl groups. The mixture was then transferred into an oil bath heated at the desired temperature for another 2 min. Then vinyl acetate was poured at once into the mixture under vigorous stirring for 5 min. The pH of this medium was observed to decrease dramatically from strong basicity to almost neutrality within 2–3 min because of the hydrolysis of vinyl acetate. Then, the mixture was precipitated with an excess volume of ethanol. The product was filtered and washed with ethanol thoroughly and then dried in a vacuum oven at 60 °C overnight.

Synthesis of various CEs

In a three-neck flask equipped with a magnetic stirrer and a condenser, 5.0 mmol of MCC (anhydroglucose units, 162 g/mol), 20 or 40 ml of DMSO, and 1.0 ml of aqueous NaOH solution (10 mol/l) were added. The mixture was stirred at room temperature for 5 min and then transferred into an oil bath (100 °C) for another 2 min. Then 30 mmol of vinyl ester was added into the mixture with vigorous stirring for 5 min. Finally, the mixture was dialyzed against ethanol, acetone and water at 50 °C for 3 days, respectively. The product was freeze-dried to obtain white powder. According to the carbon atom number of the aliphatic chain in the vinyl esters, these CEs were named CE2, CE3, CE4, CE6, CE8, CE10 and CE12; 20 ml of DMSO was used in the synthesis of CE2, CE3, CE4 and CE6, while 40 ml of DMSO was used in CE8, CE10 and CE12.

Determination of DP of MCC

Dried MCC (0.15 g) was added into a dissolving bottle with 25.0 ml of water. Then, 25.0 ml of cupri-ethylenediamine solution (CED, 1.0 mol/l) was gradually added to the dissolving bottle with magnetic stirring. The bottle was immersed in a water bath at 25 °C and placed in the dark for 10 min. Then, the limiting viscosity number of this mixture could be calculated by the efflux time determined from a viscometer. The DP of cellulose could be obtained from the following equation (Sihtola et al. 1963):

$$DP^{0.905} = 0.75 \times [\eta]$$

where DP and $[\eta]$ are the degree of polymerization of cellulose and the calculated limiting viscosity number, respectively.

## Determination of the degree of substitution of CA and CEs

The degree of substitution (DS) of CA was calculated by integration of the areas of the ^{1}H NMR peaks. An integral between 2.80 and 5.20 ppm (except the yellow section from residual water) assigned to the seven protons of the anhydroglucose unit (AGU) was used as reference, and one third of the integral of the areas of the ^{1}H NMR peaks from methyl protons was calculated as the DS of CA. The DSs of other CEs were determined by the heterogeneous saponification method (ASTM D871-96).

Characterization of various CEs

FT-IR spectra of MCC and seven as-prepared CEs were recorded on a Bruker spectrophotometer in the range of 400–4,000 cm^{-1} with a resolution of 4 cm^{-1}. A KBr disc containing 1 % finely ground sample was used for measurement. WAXD and SAXD of MCC and CEs were performed on a D8 Advance instrument (Bruker AXS) with Ni-filtered Cu Kα radiation (wavelength = 0.154 nm) from 5° to 60° and 1° to 10°, respectively. The ^{1}H NMR and solution-state ^{13}C NMR spectra were obtained on a Bruker AVIII 400-MHz spectrometer in DMSO-$d6$ with a minimum of 256 and 20,000 scans, respectively. The solvent signals were used as internal standards for both ^{1}H NMR and solution-state ^{13}C NMR. The solid-state ^{13}C NMR spectra were performed on the same spectrometer at 100 MHz in 4-mm zirconia rotors. Thermal behaviors of MCC and CEs were analyzed using TGA and DTG. TGA was performed on a TG-Q500 (TA Instruments, New Castle, DE, USA) under nitrogen flow at a heating rate of 20 °C/min from ambient temperature to 700 °C.

Results and discussion

The transesterification reaction has been applied in the synthesis of polysaccharide esters. However, most of these reactions either took a long time (hours to days)
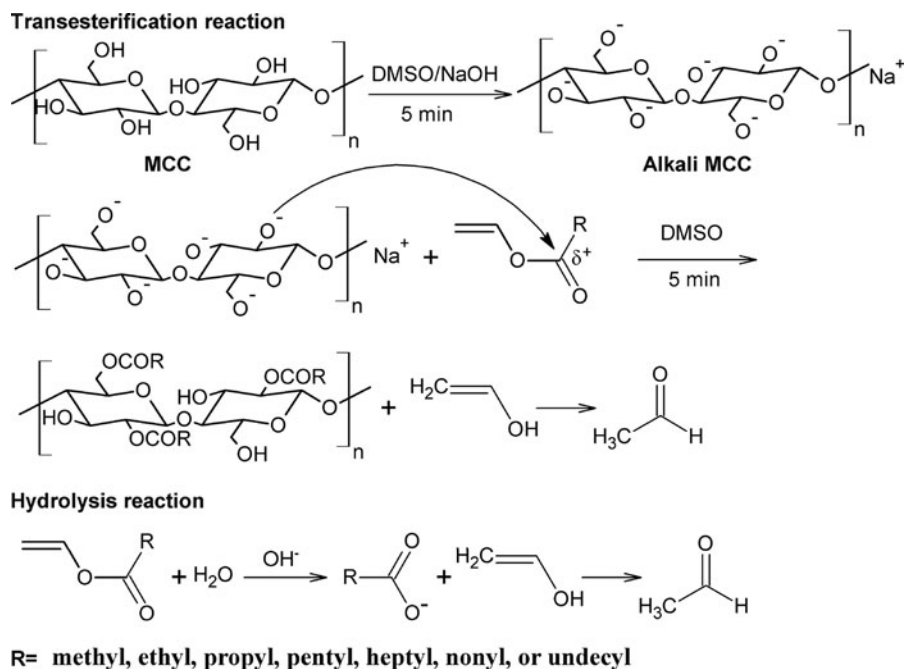
Scheme 1 Transesterification and hydrolysis reaction during the synthesis of CEs

Fig. 1 The digital and polarizing microscope images of the mixture in the reaction process
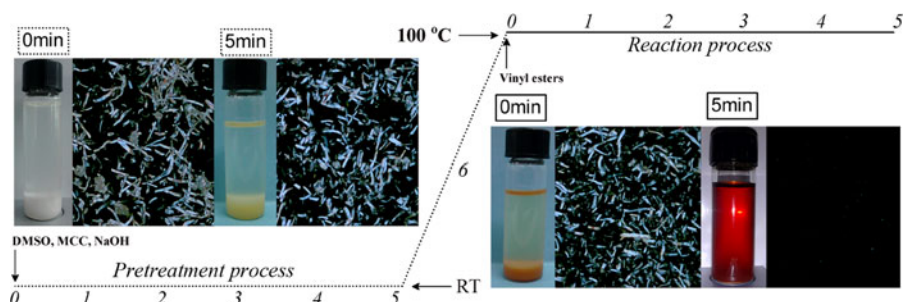
or could not react homogeneously (Dicke 2004; Gremos et al. 2011; Itoh et al. 2003; Shogren and Biswas 2010; Xie and Hsieh 2001). In this work, a novel reaction system was introduced to synthesize CEs in minutes. Scheme 1 shows the transesterification reaction (major reaction) and hydrolysis reaction (side reaction) during the synthesis of CEs. Transesterification leads to the formation of CEs, while hydrolysis causes the excessive utilization of vinyl esters.

In this work, the effects of reaction conditions on the synthesis of CA were investigated. The digital and polarizing microscope images of the mixture in the reaction process were also recorded and illustrated in Fig. 1. It is interesting to observe that almost all MCC crystals disappeared within 5 min after adding vinyl

acetate, suggesting the rapid reaction of cellulose with vinyl acetate in this new reaction system.

Effects of reaction conditions on the synthesis of CA

Table 1 shows the influences of reaction conditions on the DS of CA. The water content and molar ratio of NaOH to AGU show a significant effect on the DS of CA. The DS of CA1 (1.44) is much lower than that of CA2 (2.13) and CA3 (2.39). This is most likely because the hydrolysis of vinyl acetate is more extensive in the medium with higher water content. It was reported that low water and acid contents were required in the production of polyethylene terephthalate and biodiesel, because water and acid would lead

Table 1 Influences of reaction conditions on the DS of CA

Samples[a]	NaOH (ml)[b]	NaOH (mol/l)[c]	DMSO (ml)	NaOH/AGU (mol:mol)[d]	VAc/AGU (mol:mol)[e]	Temperature (°C)	DS[f]
CA1	2.0	2.5	8.0	2:1	6:1	100	1.44
CA2	1.0	5.0	9.0	2:1	6:1	100	2.13
CA3	0.5	10.0	9.5	2:1	6:1	100	2.39
CA4	1.0	7.5	9.0	3:1	6:1	100	1.83
CA5	1.0	10.0	9.0	4:1	6:1	100	1.41
CA6	0.5	10.0	9.5	2:1	9:1	100	2.45
CA7	0.5	10.0	9.5	2:1	12:1	100	2.51
CA8	0.5	10.0	9.5	2:1	6:1	80	2.25
CA9	0.5	10.0	9.5	2:1	6:1	120	2.42

[a] 2.5 mmol of MCC (based on AGU) is used in all the samples

[b] NaOH (ml) means the volume of aqueous NaOH used

[c] NaOH (mol/l) represents final molar concentrations of aqueous NaOH in the reaction medium

[d] NaOH/AGU means the molar ratio of NaOH to the anhydroglucose unit

[e] VAc/AGU means the molar ratio of vinyl acetate to the anhydroglucose unit

[f] DS is calculated from ^{1}H NMR

to the severe hydrolysis of dimethyl terephthalate or fatty glyceride (Fukuda et al. 2001; Schuchardt et al. 1998). Therefore, a low water content works in favor of the production of cellulose acetate with high DS. It should be noted that NaOH is insoluble in DMSO, while solid NaOH showed a poor catalytic effect due to its limited contact surface with reactants; thus, aqueous NaOH solvent was used in this work. As the amount of NaOH increases from 5.0 to 10.0 mmol, the DS of CA shows a declining tendency (from 2.13 to 1.41), which may be because excessive NaOH would result in the extensive hydrolysis of vinyl acetate (Weber et al. 1999). On the other hand, if the content of NaOH is reduced significantly, the reaction will be interrupted by the complete consumption of NaOH caused by vinyl esters hydrolysis; thus, crystals of unreacted MCC could be clearly observed in the reaction solution by an optical polarizing microscope. In addition, the DS of CA shows a slight increase with the reaction temperature or the molar ratio of vinyl acetate to AGU. When the reaction temperature was below 80 °C or the molar ratio of vinyl acetate to AGU was less than 6:1, plenty of MCC crystals still could be observed in the reaction mixture, indicating the incompletion of transesterification. It can be deduced that in the above reaction conditions, hydrolysis was more dominant than transesterification and vinyl acetate or NaOH was exhausted before the completion

of transesterification. Therefore, because of the hydrolysis competing with transesterification, any factor contributing to the hydrolysis reaction is likely to result in the incomplete transesterification of cellulose with vinyl acetate.

In addition, to investigate the degradation of cellulose in this system, the DP change of MCC in the DMSO/NaOH system as a function of time was determined. The DPs of MCC, MCC treated with DMSO/NaOH at room temperature for 5 min, and MCC treated with DMSO/NaOH at room temperature for 5 min and then treated at 100 °C for another 7 min are 211, 210 and 193, respectively. It can be seen that minor degradation of MCC indeed occurred in the DMSO/NaOH system at high temperature, but the degradation was negligible in such a short time. Furthermore, during the synthesis of CEs, the hydrolysis of vinyl esters makes the pH of this system decrease dramatically from strong basicity to almost neutrality within a short time (~ 2 min), which will decrease the degradation of products.

Synthesis of CEs

The synthesis of various CEs was performed according to the optimized condition in the synthesis of CA. In order to reduce the viscosity of the mixture during the synthesis of CE8, CE10 and CE12, 40 ml of

Table 2 Dissolution, DS and interplanar spacing of various CEs

Dissolution[b]	Samples[a]						
	CE2	CE3	CE4	CE6	CE8	CE10	CE12
Acetone	+	+	+	+	−[b]	−	−
THF	+	+	+	+	+	+	−
Pyridine	++	++	++	++	+	+	+
DMSO	++	++	++	++	+	+	−
Chloroform	+	+	+	+	−	−	−
DMF	++	++	++	++	−	−	−
DS[c]	2.02	1.28	1.53	1.47	0.79	0.89	0.76
d[d]	10.33	11.47	13.37	18.09	22.43	25.99	31.70

[a] 5.0 mmol of MCC (based on AGU), 1.0 ml of 10 mol/l NaOH, 30 mmol of vinyl esters and 20 or 40 ml of DMSO were used to synthetize these cellulose esters

[b] "+" means swellable; "++" means soluble; "−" means insoluble

[c] DS was calculated by the heterogeneous saponification method (ASTM D871-96)

[d] The interplanar spacing value was calculated according to Bragg's equation

DMSO was used instead of 20 ml. It was found that CEs with short chains (C2–C4) could dissolve in the reaction solution and rapidly form the homogeneous phase, while CEs with relatively long chains (C6–C12) could not form transparent reaction solution. The DS values of CEs are illustrated in Table 2. On the whole, the DS values of CEs showed a tendency to decrease with increasing aliphatic chain length (from 2.02 for CE2 to 0.76 for CE12). This result is probably related to the relatively long-chain vinyl esters or the decreasing solubility of CEs in DMSO with the increase of the aliphatic chain.

The dissolution of various CEs in different solvents was tested and illustrated in Table 2. It can be seen that CE2, CE3, CE4 and CE6 with short aliphatic chains could be dissolved in pyridine, DMSO and DMF, but swellable in acetone, THF and chloroform. However, CEs with long aliphatic chains (CE8, CE10 and CE12) could not be dissolved in any of these solvents, but can only swell in THF, DMSO and chloroform (except CE12). The poor dissolution of these CEs with long aliphatic chains is likely related to their relatively low DS and poor distribution of DS.

FT-IR spectra

The FT-IR spectra of MCC and all CEs are illustrated in Fig. 2. The signal at 2,957 cm^{-1} originates from the asymmetric stretching of the alpha-saturated methyl groups, while the sharp peaks at 2,924, 2,855 and 1,420 cm^{-1} are assigned to the CH$_2$ asymmetric, symmetric stretching and scissoring of the methylene groups, respectively (Jandura et al. 2000a). As the aliphatic chain of CEs grows, the area of the methylene peaks increases as compared with that of the methyl group, indicating the increase in the relative content of methylene to methyl groups. The strong signals at around 1,749 and 1,163 cm^{-1} are due to the C=O and C–C–O stretching absorption of saturated carboxylic esters (Schilling et al. 2010) and appear in all CE spectra except MCC. These characteristic signals suggest the rapid synthesis of CEs.

Wide-angle and small-angle X-ray diffraction pattern

WAXD and SAXD were carried out to investigate the crystalline structure of CEs with various aliphatic chains. Patterns of MCC, alkali MCC and their CEs are all illustrated in Fig. 3. MCC shows five characteristic peaks at around $2\theta = 14.9°$, 16.7°, 20.6°, 22.9° and 34.4°, normally assigned to the diffraction planes 101, 10$\bar{1}$, 021, 002 and 004, respectively, suggesting a typical pattern of cellulose I (Jandura et al. 2000a; Liu and Hu 2008). Alkali MCC separated before the addition of vinyl esters shows peaks with decreasing intensities at $2\theta = 12.2°$, 20.5° and 21.8°, which are assigned to the structure of cellulose II (Liu and Hu 2008). All CEs show similar patterns at the diffraction angle greater than 15.0°, and the diffraction intensity

Fig. 2 FT-IR spectra of
MCC and CEs
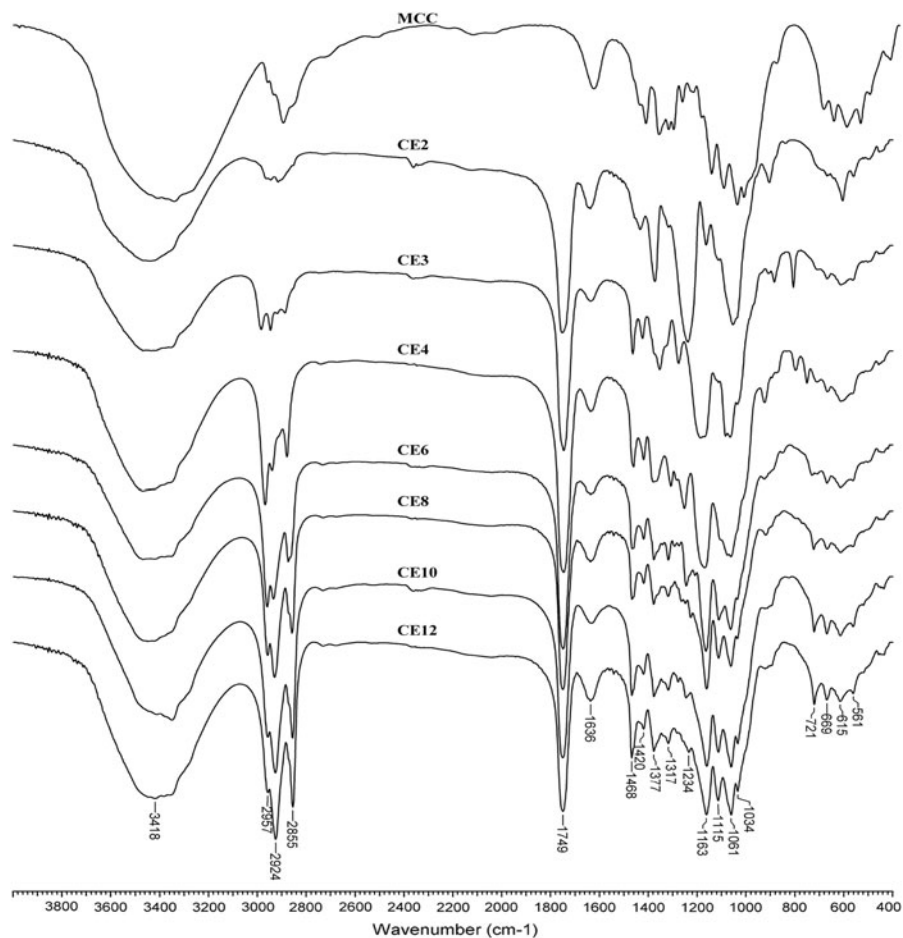
shows a trend to increase with the length of aliphatic chain. It probably suggests the low reactivity of MCC with vinyl esters with long aliphatic chains due to their stronger steric hindrance effect. However, the diffraction patterns change significantly at the diffraction angle below 15.0°. The SAXD patterns of MCC, alkali MCC, and CEs were also determined and are shown in Fig. 4. It was interesting to determine that a peak appeared in all diffraction patterns of CEs, while no peak appeared in the patterns of MCC and alkali MCC in this region, and the diffraction angle of this peak decreased regularly as the aliphatic chain increased. The interplanar spacing (d) values of the corresponding diffraction peaks of these CEs were calculated according to Bragg's equation ($n\lambda = 2d \sin \theta$) and illustrated in Table 2. According to the SAXD result, the d value showed a steadily increasing trend with the aliphatic chain length, suggesting that these obtained CEs were

organized in a layered-type structure, in line with other CEs prepared by the traditional method (Crepy et al. 2011). This can be explained as follows. The aliphatic chains, which act as side chains in the backbone of cellulose, showed strong steric hindrance in preventing MCC crystals from approaching each other. The longer the aliphatic chain is, the farther the MCC crystals are, and thus the d value increases as the length of the aliphatic chain increases (Arici et al. 2000; Lee et al. 1998).

^{1}H NMR and ^{13}C NMR

Due to the poor solubility of CE8, CE10 and CE12 in DMSO and other solvents, only ^{1}H NMR and solution-state ^{13}C NMR spectra of CE2, CE3, CE4 and CE6 are provided and illustrated in Figs. 5 and 6, respectively, while solid-state ^{13}C NMR spectra of CE6, CE8, CE10 and CE12 are shown in Fig. 7.
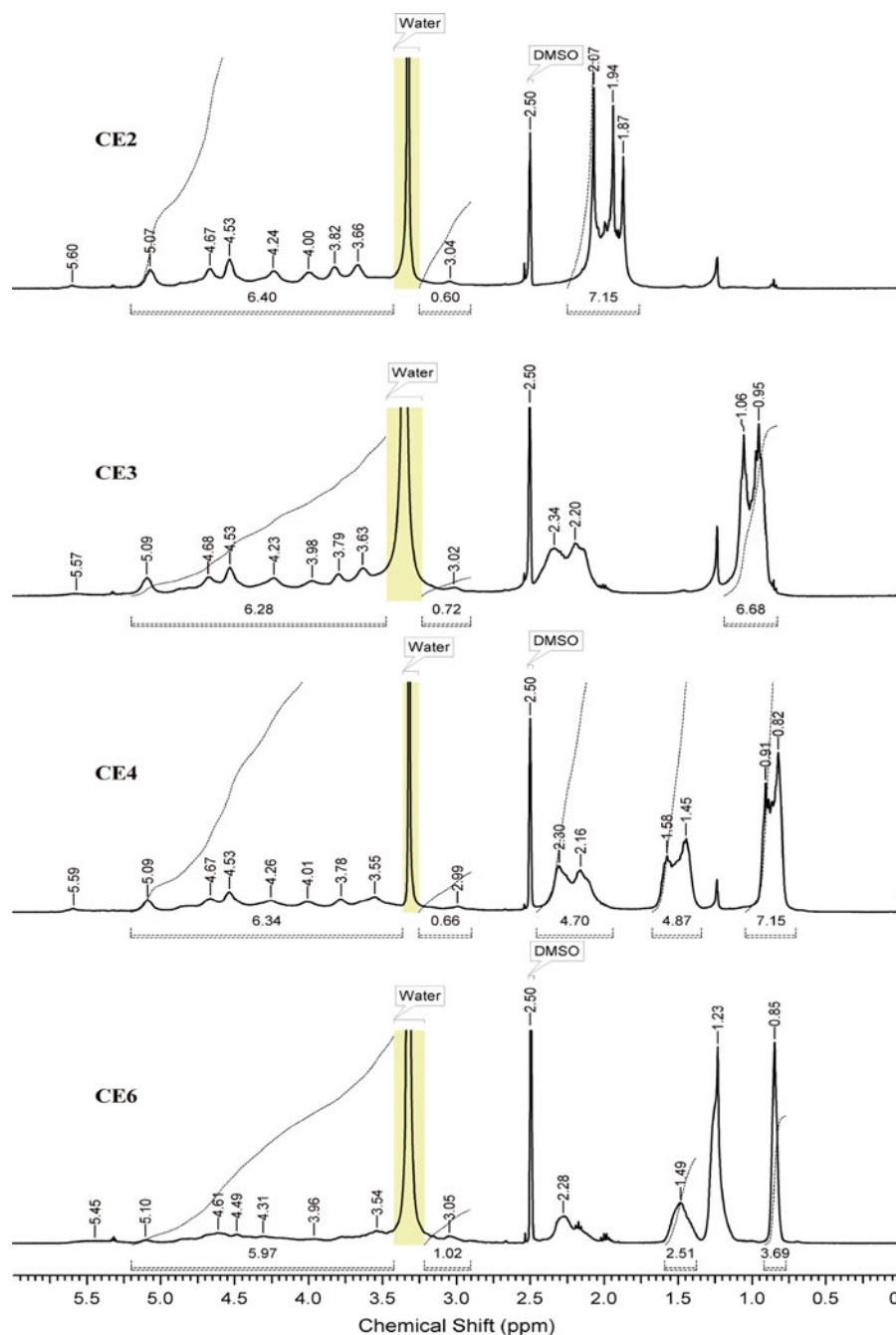
Fig. 3 WAXD patterns of
MCC, alkali MCC and CEs
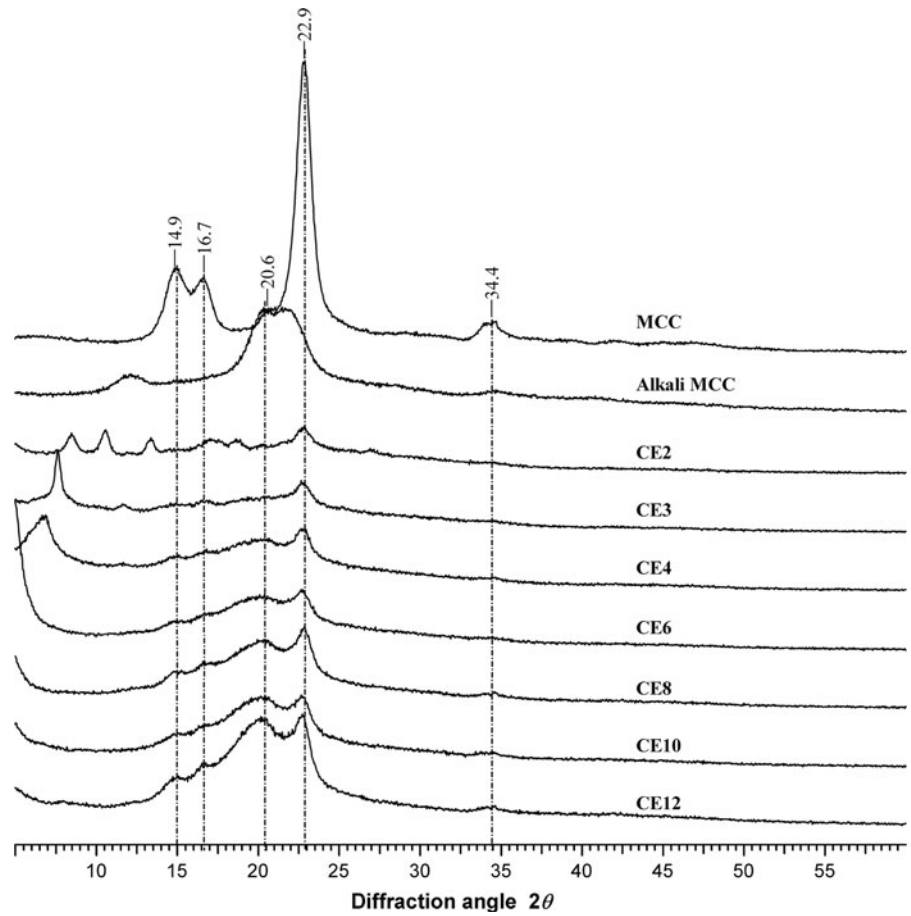
**Fig. 4** SAXD patterns of
MCC, alkali MCC and CEs
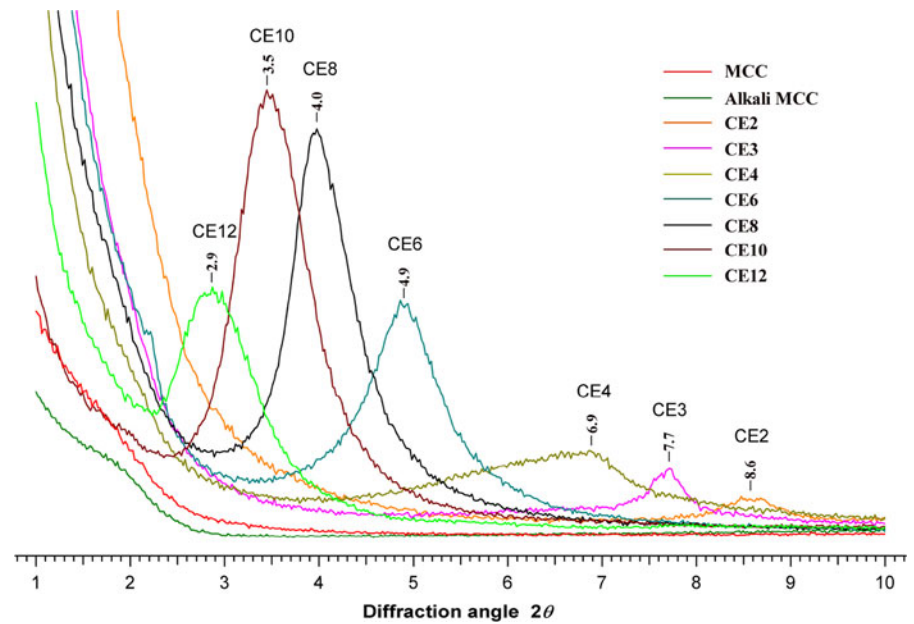
Fig. 5 ^{1}H NMR spectra of CE2, CE3, CE4 and CE6

In ^{1}H NMR spectra, the chemical shifts between 2.90 and 5.20 ppm, except the residual water signal at 3.32 ppm, belong to the seven protons of AGU (except hydroxyl protons) (Heinze and Liebert 2004), and the signals at around 5.50 ppm are related to the hydroxyl protons of AGU. The chemical shifts between 0.50 and 2.50 ppm are assigned to the protons of the substituent groups. Signals at 1.94 (1.87 and 2.07), 0.95 (1.06), 0.82 (0.91) and 0.85 ppm originated from the methyl protons of CE2, CE3, CE4 and CE6, respectively. Other signals between 0.50 and 2.50 ppm are related to the methylene chain protons of these CEs. These results again confirm the successful synthesis of CEs in minutes. The DS of
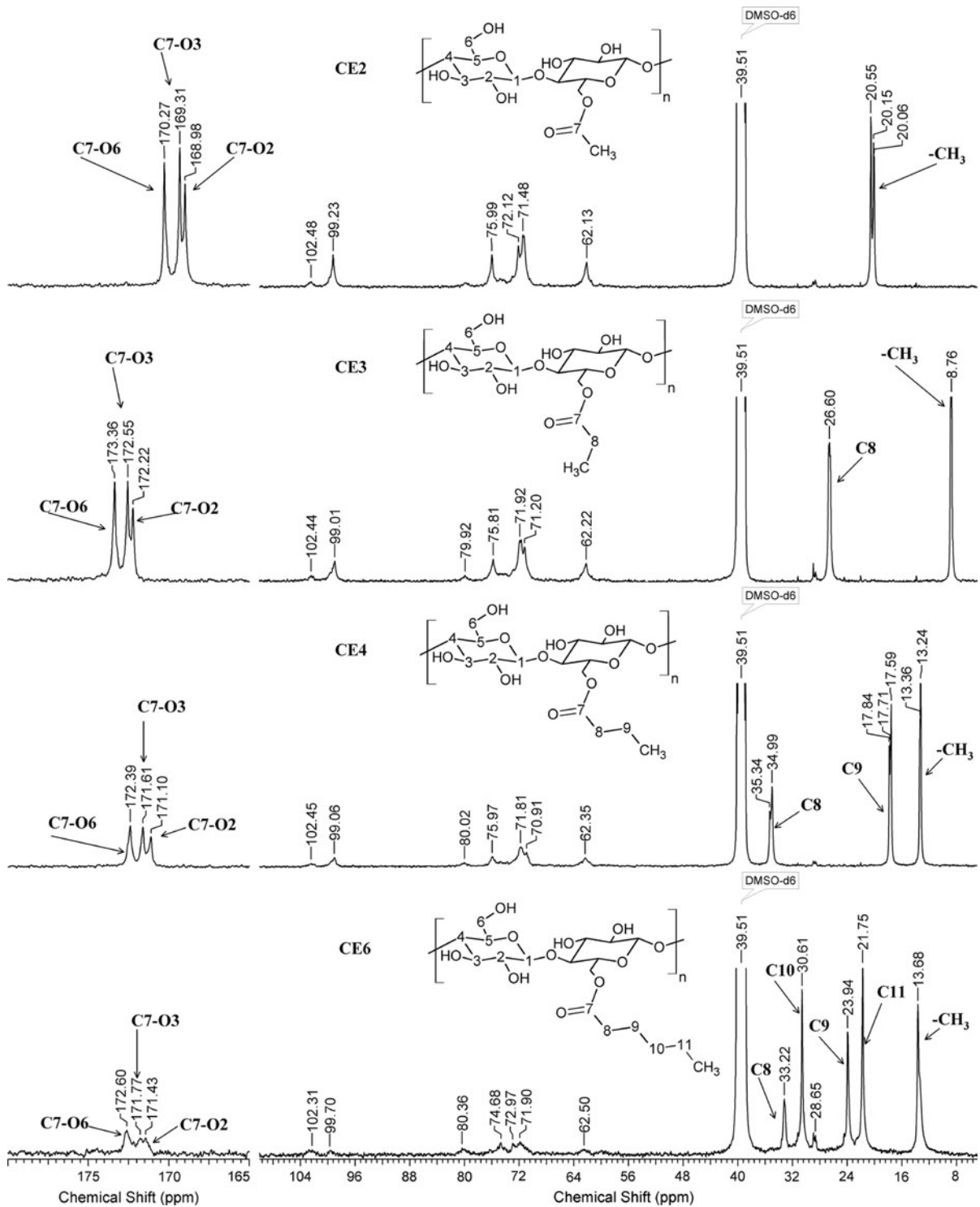
Fig. 6 Solution-state ^{13}C NMR spectra of CE2, CE3, CE4 and CE6

Fig. 7 Solid-state ^{13}C NMR spectra of CE6, CE8, CE10 and CE12
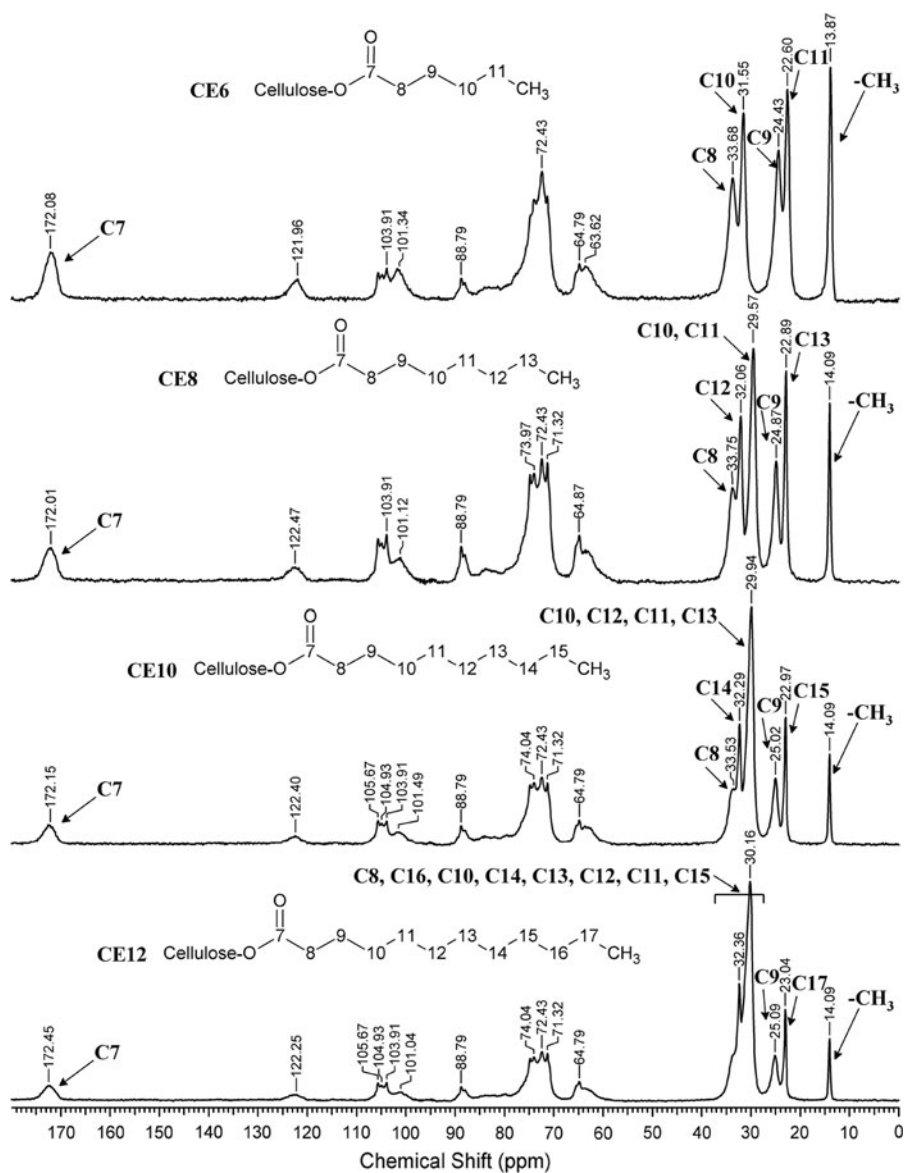
all CEs were calculated by the heterogeneous saponification method (ASTM D871-96), and the results are illustrated in Table 2. It is clear that a series of CEs with DS from 0.76 to 2.02 were synthesized within 5 min, which is in sharp contrast with hours to days for synthesizing cellulose esters using existing methods (Balser et al. 2000; Ferreira et al. 2002b; Hummel 2004; Saka 2004; Vaca-Garcia et al. 1998; Wu et al. 2004). However, CEs with long aliphatic chains show relatively low DS, indicating that vinyl esters with long aliphatic chains show low reactivity in the transesterification. It can also explain the increasing diffraction intensities in WAXD.

From the solid-state ^{13}C NMR spectra of CE6, CE8, CE10 and CE12, it can be seen that they show similar chemical shifts except the signals at 29.54–33.75 ppm. Because the resolution of solid-state ^{13}C NMR spectra is much lower than that of solution-state ^{13}C NMR, many overlaps exist in the spectra of CE8, CE10 and CE12. Both the solution-state and solid-state ^{13}C NMR spectra of CE6 are provided, and it can be seen that the chemical shifts assigned to the carbonyl carbons at different positions cannot be distinguished in the solid-state ^{13}C NMR spectra because of the relatively low resolution. The overlaps are more serious in the region of 28.00–36.00 ppm. These overlapping signals from
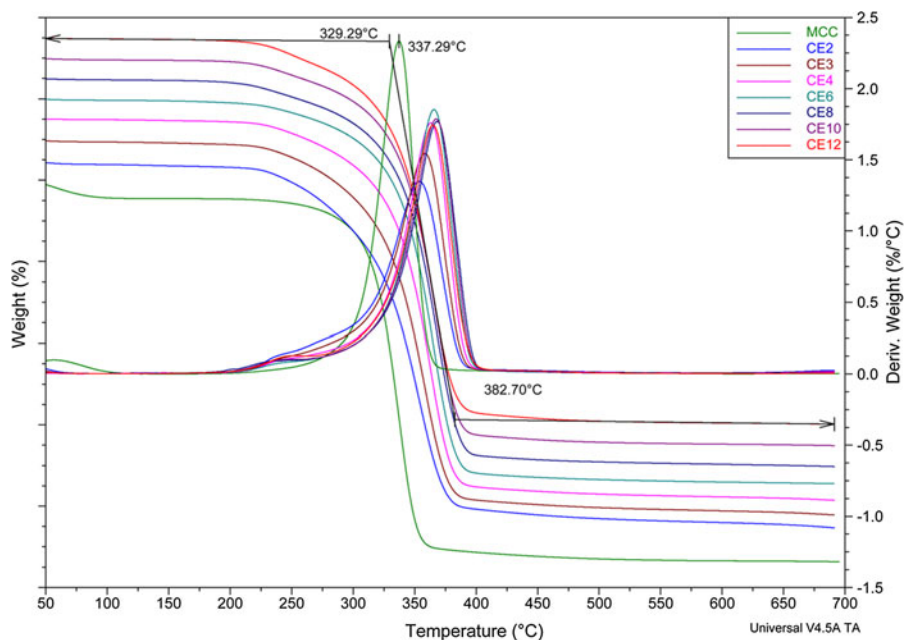
Fig. 8 TGA and DTG curves of MCC and CEs

the low to high field are depicted in Fig. 7 in the order that they should appear. Similar solid-state ^{13}C NMR spectra of long chain organic acid cellulose esters were also reported by Jandura et al. (2000a).

Thermal analysis

Step transition temperature and the temperature at the maximum weight loss rate were used to measure the relative thermal stability of products. The TGA and DTG curves of MCC and CEs are recorded and illustrated in Fig. 8 (in order to avoid overlap, the TGA curves were separated by shifting). The step transition temperature of the main decomposition and the temperature at the maximum weight loss rate from TGA and DTG are shown in Table 3. As can be seen, the onset and the end of the step transition temperature of MCC are lower than those of CEs (except the onset temperature of CE2), while the step transition of MCC finishes at a much smaller range of temperature (37.47 °C) than that of cellulose esters (49.65–61.80 °C). Furthermore, the weight loss rate peak of MCC appears at 337.29 °C, which is lower than that of CEs (353.76–368.23 °C). It indicates that the CEs synthesized in this work show higher thermal stability and a wider range of degradation than MCC. This is in

Table 3 Temperature of step transition and maximum weight loss rate of synthesized CEs

Samples	Onset (°C)	End (°C)	Maximum (°C)
MCC	314.49	351.96	337.29
CE2	311.68	373.48	353.76
CE3	319.91	376.25	358.34
CE4	328.65	379.55	363.08
CE6	333.23	382.88	365.70
CE8	333.29	385.57	368.23
CE10	332.66	384.75	367.43
CE12	329.30	382.67	364.90

line with the results from Labafzadeh's work (Labafzadeh et al. 2012), in which an increase in thermal stability was observed after the acylation of cellulose in pyridine. However, results from previous literature also reported that cellulose esters synthesized in pyridine/*p*-toluenesulfonyl chloride with organic acids or in DMAc/LiCl with the mixture of *p*-toluenesulfonic/carboxylic acid anhydride showed lower thermal stability than native cellulose (Jandura et al. 2000b; Sealey et al. 1996). Therefore, the synthesis methods and DS of CEs might affect their thermal stability to some degree.

Conclusions

Seven cellulose aliphatic esters (CEs) were heterogeneously synthesized within 5 min by transesterification under aqueous NaOH catalysis. CEs with a DS range of 0.76–2.51 could be obtained. Results obtained from FT-IR, ^{1}H, solution-state and solid-state ^{13}C NMR analysis confirmed the structure of these CEs. Water content and the molar ratio of NaOH:AGU had a marked effect on transesterification. The DS of the produced cellulose acetate decreased dramatically as the water content or the molar ratio of NaOH/AGU increased. SAXD analysis showed that the diffraction peak shifted toward a small angle with an increase in the aliphatic chain length. CEs synthesized by transesterification showed higher thermal stability and a wider range of degradation than MCC. This work offers an alternative method to rapidly prepare various CEs.

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