

New Methods for Acylation of Pure and Sawdust-Extracted Cellulose by Fatty Acid Derivatives — Thermal and Mechanical Analyses of Cellulose-Based Plastic Films

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ABSTRACT: This work deals with the synthesis of cellulosic plastic films obtained in homogeneous conditions by microwave-induced acylation of commercial or chestnut tree sawdust cellulose by fatty acids. The acylation reaction was studied according to *N,N*-dimethyl-4-aminopyridine (DMAP) amount, DMAP simultaneously playing the role of catalyst and proton trapping base. This study clearly showed that DMAP does not influence degrees of substitution (DS), massic, and molar yields. Plastic films synthesized in the absence of DMAP showed a decrease in mechanical behavior. Organic (tributylamine) or inorganic bases (CaCO_3 , Na_2CO_3) were then added to replace DMAP basic activity, and no changes were observed. Concerning thermal

and mechanical properties of plastics obtained with various bases, glass transition temperatures (T_g) and degradation temperature (T_d) were found constant whatever the base, and the best mechanical properties were obtained for films synthesized in the presence of CaCO_3 . The same remarks were made concerning the valorization of chestnut tree sawdust cellulose. Microbial biodegradation of plastic films with DS = 2.2 led to a loss of their mechanical behaviors. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 1266–1278, 2005

Key words: cellulose; catalyst-free esterification; microwave irradiation; plastic films; biodegradability

INTRODUCTION

Petroleum resources are supposed to suffer from exhaustion within the next 50–100 years, so there is a need for an alternative to petrochemistry. Much research focuses on the use of natural and renewable raw polymers for the synthesis of plastics, and cellulose may be a good candidate for this purpose.

Cellulose is the most abundant natural polymer on Earth. It is estimated that about 5×10^{10} tons of cellulose are generated each year throughout the world.¹ Cellulose accounts for 40–50% of the mass of wood.² Long-chain aliphatic acid esters of cellulose (named long-chain cellulose esters) were identified as potential biodegradable plastics because of the enzymatically labile ester bond and the *O*-glucosidic bonds of cellulose. The discovery of nondegrading solvents for cellulose, such as the lithium chloride/*N,N*-dimethylacetamide solvent system (LiCl/DMAc),³ increased the interest in its modification. In fact, reactions on cellulose in homogeneous conditions present many of advantages, as follows⁴:

- (1) they lead to cellulose derivatives with well-controlled degree of substitution;
- (2) the substitution pattern is regular along the polymer backbone; and
- (3) reactions can be done in reduced time.

Hence, cellulose fatty acid esters can be obtained in homogeneous conditions. The acylation takes place in the presence of aliphatic acids or derivatives, catalyst, and sometimes, a coupling agent. For example, carboxylic acid/pyridine/*p*-toluenesulfonic acid,⁵ carboxylic acid, or anhydride/dicyclohexylcarbodiimide (DCC)/pyrrolidinopyridine,⁶ or acyl chloride or anhydride/pyridine,^{7,8} were already used in the past. More recently, our laboratory⁹ showed that long-chain cellulose esters can be synthesized by acylation of cellulose in LiCl/DMAc with lauroyl chloride, in the presence of *N,N*-dimethyl-4-aminopyridine (DMAP) as a catalyst, using microwave irradiation as a new and very efficient way to activate reactions. Reactions realized in these conditions led to cellulose esters in only 1-min reaction time.

Concerning cellulose fatty ester purification, conventional methods were always based on the use of organic solvents. Examples quoted in the literature describe the precipitation/solubilization system^{10,11} by using methanol (or ethanol) and chloroform, re-

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spectively, and Soxhlet extraction^{12,13} (using ethanol, methanol, or acetone).

The aim of this work was the acylation of cellulose with lauroyl chloride, in LiCl/DMAc, induced by microwave irradiation with or without catalyst, and, on the other hand, in the presence of amine or inorganic bases (Scheme 1). This reaction provides an efficient synthesis of potentially biodegradable plastic films in only 1 min. We also set up a new method for long-chain cellulose ester purification, using aqueous solutions of sodium hydrogenocarbonate instead of organic toxic solvents. We will comment on the thermal and mechanical properties of the synthesized plastics and the study of their biodegradability.

EXPERIMENTAL

Materials

Microcrystalline cellulose (20 μm , Aldrich, Lyon, France), lauroyl chloride (98%, Acros, Noisy le Grand, France), N,N-dimethyl-4-aminopyridine (DMAP, 99%, Acros) tributylamine ($\geq 99\%$, Fluka, Saint-Quentin Fallavier, France), sodium hydrogencarbonate, sodium carbonate and calcium carbonate (Aldrich) were used without further purification. Solvents were purified and stored by using conventional methods. Lithium chloride (99%, Acros) was stored under vacuum. Chestnut sawdust was purchased from the "Scierie Mazières" Company, France.

Methods

Purification of chestnut cellulose

Sawdust was rid of tannins by 4×1 h of successive refluxing in ethanol/water 80/20 (v/v). After filtration and drying, lignins and hemicelluloses were extracted by the mixture dioxane/HCl 2M 90/10 (v/v) according to Monties et al.² After filtration and drying, pure chestnut cellulose was obtained.

Solubilization of cellulose in LiCl/DMAc

Both types of cellulose were dissolved by a method described elsewhere,¹⁰ consisting of solvent exchange successively using methanol and DMAc to remove the water trapped in the cellulose structure. This treated cellulose was then added to a solution of 6.7% LiCl/DMAc (w/v) and stirred until complete dissolution (2–3 h). The final solution concentration is 1 g of cellulose in 50 mL LiCl/DMAc system for either microcrystalline or chestnut cellulose.

Acylation

Lauroyl chloride was added to cellulose solutions and stirred to homogenize the mixture. This solution was

then irradiated in a microwave reactor (Prolabo Synthewave® 402) for 1 min (power output = 300 W, final temperature $\approx 110^\circ\text{C}$). In a typical experiment, 0.5 g of cellulosic substrate (25 mL of a stock solution accounting for 3.1 mmol of anhydroglucose units) was mixed with 0–11 equiv. lauroyl chloride (0–34.1 mmol, 0–7.9 mL) per anhydroglucose unit and was subjected to microwave irradiation.

Acylation in presence of organic bases

DMAP or tributylamine as first dissolved at room temperature in the cellulose solution. Then, lauroyl chloride was added, and the mixture was subjected to microwave irradiation for 1 min in the same conditions as above. The amount of organic bases varied from 0.25 to 0.5 equiv. (1.5 mmol) per anhydroglucose unit.

Acylation in the presence of inorganic bases

For experiments with inorganic bases, DMAP or tributylamine was substituted by 0.5 equiv. of CaCO_3 or Na_2CO_3 per lauroyl chloride. After adding fatty acid chloride, the reaction was activated by microwave irradiation.

Purification of synthesized cellulose esters

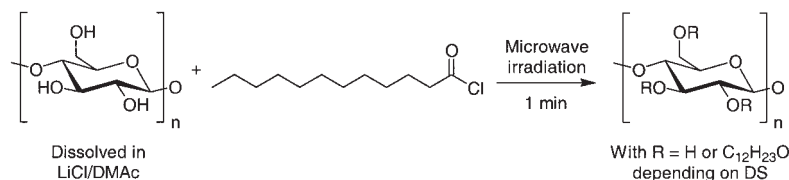
Two methods for cellulose ester purification were used.

- (1) The first method is the classical method consisting of successive precipitations and solubilizations with methanol and chloroform, respectively, and drying before casting.
- (2) The second method takes advantage of the precipitation of the reaction media by addition of an aqueous solution of sodium hydrogenocarbonate (0.4M). The precipitate was then filtered and washed once with aqueous sodium hydrogenocarbonate and then twice with hot water. Cellulose ester was allowed to dry overnight under vacuum before casting.

Casting, characterization, and degree of substitution

Each product was converted into plastic film. Cellulose esters (white or yellow–brown powder from microcrystalline or chestnut tree cellulose, respectively) were dissolved in 30 mL chloroform; then, the solvent was allowed to evaporate in air at room temperature.

All products were characterized by FTIR spectroscopy using a FTIR Perkin–Elmer Spectrum 1000 apparatus and by ^1H - and ^{13}C -NMR spectroscopy in CDCl_3 by using a Bruker DRX-400 Spectrometer (operating at 400.13 MHz); chemical shifts were measured in



Scheme 1 Acylation of cellulose by microwave irradiation without catalyst.

parts per million by using tetramethylsilane (TMS) as internal standard.

The degrees of substitution (DS = number of grafted lauroyl residue per anhydroglucose unit; $DS_{\max} = 3$) were determined by two different methods according to the solubility of cellulose esters in $CDCl_3$.

If esters were insoluble in $CDCl_3$, DS were measured by a volumetric method consisting of saponification of esters with a 0.25M NaOH alcoholic solution at 70°C for 17 h followed by pH metric titration of excess NaOH and released lauric acid sodium salt with 0.1M HCl aqueous solution, according to the formula

$$DS = \frac{M_{gu}}{(n_{fa}/m_s) - (M_{fa} - M_w)}$$

where M_{gu} is the anhydroglucose unit molecular weight = 162.14; n_{fa} is the molar number of fatty acid determined by titration (mol); m_s is the sample weight (g); M_{fa} is the fatty acid molecular weight = 202.32; and M_w is the water molecular weight = 18.02.

For $CDCl_3$ soluble cellulose esters, DS was evaluated by 1H -NMR, using integration measurement, and applying

$$DS_{NMR} = \frac{10 \times I_{CH_3}/3}{I_{sugar} + I_{CH_3}/3}$$

where I_{CH_3} is the integration for the three protons of lauric chain endgroup; and I_{sugar} is the integration of osidic protons.

Thermal analysis

Differential thermal analyses were performed with a DTA/DSC 1600 Labsys Setaram apparatus. The heating rate was set at 5°C/min until a limit of 450°C was reached. Thermogravimetric analyses were performed with an ATG Labsys Setaram apparatus by using the same program in temperature increase.

Mechanical properties

The tested samples consisted of 8 × 2 cm lamellas whose thicknesses were comprised between 150 and 200 μm. Ten tests were carried out for each film, at

20°C, using an uniaxial tensile apparatus made up of two jaws, one fixed and the other moving with a vertical velocity of 50 mm/min. The distance between the two jaws was about 3 mm at the beginning of the experiment.

Biodegradability

Cellulose-based plastic films (DS = 2.2) were suspended in ultrapure water. The medium was inoculated with a bacterial strain of *Streptomyces sampsonii*. The medium was incubated at 37°C in an orbital shaker (150 rpm) for 10 months. The same protocol was applied to another strain of the type Gram-positive bacillus *sp.* isolated during a previous work.¹⁴

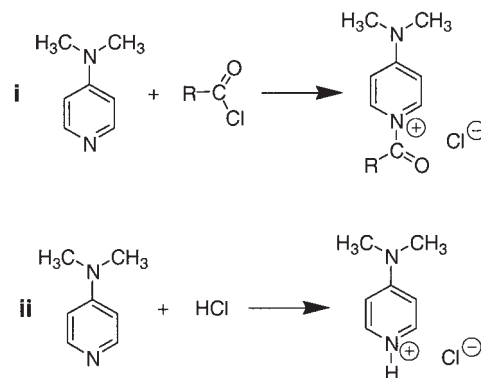
RESULTS AND DISCUSSION

Cellulose fatty esters were obtained according to Scheme 1.

Influence of DMAP

Cellulose acylation was conducted in the presence of a catalyst, such as pyridine or DMAP, leading to the formation of acylpyridinium chloride, a compound more reactive than acyl chlorides, according to the mechanism depicted in Scheme 2(i).

After solubilization of DMAP, cellulose was acylated with lauroyl chloride by microwave irradiation in a laboratory reactor. With this aim, we added lau-



Scheme 2 DMAP application during acylation reaction.

TABLE I
Cellulose Acylation (2 g/100 ml) in the Presence of DMAP, after 1 min of Microwave Irradiation

Lauroyl chloride equiv.	DMAP amount					
	0.5 equiv.			0.25 equiv.		
	DS	R_{mass} (%) ^a	R_{mol} (%) ^b	DS	R_{mass} (%) ^a	R_{mol} (%) ^b
2	^c	0.8 ^d	11	5		
3	1.57	75	27	1.54	80	29
4	1.83	120	39	1.88	178	57
5	2.04	178	54	2.24	270	77
6	2.24	280	79	2.33	290	80
8	2.46	294	78	2.41	293	79
9	2.49	306	80	2.45	322	89
10	2.54	314	81	2.66	330	88

^a Massic yield, ratio between the product weight and starting cellulose weight.

^b Molar yield, ratio between the mole number of acylated anhydroglucose unit (calculated according to the DS) and mole number of anhydroglucose unit in starting material.

^c No product was recovered by precipitation.

^d DS calculated by volumetric method.

royl chloride to the cellulose solution (DMAc/LiCl) and irradiated for 1 min (300 W power output). For purification, we applied the conventional method consisting of repeated precipitation–solubilization with methanol and chloroform, respectively. The first precipitation step resulted in the formation of methyl laurate byproduct that was eliminated after an additional solubilization–precipitation run. Table I indicates the DS, weight increase, and molar yield values obtained by acylation of cellulose when 0.25 and 0.5 equiv. of DMAP per anhydroglucose unit were used.

Results showed first that the DMAP amount did not influence DS value. Moreover, it seems that the DS reached a plateau around 2.5 for acyl chloride amount over 6 equiv. The maximum theoretical DS value of 3 was never reached. The reason for this result can be the strong steric effect induced by lauroyl chains on the remaining hydroxyl sites when $\text{DS} > 2.5$. The same interpretations can be done for massic and molar yields. The use of 4 and 5 lauroyl acid chloride equiv. gives better yields only when 0.25 equiv. of DMAP is used.

Experiments using 2 equiv. lauroyl chloride were carried out. However, no product was recovered after precipitation with methanol. Acylation was supposed to take place; otherwise cellulose would have been precipitated after methanol addition. The product ($0.3 < \text{DS} < 1.5$) obtained during this reaction was actually soluble in the DMAc/LiCl/methanol mixture. These esters thus could neither have been recovered nor analyzed.

The DMAP amounts do not show a significant influence on the reaction characteristics (DS, R_{mass} , R_{mol}). Mechanical behavior of plastic films obtained by cellulose esters casting showed that they were significantly ductile and resistant.

Reaction without DMAP

This reaction was then studied in the absence of catalyst. The evolutions of DS, mass, and molar yields are shown in Figure 1 (a–c) and compared with the results obtained with DMAP.

Figure 1 (a) ($\text{DS} = f[\text{lauroyl chloride equiv.}]$) clearly shows that, in our conditions, DMAP is not essential to catalyze cellulose acylation. Even if an acylpyridinium salt were formed, the difference in reactivity between this salt and the acyl chloride would have been too weak to play a detectable catalytic influence. Concerning curves 1 (b and c), we noticed that without DMAP, massic and molar yields tend to decrease when more than 7 acyl chloride equiv. are used. This could be a consequence of the action of the hydrochloric acid released during catalyst-free cellulose acylation. Indeed, when DMAP was used, part of this produced acid was trapped thanks to its basic activity. Without DMAP, this hydrochloric acid could hydrolyze cellulose glucosidic bounds, involving a partial degradation of polymer (Scheme 3), the small fragments being eliminated during purification.

Plastic films obtained by cellulose acylation without DMAP and after casting in chloroform are very brittle. This low ductility is also due to the decreasing polymerization degree induced by acid hydrolysis.

DMAP catalytic activity did not have any influence on DS and reaction yields, but its basic property was necessary to obtain cellulose ester plastic films with suitable mechanical behavior. Therefore, we introduced other bases in the reaction media to check this hypothesis.

Influence of other bases

Tributylamine was first used as organic base because it would be hardly evaporated during microwave ir-

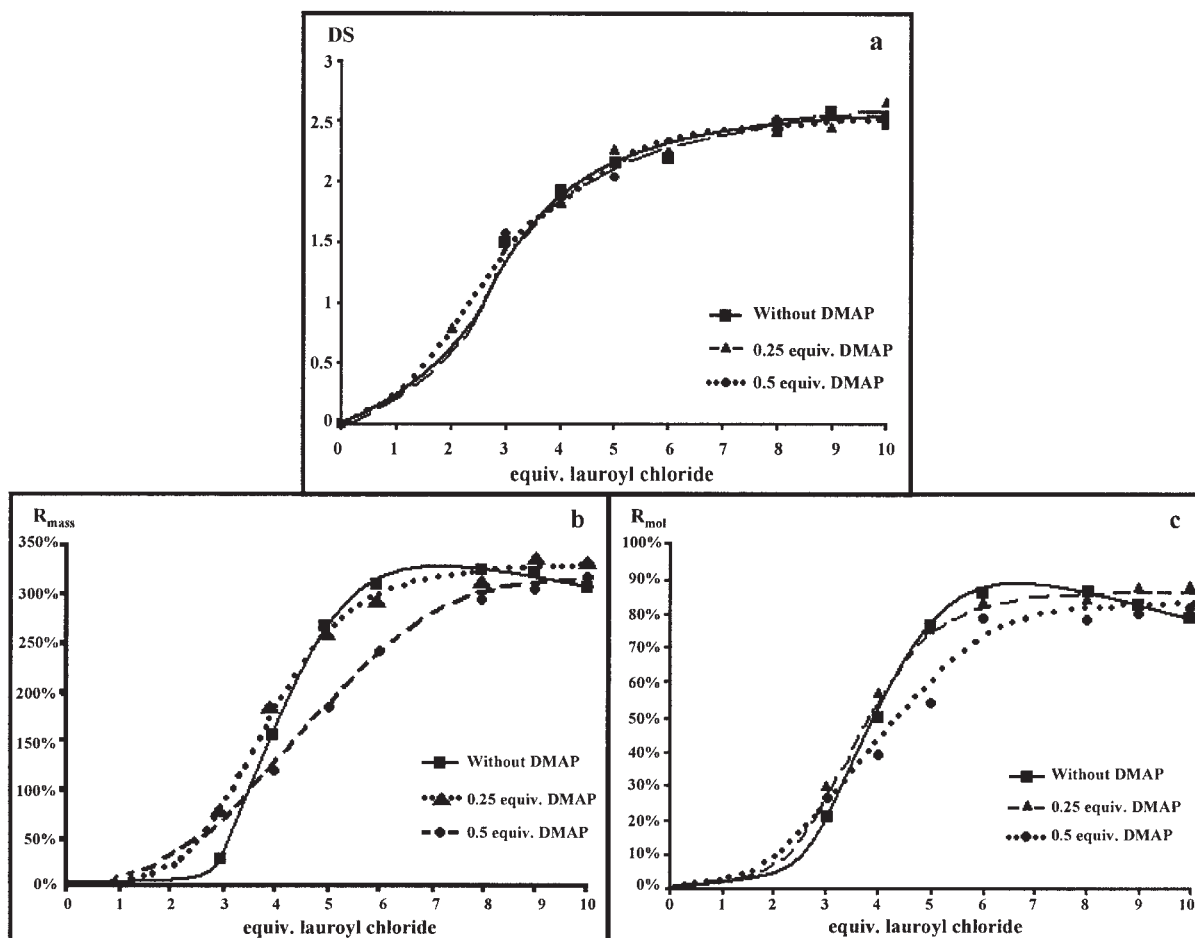
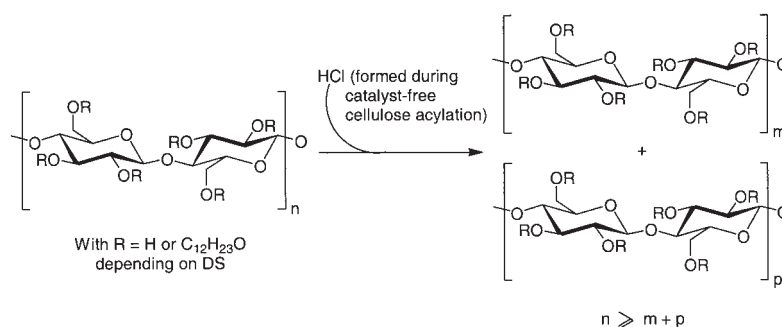


Figure 1 Evolution of cellulose acylation characteristics using various DMAP amounts (a: degree of substitution; b: massic yield; c: molar yield).

radiation ($T_{\text{eb}} = 215^{\circ}\text{C}$). The inorganic bases, calcium and sodium carbonates, were selected for their harmlessness. Moreover, their reaction with hydrochloric acid involves the formation of a salt, water, and carbon dioxide, these three byproducts being easily eliminated during purification steps.

The protocol used with these various bases consisted of the suspension (inorganic bases) or the solubilization (tributylamine) of the base, and then, in the

addition of lauroyl chloride, microwave irradiation and purification. Before activation, the cellulose solution containing base is homogeneous in the case of the tributylamine and heterogeneous when calcium and sodium carbonates were used. A difference in reaction temperature occurred after microwave activation between the homogeneous and heterogeneous solutions, these temperatures being approximately $100\text{--}110^{\circ}\text{C}$ during reaction in the presence of carbonates, and of



Scheme 3 Degradation of cellulose backbone by hydrochloric acid.

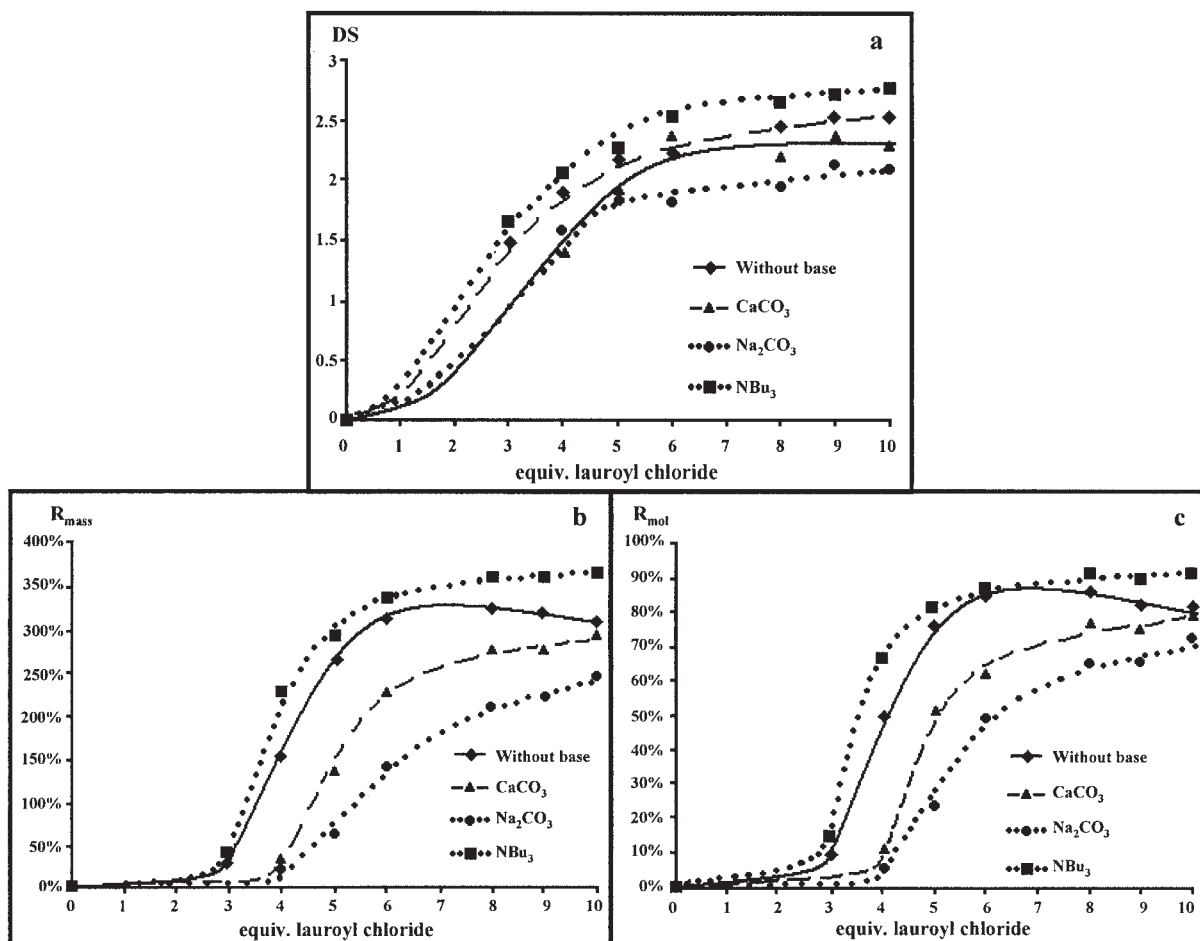


Figure 2 Evolution of cellulose acylation characteristics using various bases (a: DS; b: massic yield; c: molar yield).

approximately 130–140°C for reaction using tributylamine. Results are represented in Figure 2(a–c).

The evolution of the degree of substitution according to lauroyl chloride amount showed that the DS

obtained by reaction with tributylamine were slightly higher than these obtained without base. Cellulose esters synthesized by using carbonates had lower DS than these obtained in the presence of organic bases,

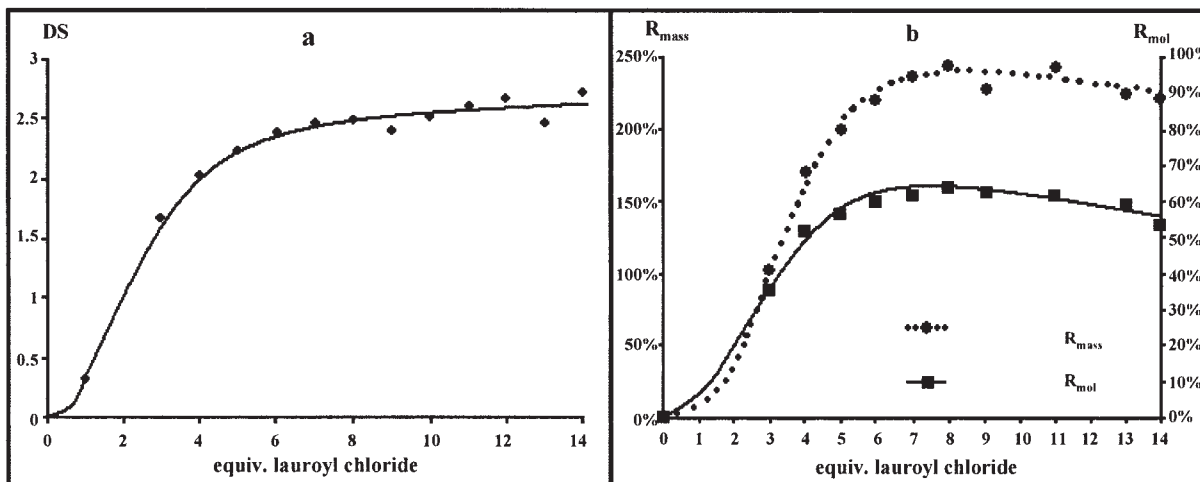


Figure 3 Evolution of the DS (a) and the massic and molar yields (b) according to lauroyl chloride amount, with 1 equiv. of DMAP.

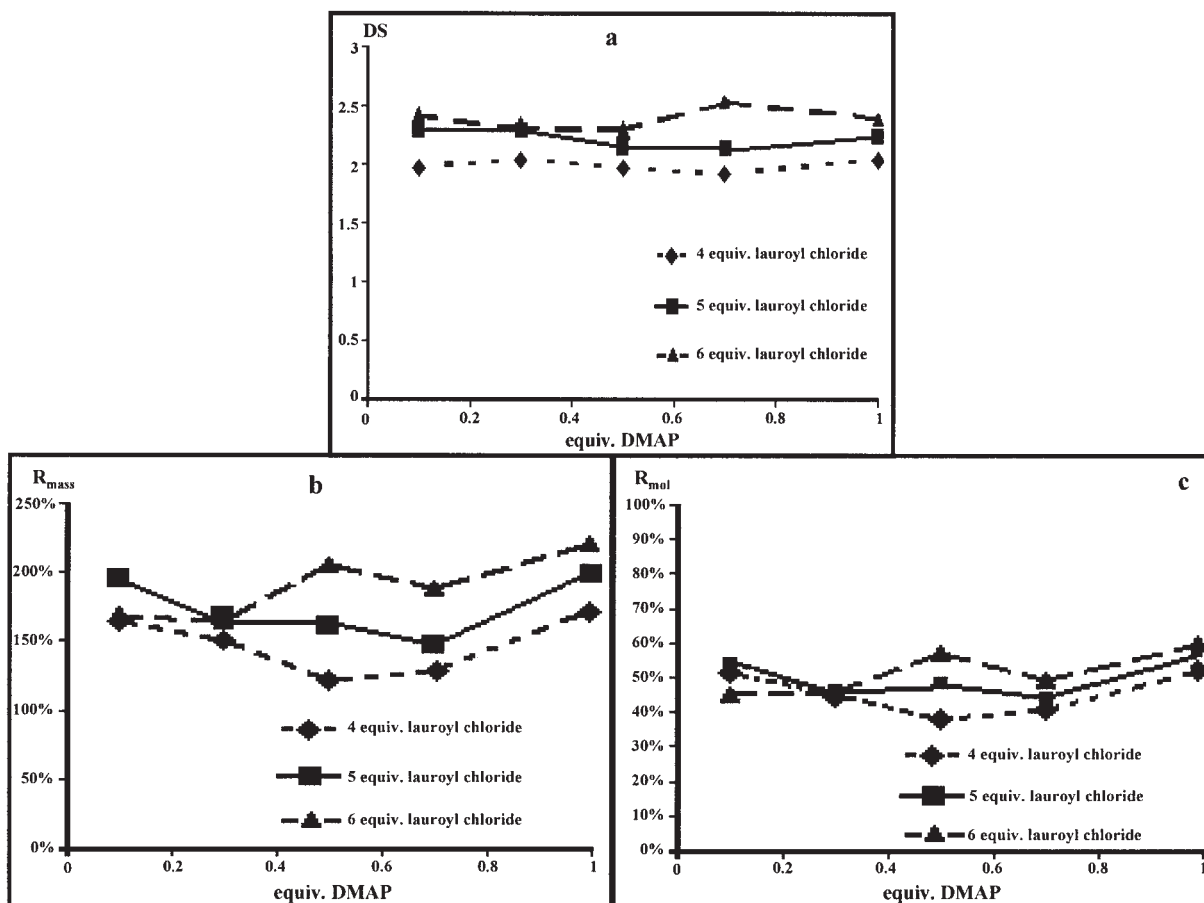


Figure 4 Evolution of the degree of substitution (a) and massic (b) and molar yields (c) according to DMAP amount.

because of reaction medium heterogeneity and evaporation of water and carbon dioxide produced after reaction between hydrochloric acid and carbonates. So, in the presence of carbonates, DS were lower than

in the presence of DMAP, itself lower than that of reactions with tributylamine.

The same comments can be made about reaction yields. In the case of massic yields, the product weight

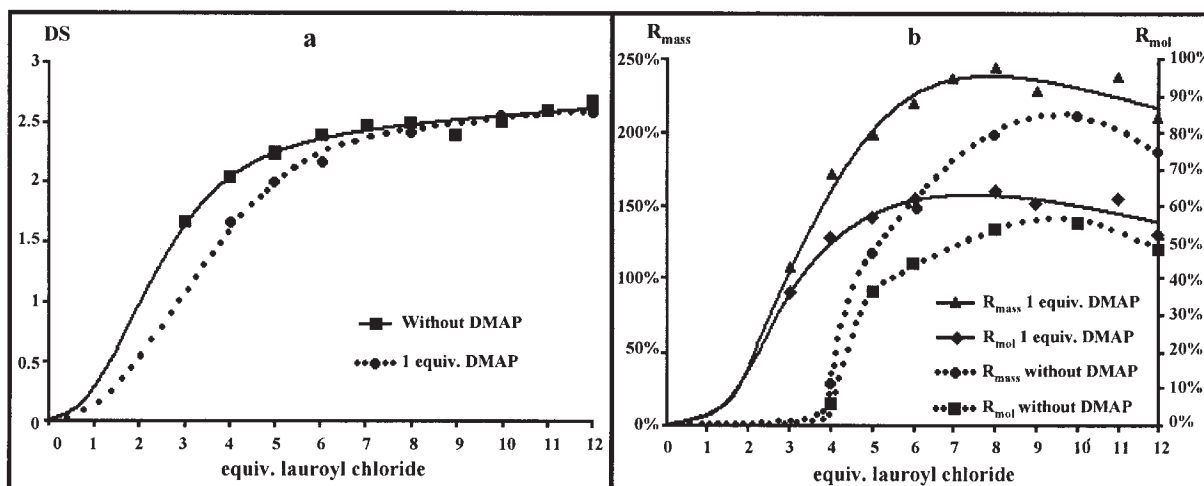


Figure 5 Results obtained for the chestnut tree sawdust cellulose acylation with or without DMAP (a: DS variation; b: massic and molar yields variation).

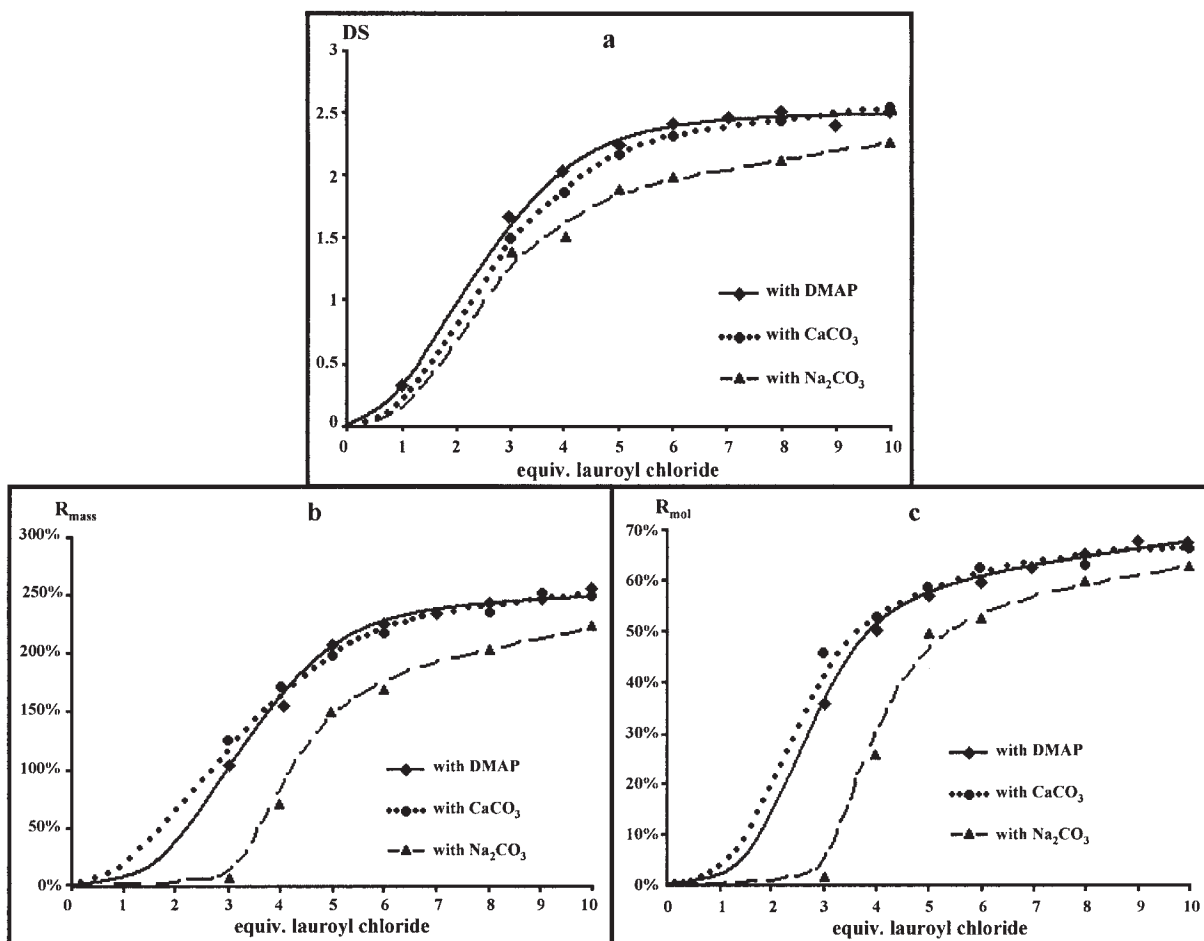


Figure 6 Evolution of cellulose acylation characteristics with various bases.

obtained is always larger in the presence of the organic bases than in the presence of inorganic bases. This massic yield reached a plateau near 360% when tributylamine was used, but no plateau value was obtained when inorganic bases were used. This remark is also valid for the molar yields.

Cellulose esters obtained by this protocol were converted into plastic films by casting. These plastics were also ductile and easy to handle whatever the base used. The most promising basic compounds are calcium and sodium carbonates because of their harmlessness.

Acylation of chestnut tree sawdust cellulose

Chestnut tree cellulose was obtained from corresponding sawdust by successive extractions of tannins, lignins, and hemicelluloses with 42% massic yield. After solubilization in LiCl/DMAc , cellulose was acylated by microwave irradiation, in the same reaction conditions as commercial cellulose.

As for the study of microcrystalline cellulose acylation, we studied the variation of the acylation character-

istics (DS, R_{mass} , and R_{mol}) for chestnut tree sawdust cellulose obtained by acid hydrolysis in dioxane. Initially, the DS variations and reaction yields were studied according to acyl chloride equivalents, using 1 equiv. of DMAP. Results are illustrated in Figure 3 (a, b).

The variation of the reaction characteristics was in agreement with that obtained for commercial microcrystalline cellulose.

Influence of DMAP amount

The influence of DMAP amount on reaction characteristics was studied using 4, 5, and 6 lauroyl chloride equiv., which corresponded to the lowest amounts necessary to obtain plastic films, as shown for model cellulose (Fig. 4).

As in the case of microcrystalline cellulose, DMAP amount did not have any influence on reaction characteristics. This encouraged us to realize the same study in the absence of DMAP. These reactions were carried out using 0 to 12 lauroyl chloride equiv. per anhydroglucose unit. The results [Fig. 5 (a, b)] were

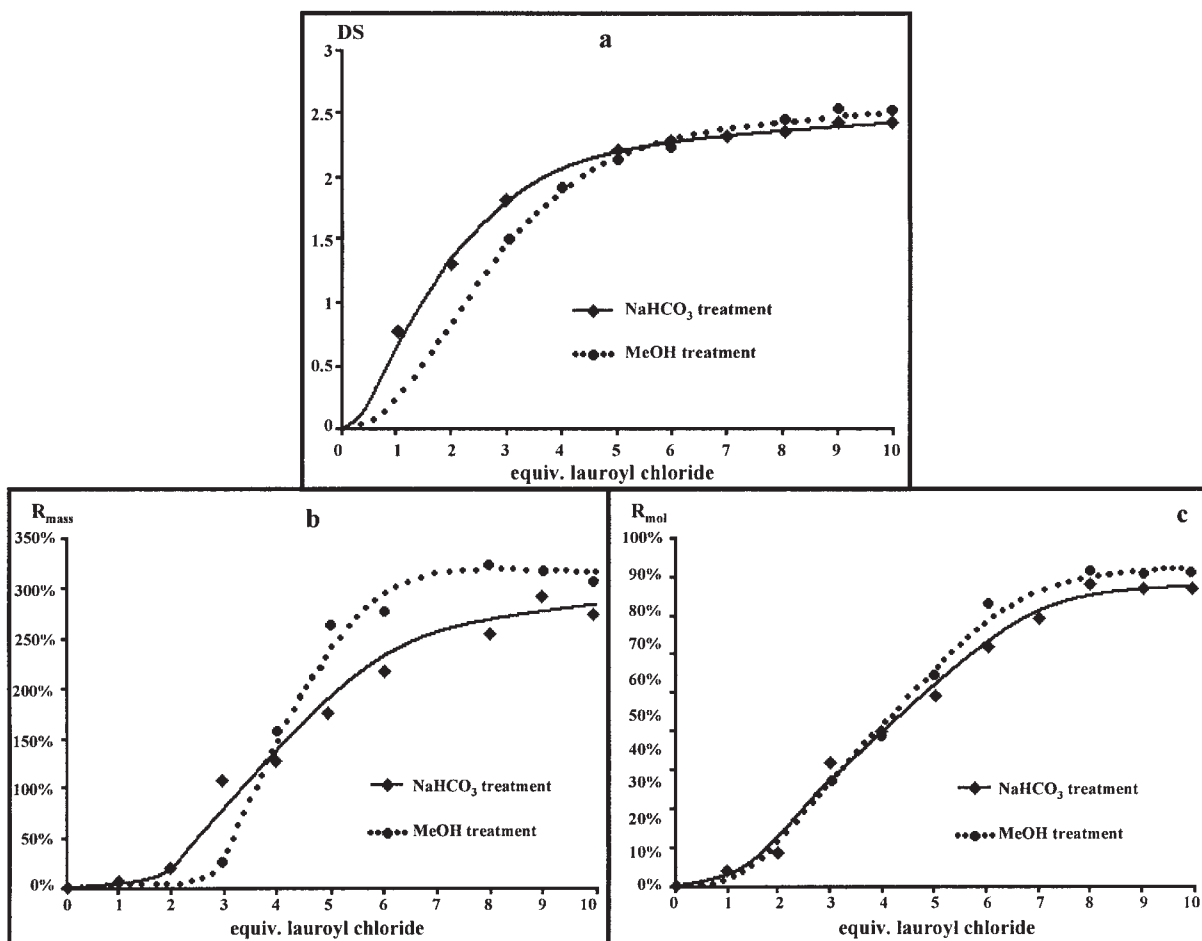


Figure 7 Influence of purification treatment on the DS (a), massic (b), and molar yields (c) variation of the cellulose acylation reaction.

compared to these obtained when 1 equiv. of DMAP was used.

Even if DS were unchanged in both cases, the absence of DMAP induced massic and molar yields lower than these obtained when DMAP was used. Furthermore, plastic films obtained after acylation without DMAP are very brittle, whereas those synthesized with DMAP are more ductile. This tends to support our assumption on destroying acid hydrolysis.

To avoid cellulose ester hydrolysis by hydrochloric acid, chestnut tree sawdust cellulose acylation was again carried out by using calcium or sodium carbonate instead of DMAP.

Influence of carbonates on chestnut tree sawdust cellulose acylation

By applying the method developed for microcrystalline cellulose, we studied the effect of the two inorganic bases—calcium carbonate and sodium carbonate—on chestnut tree sawdust cellulose acylation (Fig. 6).

We observed the same trends as these obtained with microcrystalline cellulose. Comparing the two inorganic

bases, we concluded as for microcrystalline cellulose that DS, massic, and molar yields obtained with calcium carbonate were higher than these obtained by using sodium carbonate. Plastic films obtained after casting in chloroform had the same aspect in every case.

Influence of purification treatment

After dissolution, we acylated cellulose with lauroyl chloride without any catalyst by microwave irradiation in a laboratory reactor. In this way, we added lauroyl chloride to the cellulose solution (DMAc/LiCl) and irradiated for 1 min with 300 W power output. For purification, we applied the conventional method consisting of precipitation–solubilization with methanol and chloroform, respectively. Two precipitations were necessary for complete elimination of methyl laurate formed as byproduct during the first precipitation (action of methanol on excess lauroyl chloride). The major drawback of this purification method was the use of toxic solvents in large amounts to obtain pure cellulose esters.

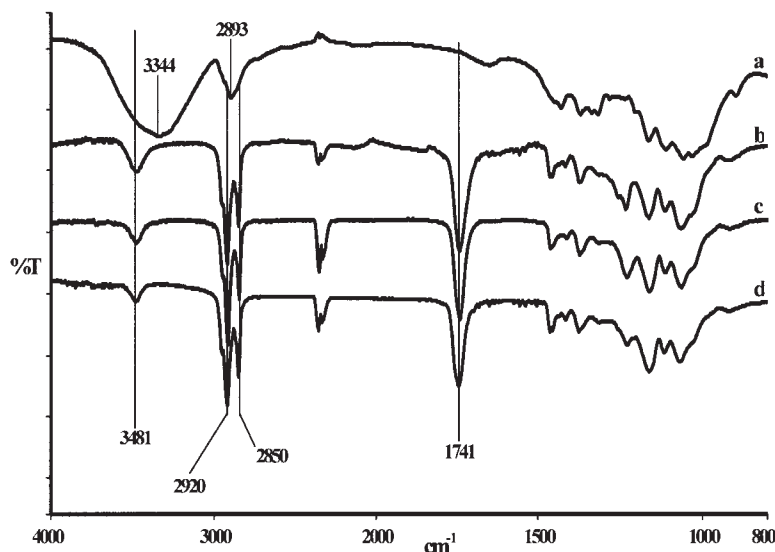


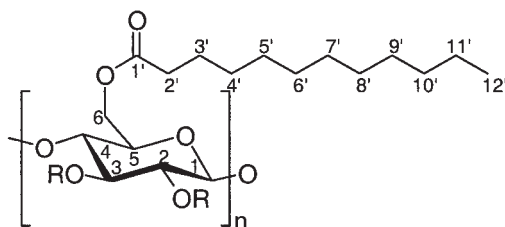
Figure 8 Infrared spectra of microcrystalline cellulose (a) and cellulose esters with DS 1.5 (b), 1.9 (c), and 2.5 (d) in solid phase.

To avoid their use, we set up a new purification method based on precipitation of cellulose ester by adding an aqueous solution of NaHCO_3 . After filtration, solid ester was washed twice with water and dried under vacuum. The filtrate is an aqueous solution of surfactant (sodium laurate), very difficult to filter on paper because it leads to the fast filling of the filter paper. Cellulose esters were dried in vacuum and converted into plastic film by casting. This purification led to the total elimination of unreacted lauroyl chloride by its conversion into the corresponding water-soluble fatty acid sodium salt. To check the purification method effectiveness, cellulose esters were dissolved again in chloroform and precipitated

by methanol addition. After filtration, the filtrate was recovered and dried. This experiment showed that esters were pure and that purification of these cellulose esters by NaHCO_3 treatment was appropriate. This new treatment was applied to cellulose esters synthesized without DMAP, and without base, starting from dissolved microcrystalline cellulose; we then studied the influence of the purification method on the characteristics of the reaction (Fig. 7).

These results showed that this treatment did not influence the variation of cellulose ester degree of substitution. On the other hand, the analysis of the massic yield variation showed that a considerable cellulose ester amount was not recovered after purifica-

TABLE II
Chemical Shifts of Cellulose Ester in ^1H and ^{13}C NMR Spectroscopies



With $\text{R} = \text{H}$ or $\text{C}_{12}\text{H}_{23}\text{O}$
depending on DS

Position in sugar	^1H δ (ppm)	^{13}C δ (ppm)	Position in side chain	^1H δ (ppm)	^{13}C δ (ppm)
1		114.2	1'	—	173.2, 173.6, 174.0
2		73.4	2'	2.32	36.7
3		74.9	3' to 11'	1.26	22.7 to 29.7
4		82.0	12'	0.88	14.1
5		76.2			
6	3.0 to 5.3	62.3			

tion. This was attributed to the filtration problems. The product loss could, thereafter, be reduced by use of Soxhlet thimbles, allowing a fast and efficient filtration of cellulose ester.

We also studied the influence of the purification treatment on reaction characteristics for reactions using inorganic bases (CaCO_3 , Na_2CO_3). The results in this case were identical to these obtained previously.

Spectral analysis

Infrared analyses were carried out on microcrystalline cellulose esters by direct transmittance of the beam through plastic film. IR spectra of cellulose esters with DS of 1.5, 1.9, and 2.5 were compared to the starting cellulose one (Fig. 8).

These spectra were similar to these obtained in previous works for lauroyl cellulose esters.¹⁵ They showed a decrease of 3344 cm^{-1} band corresponding to hydroxyl group and a shift around 3481 cm^{-1} due to the disappearance of hydroxyls and obviously of the hydrogen bonds of starting cellulose. This decrease in intensity happened with the appearance of a band around 1741 cm^{-1} characteristic of ester functions. Moreover, we noticed an increase in width for the band around 2900 cm^{-1} corresponding to C—H stretching of cellulosic backbone and fatty chains. Comparing cellulose esters according to their DS, a slight extinction of the hydroxyl band was correlated with the increase in the DS.

Concerning NMR data, signal observed for ^1H and ^{13}C analysis are given in Table II. The ^1H -NMR spectra showed peaks between 0.8 and 2.2 ppm, corresponding to alkyl groups of lauroyl side chain, and other figures between 2.8 and 5 ppm are attributed to anhydroglucose unit protons. The missing acidic proton characteristic signals ($\delta = 12\text{ ppm}$) of lauric acid and of aromatic signals corresponding to catalyst protons also proves the efficiency of the purification.

The ^{13}C -NMR spectra showed three signals at 173.2, 173.6, and 174.0 ppm, corresponding to carbonyl groups linked to sugar carbons C-2, C-3, and C-6, respectively. Literature indicates that C-6 position is substituted, preferentially to C-2 and then to C-3.⁶

No difference was observed between IR and NMR spectra of cellulose esters obtained by the different synthesis pathways exposed previously.

Comparison of mechanical properties of various samples

The mechanical characteristics recovered from cellulose-based plastic film tensile tests were the elastic modulus, E (MPa), the tensile failure stress, σ_f (MPa), and the failure strain level, ε_f (%).

Uniaxial mechanical tensile tests were performed on microcrystalline cellulose ester plastic films (DS = 2.2)

TABLE III
Mechanical Properties of Cellulose-Based Plastic Films with DS = 2.2

Base	Elastic modulus E (MPa)	Tensile failure stress σ_f (MPa)	Tensile strain level ε_f (%)
No base	47.4	12.3	314
Tributylamine	54.7	17.0	422
DMAP	46.0	16.4	705
Calcium carbonate	56.3	22.5	687

with a constant traction velocity of 50 mm min. The sample sizes were $8 \times 2\text{ cm}$ but the part on which traction was exerted lied between 2 and 3 mm, the remainder of the sample being wedged in apparatus bites. The thickness of the samples was measured in 12 points and is on average $150\text{ }\mu\text{m}$ for each one. For each plastic, 10 samples were tested and the results for each plastic film indicated in Table III are the average of these 10 sample characteristics.

In a general way, results showed elastic moduli around 50 MPa, tensile strain level higher than 300%, and tensile failure stress between 12 and 22 MPa. With equal degrees of substitution (2.2), the use of a base involved a very significant increase in tensile strain level. Moreover, the use of calcium carbonate to replace DMAP involved an increase in elastic modulus (+8 MPa) and tensile failure stress (+6 MPa). The best mechanical characteristics were obtained by using calcium carbonate as base.

The mechanical properties (elastic modulus, E , tensile strain level, ε_f , and tensile failure stress, σ_f) of some largely used commercial polymers are indicated in Table IV.¹⁶ Polyethylene (PE) is largely used in packaging but also in the agricultural field (covers) or textile industry. Polypropylene (PP) is used in automobile engineering or cloth bag industry. PE and PP are both materials we would like to replace by cellulose-based material. Cellulose acetate and cellulose acetate butyrate film mechanical properties were also compared to long-chain cellulose ester film ones.

Compared to cellulose acetate and acetobutyrate, we noticed an elastic modulus lower for long-chain cellulose ester plastic films with DS = 2.2 (Table III) but an acceptable tensile failure stress and a better tensile strain level. If results obtained for lauroyl cellulose ester plastic films were compared to the commercial petrochemical plastic mechanical properties (Table IV), the following have been observed:

- (1) the cellulose plastic films elastic moduli were always lower than these of traditional plastics; and
- (2) their tensile failure stress and tensile strain level were equivalent to these obtained for linear low-density polyethylene.

TABLE IV
Mechanical Properties of Some Commercial Plastic Materials

Polymer	Elastic modulus E (MPa)	Tensile failure stress σ_R (MPa)	Tensile strain level ε_R (%)
Cellulose triacetate	1000–4000	12–110	15–55
Cellulose acetate-butyrate	300–2000	20–60	30–60
Low-density PE	150	15	500
Low-density linear PE	250	20	200–900
High-density PE ($M \approx 3 \times 10^4$ g mol ⁻¹)	800–1200	35	200–800
High-density PE ($M = 1$ to 5×10^6 g mol ⁻¹)	200–600	35	200–500
Polypropylene	1300	40	400

Thermal analysis

Glass transition temperature (T_g), measured by differential thermal analyses, corresponds to the transition temperature from the vitreous state to the rubbery state of a polymer. In our case, the T_g 's were determined for several types of plastic films focusing our attention on the effect of the base used during acylation on T_g for cellulose esters with DS = 2.2. We found that T_g 's were independent of the base used, around $160 \pm 5^\circ\text{C}$. These T_g values are in accordance with the literature, where they varied between 160 and 75°C for cellulose esters with DS ranging between 2.47 and 2.99, respectively.¹³ The polymerization degree of cellulose ester did not seem to influence T_g . To support this observation, we also carried out T_g measurements for chestnut tree sawdust cellulose esters with DS = 2.2. In this case, T_g remained unchanged around $160 \pm 5^\circ\text{C}$.

Degradation temperatures, T_d , of microcrystalline cellulose ester with DS = 2.2 were measured by thermogravimetric analysis, sampling with 30 mg of plastics. These experiments showed degradation temperatures between 200 and 215°C regardless of the base used during the acylation reaction. The T_d values recorded in these experiments are in agreement with the literature.⁵

Biodegradability

Previous works in our laboratory⁹ concerning biodegradability of cellulose-based plastic films were carried out on cellulose esters with DS = 0.7, using *Chromobacterium violaceum*, a bacterial strain isolated from compost. A subsequent weight loss ($\approx 15\%$) was observed. This biodegradation is somewhat higher than those reported by other groups¹⁷ (5% for DS = 0.3). To evaluate the biodegradability of cellulose esters with higher degrees of substitution, biodegradability assays were carried out on microcrystalline cellulose ester plastic films with DS = 2.2, using two bacterial strains. One of these strains was isolated by bacterial screening during a previous work¹⁴: it is Gram-positive bacillus whose identification is in hand. The other

strain is *Streptomyces sampsonii*, a filamentous Gram-positive bacterium-filament leading to short elements in the shape of Gram-positive bacillus.

Initially, two plastic samples were suspended in ultrapure water, each one with a bacterium strain, under stirring at 37°C . After 2 months, these plastics had lost their ductility and became very brittle. A control experiment carried out under the same conditions and without bacterium had not shown any change in plastic film mechanical properties. These material ductility modifications clearly showed the microbial attack on cellulosic plastic films. After 10 months, the two plastics were reduced into small pieces of approximately 0.4 cm. The reference sample, suspended in water, underwent no modification. Moreover, plastic film colors changed after incubation with bacteria, from colorless to yellow, supporting the bacterial attack hypothesis.

CONCLUSION

We applied a new catalyst-free cellulose acylation method and improved the efficiency of sodium and calcium carbonate instead of DMAP to limit cellulose hydrolysis during reaction. This method was successfully applied to cellulose extracted from chestnut tree sawdust. Moreover, a new purification method of cellulose esters was developed by using an aqueous solution of sodium hydrogenocarbonate instead of traditionally used methanol and chloroform. The study of cellulose esters mechanical properties showed that the use of calcium carbonate was much more efficient to obtain plastic films having best mechanical characteristics. The study of the biodegradability was very encouraging since we showed that microorganisms were able to modify the apparent plastic film ductility of cellulose esters with high DS.

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