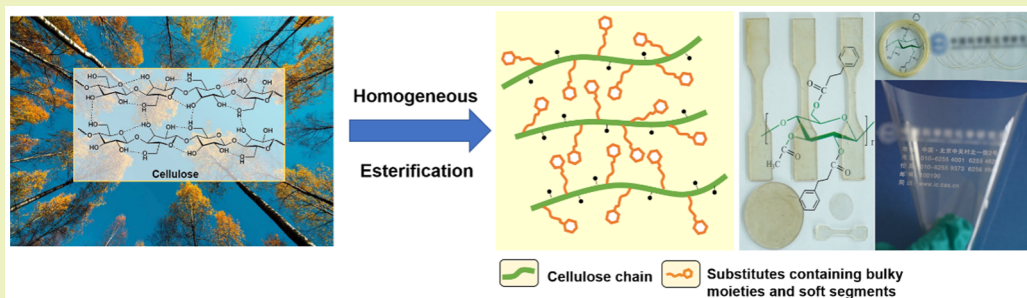


Novel Thermoplastic Cellulose Esters Containing Bulky Moieties and Soft Segments

Zhangyan Chen,^{†,‡} Jinming Zhang,^{*,†,§} Peng Xiao,[†] Weiguo Tian,[†] and Jun Zhang^{*,†,‡,§}[†]CAS Key Laboratory of Engineering Plastics, CAS Research/Education Center for Excellence in Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences (CAS), Beijing 100190, China[‡]University of Chinese Academy of Sciences, Beijing 100049, China

S Supporting Information



ABSTRACT: It is still challenging to convert cellulose into melt-processable materials because natural cellulose, which has a strong hydrogen bonding network, degrades before melting. Herein, a series of novel cellulose-based thermoplastics were successfully designed and fabricated by a simple and efficient homogeneous esterification of cellulose in an ionic liquid. Introducing ester substituents containing both bulky moieties and soft segments can improve the mobility of the cellulose chain, and the glass transition temperatures (T_g s) appeared in the resultant cellulose esters. In particular, when the ester substituents consisted of bulky terminal moiety and soft middle segment, T_g s of the corresponding cellulose esters were relatively low (80–160 °C), indicating these cellulose materials were suitable for melt processing. Accordingly, these thermoplastic cellulose esters can be processed into transparent disks, dumbbells, fibers and flexible films by traditional injection molding, melt extrusion, and hot pressing without any external plasticizers. Therefore, this work provides a simple and engineering method to construct melt-processable bioplastics from cellulose.

KEYWORDS: Cellulose, Cellulose esters, Homogeneous esterification, Glass transition, Melt processing

■ INTRODUCTION

Cellulose, the major component of lignocellulosic biomass produced by plant photosynthesis, is the most abundant biorenewable and biodegradable resource on Earth and has an estimated annual yield of 1.5×10^{12} tons.¹ Efficient and environmentally friendly utilization of cellulose not only reduces dependence on fossil resources but also protects our environment.² However, due to plenty of intermolecular and intramolecular hydrogen bonds, cellulose is insoluble in common solvents and not melt processable as well. Although chemical modification such as esterification and etherification provides processable cellulose derivatives, to date, the industrial processing and practical applications of cellulose-based materials (films, fibers, coatings, and molded plastics) are dominated by solution methods^{3–5} that require hazardous chemicals like acetone and cause substantial environmental damage due to the release of toxic gases and solvents. In contrast, the melt processing of cellulose materials has drawn increasing attention because it is simple, efficient, and environmentally friendly. The conversion of cellulose into melt-processable materials is quite attractive.

The key to achieve thermoplastic processing of cellulose is to eliminate the hydrogen bonding network. Schroeter and Felix discovered that pure cellulose could be plastically deformed using a combination of mechanical shear, uniaxial pressure, and laser irradiation.⁶ However, this process of destroying hydrogen bonds in cellulose requires a substantial amount of energy and is too harsh for industrial production. Recently, Wu et al. noted that the addition of a large quantity of 1-butyl-3-methylimidazolium chloride (BmimCl) ionic liquid as the plasticizer could also disturb the hydrogen bonding network in cellulose, and the melt-processable cellulose/BmimCl composites were obtained.⁷ However, even if the migration of BmimCl is not considered, the high moisture sensitivity and toxicity of the resultant composites, due to the high content of BmimCl, makes these materials impractical for many applications.

Chemical modification can convert hydroxyl groups to esters, ethers, or other functional groups, which consequently destroys

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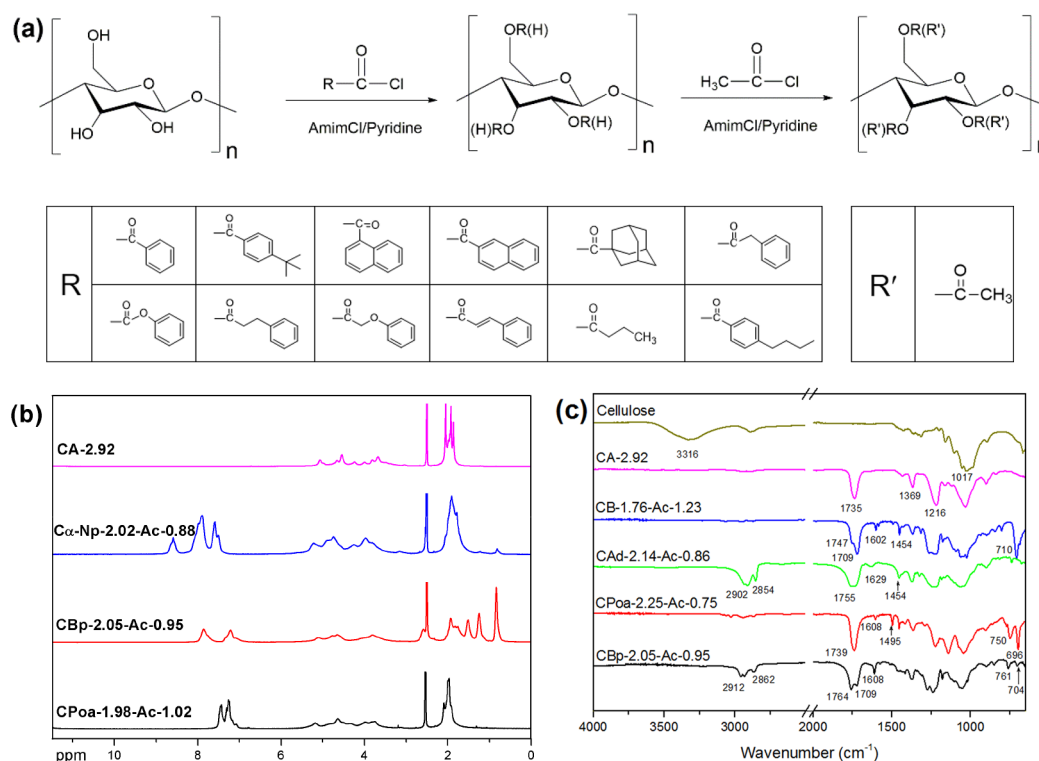


Figure 1. (a) Synthetic routine of cellulose mixed esters. (b) Representative ¹H NMR spectra of cellulose mixed esters. (c) Representative FTIR spectra of cellulose and cellulose mixed esters.

the hydrogen bonding network in cellulose. Additionally, this process can endow cellulose-based materials with many new properties, including good solubility,^{8–10} electrical properties,^{11,12} optical performance,^{13,14} adsorption and separation capabilities,^{15,16} hydrophobicity^{17,18} and stimuli responsiveness.^{19–22} An initial success in the field of melt-processable cellulose derivatives was the development of cellulose acetate. Subsequently, other cellulose short-chain aliphatic esters, such as cellulose acetate propionate and cellulose acetate butyrate, have been also processed by injection molding. They represent a class of commercially important thermoplastic polymers in the fiber, film, and filter industries.^{3,23} However, melt processing of these classical cellulose esters is not easy because the decomposition temperatures (*T_d*s) and the flow temperatures (*T_f*s) are very close; i.e., the processing window is too narrow. Thus, during melt processing, a large amount of small molecule plasticizer is required. Unfortunately, the inevitable migration of the external plasticizers will weaken the performance and decrease the lifetime of the cellulose plastics.^{3,24,25} It seems that cellulose long-chain aliphatic esters can solve this dilemma because the long-chain fatty acid groups not only disrupt the hydrogen bonds in cellulose but also act as internal plasticizers.^{26–30} However, it is difficult to synthesize cellulose long-chain aliphatic esters because of the poor reactivity and steric effect of the long-chain fatty acyl chloride or long-chain fatty acid. To increase the reaction rate and transformation efficiency, high reaction temperatures, long reaction times, basic catalysts, or/and special acylation reagents are often employed.^{31–34} However, these conditions can cause serious degradation of the cellulose, and they can make the process more expensive and tedious. In addition, polylactic acid (PLA)^{35–38} and polycaprolactone (PCL)^{39–42} grafted onto cellulose can also serve as an efficient internal plasticizer.

However, a high content of the grafting polymer is necessary to achieve suitable thermoplasticity, which results in a decrease in thermal stability and an increase in fragility. Therefore, although despite many attempts made in this regard, the synthesis of cellulose-based melt-processable materials is still a challenging and appealing target for real-world applications.

Recently, we found that bulky ester groups, such as diphenyl phosphate, could significantly improve the mobility of cellulose ester chains, and the melt-processable cellulose acetate diphenyl phosphate was synthesized.⁴³ Herein, a series of cellulose esters containing bulky moieties and/or soft segments were homogeneously synthesized in the ionic liquid 1-allyl-3-methylimidazolium chloride (AmimCl). The influence of the structural characteristics of the bulky moieties (volume) and soft segments (length, chemical composition, and location) of the substituents on the thermal behavior and melt processability of cellulose esters was investigated. Eventually, several novel cellulose-based thermoplastics were obtained and could be readily processed into different shapes by traditional melt processing, indicating the great potential of these cellulose esters in practical applications.

EXPERIMENTAL SECTION

Materials. Microcrystalline cellulose with degree of polymerization (DP) of 90 and 220 and cotton pulp with DP of 382 and 650 were dried under vacuum at 60 °C for 48 h before use. The ionic liquid AmimCl was synthesized according to our previous work.^{44,45} All the acyl chlorides used in this study were purchased from J&K Scientific Ltd. Other chemicals were obtained from Beijing Chemical Reagent Co., China. All reagents were of analytical grade and used without further purification.

Synthesis. Cellulose mixed esters were synthesized according to Figure 1a. A typical procedure is given below. Cellulose (1.0 g) was dispersed in 19.0 g of AmimCl. After stirring at 80 °C for 1 h, a transparent cellulose/AmimCl solution (5 wt %) was obtained. Then,

at 50 °C, 0.73 g of pyridine and the first acyl chloride were added according to the prescribed feed ratios. After the given reaction time, 1.96 g of acetyl chloride was added to react with the remaining hydroxyl groups. Subsequently, the products were precipitated in methanol or isopropanol, and the white floccules were collected by filtration. After washing three times with methanol or isopropanol, the product was redissolved in dimethyl sulfoxide (DMSO), precipitated again in methanol or isopropanol and washed another three times. Finally, the products were filtered and dried under vacuum at 60 °C for 24 h before characterization.

Measurements and Characterization. ^1H NMR spectra were acquired on a Bruker AV-400 NMR spectrometer with 16 scans at room temperature in $\text{DMSO}-d_6$. A few drops of trifluoroacetic acid- d_1 were added to shift the signals of the free hydrogens downfield. The degree of substitution (DS) value of each of the cellulose mixed esters was calculated from their ^1H NMR spectra. FTIR spectra were recorded with a Nicolet 6700 FT-IR spectrometer (Thermo Fisher, USA) from 650 to 4000 cm^{-1} with 16 scans.

Differential scanning calorimetry (DSC) was conducted on a TA-Q2000 differential scanning calorimeter (TA Instruments, USA) under a nitrogen atmosphere. To provide the same thermal history before the measurements, each sample was heated to 240 °C at a scanning rate of 20 °C/min and maintained at 240 °C for 5 min. Then, the samples were cooled to 20 °C, kept for 5 min, and quenched to room temperature. All the reported glass transition temperatures (T_g s) were calculated from a second scan.

Thermal flow behaviors of the samples were observed by an Olympus BX5.1 optical microscope equipped with a Linkam THMS 600 hot-stage device. A small piece of the sample was sandwiched between two cover glasses and heated from 20 to 260 °C at a rate of 10 °C/min. The whole process was recorded by taking photos at the desired temperature intervals. The temperature, at which the cellulose ester was completely transparent and flowed, was recorded as the melt flow temperature (T_f).

Dynamic mechanical analysis (DMA) was carried out on a TA Instruments DMA Q800. The film was obtained by solution evaporation in a polytetrafluoroethylene (PTFE) mold. The specimen was a thin rectangular strip with dimensions of 15 mm $\times$ 4 mm $\times$ 0.06 mm. The measurements were performed in tensile mode at a constant frequency of 1 Hz over a temperature range from -150 to 150 °C and a heating rate of 3 °C/min in a nitrogen atmosphere.

Thermogravimetric analysis (TGA) was conducted on Perkin-Emmer Pyris 1 and TGA 7 thermogravimetric analyzer in nitrogen and air atmosphere, respectively. Each sample was heated from 50 to 750 °C at a rate of 20 °C/min.

Thermal Processing. The dumbbell-shaped samples were prepared by injection molding with a Haake mini-jet system. The injection temperature was 160 °C, and the mold temperature was controlled at 60 °C. The pressure was 850 bar. Fibers were shaped by melt spinning with a Haake-SWO 556-0031 melt flow speed indicator. Approximately 4 g of copolymer was put into the barrel of the device, heated at a rate of 40 °C/min up to 180 °C, kept at this temperature for 2 min, and then extruded through a capillary under a constant load of 1.2 kg. The extruded fiber was taken up at a rate of 10 m/min at room temperature. The disks and flexible films were prepared by hot pressing at 150 °C.

RESULTS AND DISCUSSION

Synthesis and Characterization of Cellulose Esters.

Cellulose contains a large number of hydroxyl groups at the C2, C3, and C6 positions of each monomer. Thus, it is susceptible to chemical modifications such as esterification and etherification. However, the existence of numerous hydroxyl groups in cellulose also generates an extensive hydrogen bonding network, which causes cellulose to be neither soluble nor meltable; therefore, cellulose derivatives can only be produced through the heterogeneous techniques used in industry. The heterogeneous reactions have some inevitable problems, such

as uneven distribution of substituents, side reactions, considerable degradation of the cellulose, and long reaction time. Furthermore, it is impossible to directly control the synthesis and chemical structure of the resultant cellulose esters. Recently, this predicament has been solved using emerging novel cellulose solvents. In particular, ionic liquids (ILs) have provided a new method for the homogeneous synthesis of cellulose derivatives at the molecular level.^{46–50} As a new kind of aprotic solvent, ILs are thermally stable, chemically inert, and highly polar; hence, they are ideal media for the homogeneous derivatization of cellulose. In fact, many conventional cellulose esters and a variety of novel and functional cellulose derivatives have been successfully synthesized in ILs.^{49–56} Compared with traditional heterogeneous derivatization, the homogeneous synthesis of cellulose esters in ILs has several obvious advantages, such as high efficiency, high yield, mild reaction conditions, no or few byproducts, simple separation, and easy solvent recovery. More importantly, the structure of the cellulose derivatives can be precisely controlled with different reaction conditions.

In our work, taking advantage of the merits of the homogeneous esterification in ILs, a series of cellulose mixed esters with well-defined structures were synthesized by first incorporating the ester groups containing bulky moieties and/or soft segments and then completely substituting the remaining hydroxyl groups with acetyl groups, as shown in Figure 1a. By adjusting the feed ratio, reaction temperature, and duration of the first step, the structures of the resultant cellulose mixed esters were precisely controlled (Figures S1–S27 and Tables S1–S13). In the first step, as the feed ratio increases, the DS value of the substituents increases dramatically. Take cellulose phenyl carbonate (CPcm) for example. When the molar ratio of phenyl carbonochloridate to anhydroglucose units (AGU) increased from 2:1 to 4:1 at 50 °C for 1 h, the DS value of the phenoxycarbonyl groups increased from 0.90 to 2.07 (Table S13). An increase in the reaction temperature accelerated the reaction and improved the DS value. For instance, during the esterification of cellulose with β -naphthoyl chloride, under the same conditions of a molar ratio of 3:1 (β -naphthoyl chloride to AGU) and reaction time of 1 h, increasing the reaction temperature from 50 to 80 °C led to an increase in the DS value from 1.67 to 2.39 (Table S4). Prolonging the reaction time also favors a high DS value. During the reaction between cellulose and *n*-butyryl chloride in a molar ratio of 2:1 at 50 °C, increasing the reaction time from 1 to 2 h results in an increase in the DS value from 1.36 to 1.64 (Table S2). In addition, different acyl reagents exhibit diverse reactivities. Obviously, the acyl reagents with larger volumes show lower reactivities. Therefore, to obtain cellulose esters with similar DS values, the reactions between cellulose and larger substituents required greater feed ratios, longer reaction times, and higher reaction temperatures. Even so, the conditions for the reactions of cellulose and larger substituents are mild, because these are the homogeneous solution reaction in ILs, and the reactivities of the bulky acyl reagents used in this study are higher than those of the classical long-chain fatty acyl chlorides. In our synthetic process, the reaction temperatures are below 80 °C, and the reaction times are no more than 2 h (Tables S1–S13).

Typical ^1H NMR and FTIR spectra of cellulose mixed esters are shown in Figure 1b and 1c, respectively. The signals from 2.8 to 5.5 ppm were assigned to the protons of the cellulose backbone. The peaks at 6.8–9.0 ppm and 0.6–2.1 ppm can be

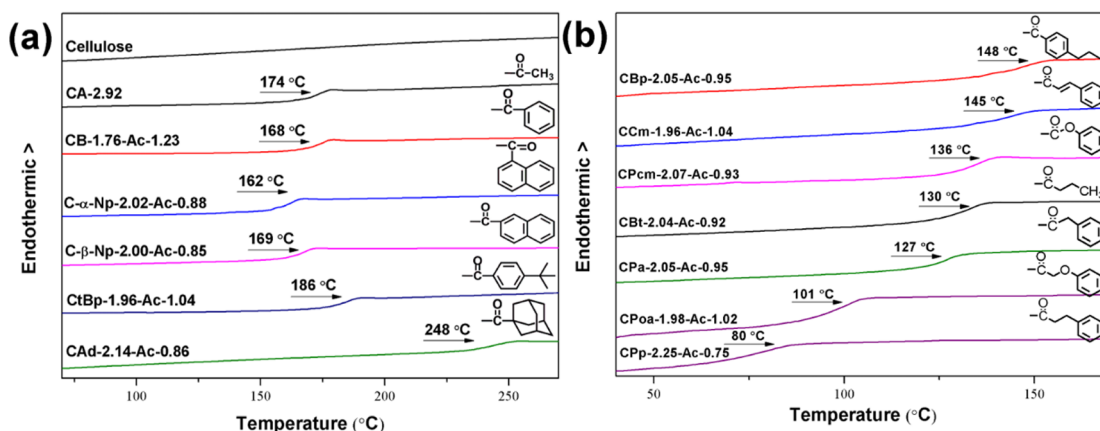


Figure 2. DSC curves of (a) cellulose and cellulose mixed esters containing bulky moieties and (b) cellulose mixed esters containing both bulky moieties and soft segments.

attributed to the protons of the phenyl rings and alkyl groups, respectively, confirming that the acyl groups have been successfully incorporated into the cellulose. The DS values of cellulose mixed esters were calculated from the ^1H NMR spectra (Figures S1–S27). In comparison with the FTIR spectrum of cellulose, the complete disappearance of the hydroxyl peak at $3000\text{--}3500\text{ cm}^{-1}$ indicates that all the hydroxyl groups in cellulose have been modified. Meanwhile, some new characteristic peaks appear. The peaks at $1700\text{--}1800\text{ cm}^{-1}$ are attributed to $\text{C}=\text{O}$ stretching in esters. The signals at $1450\text{--}1610\text{ cm}^{-1}$ and $700\text{--}800\text{ cm}^{-1}$ correspond to aromatic $\text{C}=\text{C}$ stretching and C-H out-of-plane bending of phenyl rings. These results confirm that cellulose mixed esters with well-defined structures were synthesized as expected.

Thermal Properties and Dynamic Mechanical Properties of Cellulose Esters. The glass transition in noncrystalline polymers is a macroscopic manifestation of the motions of macromolecular chains suddenly becoming significantly easier; therefore, the glass transition temperature (T_g) substantially depends on the intermolecular interactions between macromolecular chains. By conventional DSC, unmodified cellulose has no glass transition prior to its decomposition (Figure 2a) due to the existence of strong hydrogen bonding interactions. The conversion of all the hydroxyl groups to ester groups destroys the hydrogen bonding interactions, increases the distance between the molecular chains, and improves the free volume and mobility of the macromolecular chains. Thus, obvious T_g s of cellulose esters appear, as shown in Table 1 and Figure 2a.

The effect of the size of different substituents on the T_g of cellulose esters is thoroughly demonstrated (Table 1 and Figure 2a). The cellulose esters with common bulky moieties, such as phenyl groups and naphthyl groups, have similar T_g s as cellulose acetate. However, bulkier groups, like adamantane and 4-*tert*-butylphenyl groups, increased the T_g (CAd-0.90-Ac-2.10, $T_g = 212\text{ }^\circ\text{C}$), and a higher DS value of the adamantane derivative would further raise the T_g (CAd-2.14-Ac-0.86, $T_g = 248\text{ }^\circ\text{C}$) because the adamantane group increases the steric hindrance and results in a regular arrangement of molecular chains.⁵⁴ The results reveal that the bulky groups have two opposing effects on the T_g of cellulose esters. On one hand, the increase in the free volume caused by bulky groups would decrease the T_g . On the other hand, the steric hindrance of bulky groups would raise the T_g . Therefore, ester groups with suitable volumes can promote the mobility of the cellulose

molecular chains, while oversized rigid ester groups will increase the T_g of cellulose esters.

Furthermore, because soft segments can act as internal plasticizers, a series of ester groups containing both bulky moieties and soft segments were introduced to improve the mobility of the cellulose chains. The influence of location, length, and structure of the soft segments on the T_g s of cellulose esters was investigated, and the results are shown in Table 1 and Figure 2b. The addition of soft segments significantly decreases the T_g s of cellulose esters. The cellulose benzoate (CB-1.76-Ac-1.23) has a T_g of $168\text{ }^\circ\text{C}$. After introduction of a butyl group, the corresponding cellulose ester CBp-2.05-Ac-0.95 gives a markedly lower T_g of $148\text{ }^\circ\text{C}$. Furthermore, comparing CBp-2.05-Ac-0.95 ($T_g = 148\text{ }^\circ\text{C}$) with CPp-2.25-Ac-0.75 ($T_g = 80\text{ }^\circ\text{C}$) suggests that substituents with soft middle segments and bulky terminal moieties are more efficient in decreasing the T_g of cellulose esters. That is, for improving the mobility of the cellulose chains, substituents with soft segments located between the bulky moiety and the cellulose chain are superior to those with the soft segments located at the end of bulky groups directly attached to the cellulose chain. Additionally, for substituents with soft middle segments and bulky terminal moieties, longer soft segments cause lower T_g s. Moreover, a change in the chemical composition of the soft segments has a significant effect on T_g of cellulose esters because it changes the degrees of flexibility of the pendant ester groups and thereby changes the freedom of the overall macromolecular chain. For instance, when the alkyl chain in the soft segments is replaced by an oxygen atom and a double bond, the T_g of the corresponding cellulose esters is substantially higher, e.g., CPp-2.25-Ac-0.75 ($T_g = 80\text{ }^\circ\text{C}$) and CCm-1.96-Ac-1.04 ($T_g = 145\text{ }^\circ\text{C}$), CPp-2.25-Ac-0.75 ($T_g = 80\text{ }^\circ\text{C}$) and CPoa-2.05-Ac-0.95 ($T_g = 101\text{ }^\circ\text{C}$), or CPa-2.05-Ac-0.95 ($T_g = 127\text{ }^\circ\text{C}$) and CPcm-2.07-Ac-0.93 ($T_g = 136\text{ }^\circ\text{C}$). Therefore, a long alkyl segment located between the bulky group and the cellulose chain is the best choice for enhancing the mobility of the cellulose chain.

It should be noted that bulky terminal moieties also play an important role in improving the mobility of the molecular chains. For CPp-2.25-Ac-0.75 ($T_g = 80\text{ }^\circ\text{C}$), if the terminal phenyl ring is replaced by a methyl group, the T_g of the corresponding cellulose ester (CBt-2.04-Ac-0.92) is significantly increased to $127\text{ }^\circ\text{C}$.

All of the above results suggest that the combination of bulky moieties and soft segments, especially substituents with soft

Table 1. Effect of Different Structures of Cellulose Mixed Esters on Glass Transition Temperatures (T_g s) and Melt Flow Temperatures (T_f s)^a

Samples	Acyl groups (R)	DS _R	DS _{Ac}	DS _{Total}	T_g /°C	T_f /°C
CA-2.92		2.92	2.92	2.92	174	N/A
CB-1.06-Ac-1.93		1.06	1.93	2.99	168	230
CB-1.76-Ac-1.23		1.76	1.23	2.99	168	230
CtBp-1.15-Ac-1.85		1.15	1.85	3.0	184	N/A
CtBp-1.96-Ac-1.04		1.96	1.04	3.0	189	N/A
Cα-Np-1.00-Ac-2.00		1.00	2.00	3.0	167	240
Cα-Np-2.02-Ac-0.88		2.02	0.88	2.90	162	240
Cβ-Np-1.16-Ac-1.70		1.16	1.70	2.86	173	240
Cβ-Np-2.00-Ac-0.85		2.00	0.85	2.85	169	240
CAd-0.90-Ac-2.10		0.90	2.10	3.0	212	N/A
CAd-2.14-Ac-0.86		2.14	0.86	3.0	248	N/A
CPa-0.98-Ac-1.98		0.98	1.98	2.96	140	200
CPa-2.05-Ac-0.95		2.05	0.95	3.0	127	180
CPp-1.02-Ac-1.92		1.02	1.92	2.94	109	180
CPp-2.25-Ac-0.75		2.25	0.75	3.0	80	150
CCm-1.10-Ac-1.99		1.01	1.99	3.0	147	230
CCm-1.96-Ac-1.04		1.96	1.04	3.0	145	230
CPoa-1.10-Ac-1.90		1.10	1.90	3.0	123	210
CPoa-1.98-Ac-1.02		1.98	1.02	3.0	101	190
CPcm-0.90-Ac-2.10		0.90	2.10	3.0	155	230
CPcm-2.07-Ac-0.93		2.07	0.93	3.0	136	210
CBt-1.06-Ac-1.85		1.06	1.85	2.91	146	230
CBt-2.04-Ac-0.92		2.04	0.92	2.96	130	210
CBp-0.94-Ac-2.04		0.94	2.04	2.98	149	230
CBp-2.05-Ac-0.95		2.05	0.95	3.0	148	230

^a"N/A" means that the melt flow phenomenon is not available during the temperature increases from 20 to 260 °C.

middle segments and bulky terminal moieties, could substantially improve the mobility of the cellulose chains. Based on this principle, a series of novel cellulose esters with T_g s from 80 to 160 °C were synthesized.

In our previous research, the large volume of diphenyl phosphate was recognized as the main reason for the low T_g of

cellulose acetate diphenyl phosphate.⁴¹ According to the above principle, the oxygen (O) between the benzyl and the phosphorus (P) atom should also play a key role in decreasing the T_g of the cellulose ester. To test this hypothesis, we synthesized cellulose acetate diphenyl phosphite (DS_{DPi} = 1.18, DS_{Ac} = 1.76, T_g = 167 °C), which exhibits a much higher T_g than cellulose acetate diphenyl phosphate (DS_{DPa} = 1.19, DS_{Ac} = 1.53, T_g = 97 °C). Such a remarkable difference proved the striking effect of the combination of bulky moieties and soft segments on reducing the T_g of cellulose esters.

To study the influence of the degree of polymerization (DP) of the cellulose esters on their thermal behavior, four kinds of cellulose with different DP values from 90 to 650 were selected to synthesize CPoa-Ac. The results indicate that the T_g s of all the CPoa-Ac are approximately 100 °C (Table 2), despite their dramatically different DP_w values (66–1703). Thus, in the case of cellulose esters, DP values from 90 to 650 have no obvious influence on T_g . Although DP has no influence on T_g , it has an impressive effect on the dynamic mechanical properties of the cellulose ester, which is consistent with the previous works.^{35,57–60} As shown in Figure 3, CPoa-Ac with higher DPs always have higher storage moduli at a given temperature. For instance, at 30 °C, as DP_w increases from 701 to 892 and 1703, the storage moduli of the CPoa-Ac increased from 1.2 GPa (CPA2) to 1.4 GPa (CPA 3) to 1.8 GPa (CPA 4), respectively. Notably, because the molecular weight of CPA1 (DP_w = 66) is so low, it is impossible to cast a film for a DMA test. In addition, the storage moduli of the CPoa-Ac rapidly decrease to zero near 105 °C, which is consistent with their T_g s. Therefore, DP is a very important parameter for adjusting the mechanical properties of cellulose esters, and vice versa, the mechanical properties of cellulose esters could be controlled by their DPs.

Thermal Flow Behaviors of Cellulose Esters. The optical micrographs in Figure 4 show the thermal flow behaviors of the cellulose mixed esters at different temperatures. The pure cellulose acetate (CA-2.92) is difficult to melt, and it does not even soften at 240 °C. The introduction of acetyl groups effectively destroys the hydrogen bonding networks. However, due to the small volume of acetyl groups and the inherent rigidity of cellulose backbones,^{61–64} the thermal motion of macromolecular chains is still poor; thus, CA-2.92 would not flow without external plasticizers. In contrast, after a bulky pendant group, like α-naphthoate, is introduced into the cellulose chain, the distance between the macromolecular chains increases significantly, and as a result, the free volume and mobility of the molecular chains is improved. Therefore, the obtained cellulose α-naphthoate acetate (Cα-Np-2.02-Ac-0.88) will soften at 190 °C and become transparent at 240 °C. Because soft segments can act as internal plasticizers,^{26–29} the combination of bulky moieties and soft segments can further reduce the intermolecular interactions of the cellulose ester chains and improve the thermoplastic properties of cellulose esters, such as CBp-2.05-Ac-0.95 (T_f = 230 °C) compared to CPoa-1.98-Ac-1.02 (T_f = 190 °C). Unfortunately, when the soft segments are located at the end of the ester substituent, the long alkyl side chains will form additional van der Waals interactions, which results in entanglement or even assembly into regular structures^{29,30,65,66} hindering the motion of the molecular chains. Therefore, for ester substituents with long soft segments located between the bulky group and the cellulose backbones, which can weaken or even eliminate the above van der Waals interactions and

Table 2. Synthesis Conditions, DS, DP, and T_g of Cellulose Phenoxyacetate Acetate (CPoa-Ac)^a

Samples	Cellulose		Molar ratio of phenoxyacetyl chloride/AGU	T (°C)	CPoa-Ac			
	DP _n	Concentration (wt %)			DS _{Poa}	DS _{Ac}	DP _w	T_g
CPA1	90	5%	3.5:1	50	2.05	0.95	66	102
CPA2	220	5%	4.0:1	50	1.98	1.02	701	101
CPA3	382	2%	5.0:1	50	1.93	1.07	892	100
CPA4	650	2%	5.0:1	60	2.00	1.00	1703	102

^aDP_w was measured by gel permeation chromatography with tetrahydrofuran as the mobile phase and polystyrene as the standard substance.

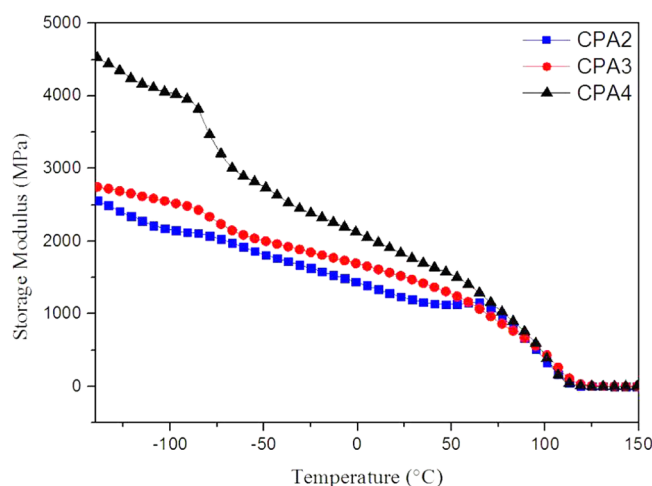


Figure 3. DMA curves of CPoa-Ac with different DPs.

entanglements between the pendant substituents, the corresponding cellulose esters show the lowest melt flow temperatures (CPp-2.25-Ac-0.75, T_f = 150 °C).

Thermoplastic Processing of Cellulose Mixed Esters. The thermoplastic processing properties of noncrystalline polymers depend on the difference between the onset decomposition temperature (T_{onset}) and T_f . The T_{onset} of the traditional cellulose esters, such as cellulose acetate (CA-2.92) and cellulose acetate butyrate (CBt-2.04-Ac-0.92), is about 340

°C, while almost all of cellulose mixed esters with bulky moieties have a higher T_{onset} , 360–380 °C (Figure S28 and Table S14). That is to say, the traditional cellulose esters, such as cellulose acetate and cellulose acetate butyrate, have a relatively low T_{onset} and a high T_f , while the cellulose mixed esters with the ester substituents consisted of bulky terminal moiety and soft middle segment have a high T_{onset} and a strikingly low T_f . Therefore, the cellulose mixed esters with the ester substituents consisting of bulky terminal moieties and soft middle segments show excellent thermoplastic properties and can be processed by traditional melt-processing methods. They were processed into disks, dumbbell-shaped splines, fibers, and flexible thin films by hot pressing, melt extrusion, and injection molding (Figure 5). In addition, the excellent uniformity and transparency of the products, and especially the good flexibility of the film, provide a solid foundation for the large-scale applications of these thermoplastic cellulose esters.

CONCLUSION

In this work, ester groups consisting of bulky moieties and soft segments were incorporated into cellulose by homogeneous esterification in the ionic liquid AmimCl. The DS value of the substituents was effectively controlled by adjusting the reaction conditions. The relationship between the structure of the substituents and the melt processability of these cellulose esters indicated that the synergistic effects of the bulky moieties and the soft segments could substantially decrease the T_g s and T_f s of cellulose esters. The resultant cellulose esters were readily

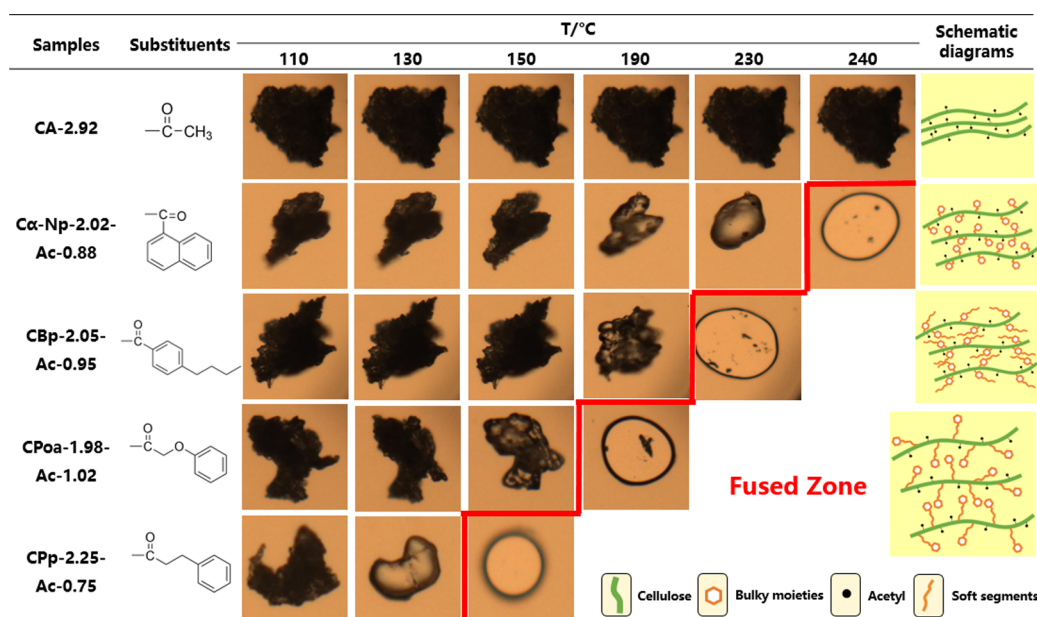


Figure 4. Optical micrographs and structures of different cellulose mixed esters at different temperatures.

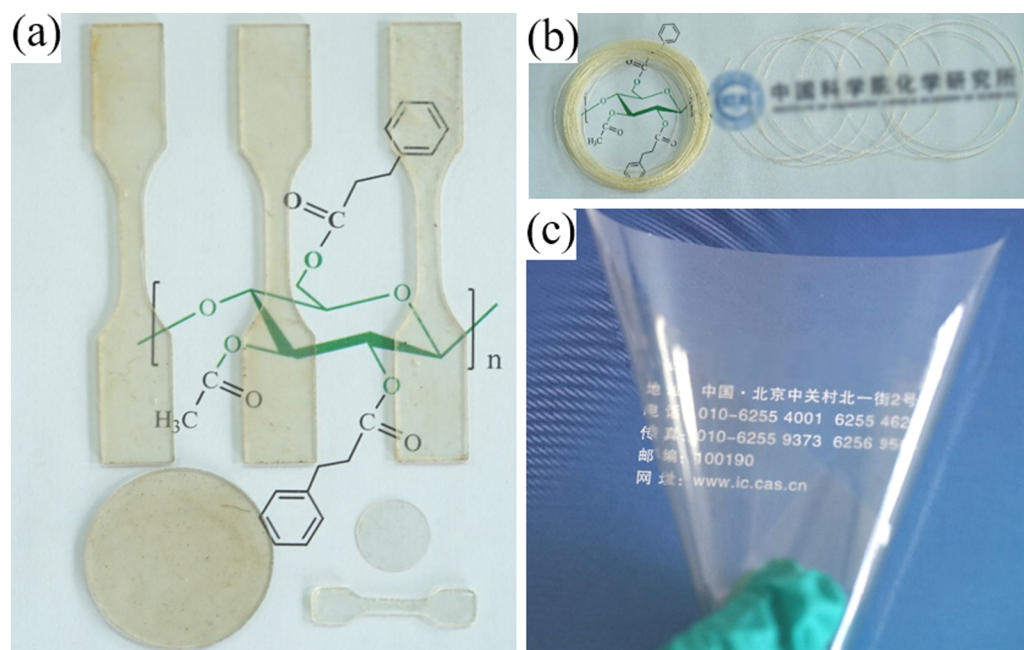


Figure 5. Photographs of CPp-2.25-Ac-0.75 with different material forms produced by traditional melt processing methods. (a) Transparent disks and dumbbells, (b) fibers, and (c) flexible thin film.

melt-processed into plastics with high transparency and good flexibility by hot pressing, melt extrusion, and injection molding. Moreover, because of the excellent biodegradability, nontoxicity, and low-cost of cellulose derivatives, this work provides a simple and engineering method for constructing melt-processable bioplastics from cellulose.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acssuschemeng.7b04466](https://doi.org/10.1021/acssuschemeng.7b04466).

Synthetic routine and reaction conditions, NMR spectra of various cellulose esters, and TGA characterization of various cellulose esters. (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: zhjm@iccas.ac.cn (J. M. Zhang).

*E-mail: jzhang@iccas.ac.cn (J. Zhang).

ORCID

Jinming Zhang: 0000-0003-3404-4506

Jun Zhang: 0000-0003-4824-092X

Notes

The authors declare no competing financial interest.

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