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Synthesis of Plastic Films from Inulin by Acylation

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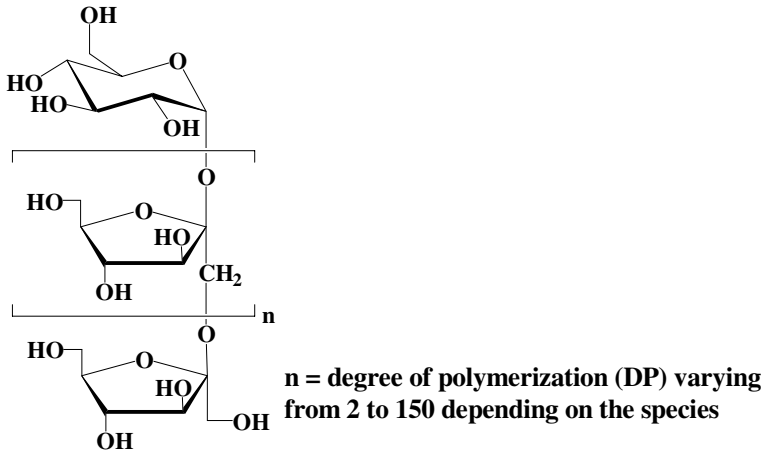
Summary

In this preliminary study, inulin, a fructooligosaccharide extracted from chicory roots, was converted into plastic films by acylation in homogeneous media and under conventional heating, using methacryloyl and lauroyl chlorides as acylating reagents and *N,N*-dimethyl-4-aminopyridine as basic catalyst. Products were analyzed by FT-IR and ^{1}H NMR spectroscopies to confirm their structures. A preliminary study of their thermal properties was also achieved.

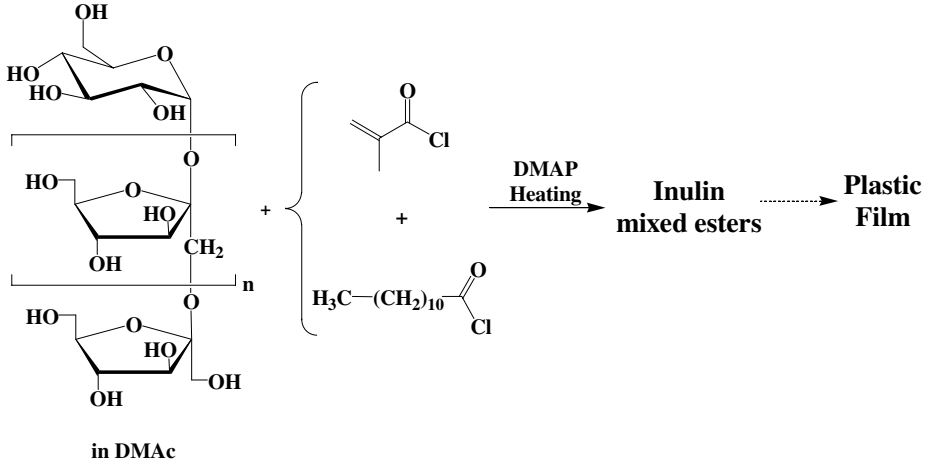
Introduction

Petroleum reserves will be exhausted in less then one century, so it is necessary to find another raw material for the fuel area, but also for plastic industry. Since few years, the use of natural polymers is a proposed alternative for the substitution of this non-renewable petroleum. In fact, biocarburants (bioethanol, bioesters…) are now well known and their use is growing up. But the valorization of agricultural or forestry byproducts can also lead to raw materials of great importance for the synthesis of biodegradable materials. In this last research area, we study the possible valorization of chicory roots (*Cichorium intybus*), an agricultural byproduct of importance in the North of France, to produce potentially biodegradable plastic films. The analysis of its chemical composition reveals principally polysaccharides such as cellulose, hemicelluloses and inulin. Inulin is a reserve carbohydrate of these plants, consisting mainly in β-(2→1)-fructosylfructose units with often, but not always, a α-D-glucopyranose unit at the reducing end (scheme 1). This fructopolysaccharide represents around 20 wt. % of the roots.



Scheme 1. Chemical structure of inulin.

Inulin is well known for its prebiotic properties,[1] but its derivatives have also been described as potential drug carriers and for its drug delivery abilities.[2,3] Concerning material applications, this polysaccharide was associated to Eudragit to obtain a biodegradable coating for specific colon disease targeting.[4] but all these biological applications are not sufficient enough for the utilization of inulin stock.
For the first time, our laboratories present a new and original way for the valorization of chicory root inulin. The aim of this work was to convert inulin into potentially biodegradable plastic films by its chemical acylation with methacrylic and lauric chains (scheme 2).



Scheme 2. Acylation of inulin with lauroyl and methacryloyl chlorides to obtain plastic films.

Experimental part

Materials

Commercial inulin (average DP=10, Orafti, Belgium), lauroyl chloride (98%, Acros), methacryloyl chloride (97%, stabilized by MEHQ, Acros), N,N-dimethyl-4-aminopyridine (DMAP, 99%, Acros), chloroform, methanol and N,N-dimethylacetamide (DMAc, 99+%, Acros) were used without further purification. Inulin was stored under vacuum and methacryloyl chloride was stored at 4°C.

Methods

Synthesis of Inulin-Based Plastic Films

Commercial inulin was first dissolved in N,N-dimethylacetamide (DMAc) and then acylated using acyl chloride reagent in the presence of N,N-dimethyl-4-aminopyridine (DMAP) as a basic catalyst.

In a typical procedure, inulin (2 g, 12.34 mmol) and DMAP (3 equiv, 4.52 g, 37 mmol) were first dissolved in 30 mL of DMAc. Either methacryloyl chloride, or lauroyl chloride or a mixture of both acyl chlorides, was added to the solution containing inulin. The reactional medium was stirred at various temperatures (room temperature to 80°C) during various times (30 min to 24 hours). At the end of the reaction, the product was purified by conventional method consisting in precipitation-dissolution using methanol and chloroform respectively.

Film Forming, Chemical Characterization, NMR and Infra-Red Spectroscopy

After purification, a casting was achieved to convert inulin esters into plastic films. This step consists in the solubilization of the product in 30 mL dichloromethane followed by slow evaporation of the solvent in the air at room temperature.

Every product was characterized by FT-IR spectroscopy using a FT-IR Bruker Vector 22 apparatus and by ^{1}H NMR spectroscopy in $CDCl_3$ using a Bruker DRX-300 Spectrometer (operating at 300.13 MHz). The degrees of substitution (DS = number of grafted chains per anhydrofructose unit; DS_{max} = 3) were determined by ^{1}H NMR (using integration measurement), and confirmed by FT-IR spectroscopy and volumetric method.[5]

Thermal Properties

Thermogravimetric analyses were performed with a Setaram TGDTA92 ® apparatus. The temperature program was to heat inulin ester plastic films (20 mg) from 20°C to 400°C at 5°C/min.

Calorimetric analyses were performed using a Differential Scanning Calorimeter PerkinElmer Pyris 1®. The heating rate was set at 20°C/min for the first ramp until 170°C, the sample was then cooled to 30°C and heated again until degradation temperature (determined by thermogravimatric analysis).

Results and discussion

Acylation of Inulin to Obtain Plastic Films

It is well known that cellulose can be converted into plastic films by fatty acylation, fatty acid chains are used as internal plasticizer.[6] We first used lauroyl chloride (LCl, 5 equiv. per anhydrofructose unit) as acylating reagent. After 30 minutes stirring at 80°C, the product was isolated after precipitation with methanol as a yellow oil, characterized by FT-IR and NMR spectroscopies as a lauroyl inulin ester. But this inulin ester could not be transformed into a plastic film.

Taking into account these results, and knowing the possibility to transform inulin into hydrogels by partial methacryloylation,[7] we achieved the acylation of inulin with methacryloyl chloride (MCl, 5 equiv per anhydrofructose unit), which led to a yellow gel and not to a plastic. FT-IR and NMR spectroscopies confirmed that this product was methacrylic inulin esters.

Previous works with cellulose [8] have shown that its acylation with lauroyl chloride led to plastic film formation. Thus lauroyl chains were introduced onto methacrylated inulin as internal plasticizer. In a typical experiment, inulin was acylated by an equimolar mixture of methacryloyl and lauroyl chloride (4 equiv of acyl chloride per anhydrofructose unit), at 80°C under stirring using DMAP as catalyst. Unfortunately, this experiment did not lead to a plastic film, but to a yellow oil which FT-IR and ^{1}H NMR spectra identified as a mixture of lauric and methacrylic inulin ester.

In order to analyze the importance of the acyl chloride addition order, lauroyl chloride (2 equiv) was first reacted with inulin and then methacryloyl chloride (2 equiv) was grafted onto the inulin lauric esters, leading to a plastic film. Other experiments were conducted using a mixture of lauroyl and methacryloyl chlorides, also leading to plastic films. The following experiments were focused on the influences of methacryloyl chloride / lauroyl chloride ratio. Experimental conditions of reactions leading to plastics are described in Table 1.

Table 1. Reaction conditions to obtain plastic films from inulin.

Essay	First step conditions	Second step conditions	R_{mass} (%)[a)]	DS[b)]	Ratio L/M[c)]
1	LCl (1 equiv) 80°C, 0.5 h	MCl (2 equiv) RT, 24 h	112	1.8	1/9
2	LCl (2 equiv) 80°C, 0.5 h	MCl (1 equiv) RT, 24 h	26	1.6	2/3
3	LCl (2 equiv) 80°C, 0.5 h	MCl (3 equiv) 40°C, 24 h	150	2.0	1/4
4	LCl (1 equiv) + MCl (3 equiv) 40°C, 24 h		20	2.0	1/9
5	LCl (2 equiv) + MCl (2 equiv), 80°C, 2h		66	1.9	1/4

[a)] Rmass: mass yield; [b)] DS: degree of substitution; [c)] L/M: laurate/methacrylate

Degrees of substitution (DS) and laurate/methacrylate (L/M) ratios were determined by a volumetric method (after saponification of inulin mixed esters) and FT-IR spectroscopy (using methyl methacrylate and methyl laurate as standards) respectively. Every product obtained as described in Table 1 was converted into plastic films by casting (dissolution of the inulin mixed ester in dichloromethane and slow evaporation in the air). Products 1 to 3 were yellow sticky films, product 4 was yellow and brittle, and 5 (figure 1) was white, translucent but neither sticky nor brittle.

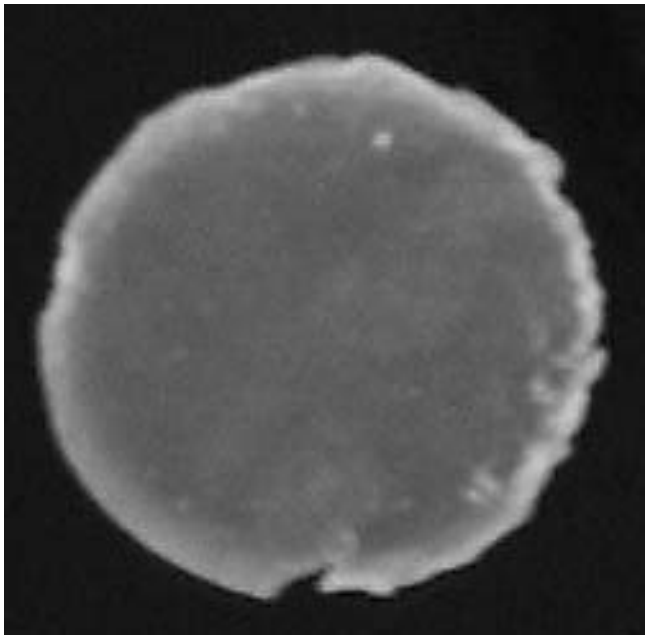


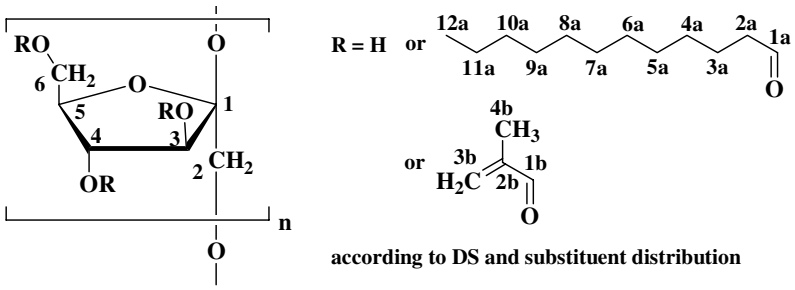
Figure 1. Photograph of the inulin-based plastic film 5.

According to this preliminary study, the best reaction conditions for the preparation of good quality plastics were to introduce together an equimolar ratio of methacryloyl and lauroyl chlorides in a solution of inulin containing DMAP, and to heat the reaction medium at 80°C for 2 hours. Fortunately, the other products could be investigated for their characteristics in adhesive material area.

Analyses of Inulin-Based Plastic Films

These films based on inulin were analyzed by NMR spectroscopy. Every product ^{1}H NMR spectrum shows similar characteristic signals corresponding to inulin protons, methacrylic moiety protons and lauric moiety protons (Table 2).

Table 2: ^{1}H NMR signal of inulin laurate/methacrylate mixed esters.



Inulin skeleton		Lauric chains		Methacrylic chains	
Protons	δ (ppm)	Protons	δ (ppm)	Protons	δ (ppm)
H1-H6	3.0-5.0 (m)	H2a	2.32 (t, J=6.9 Hz)	H4b	1.88 (s_e)
		H3a	1.63 (m)	$H3b_1$ and $H3b_2$	5.70 and 6.15 ($2s_e$)
		H4a-H11a	1.21 (m)		
		H12a	0.89 (t, J=7.1 Hz)		

These films were also characterized by FT-IR spectroscopy using a diamond ATR equipment, allowing the direct analysis of the film. Spectra of starting inulin and plastic film 5 are described by the figure 2.

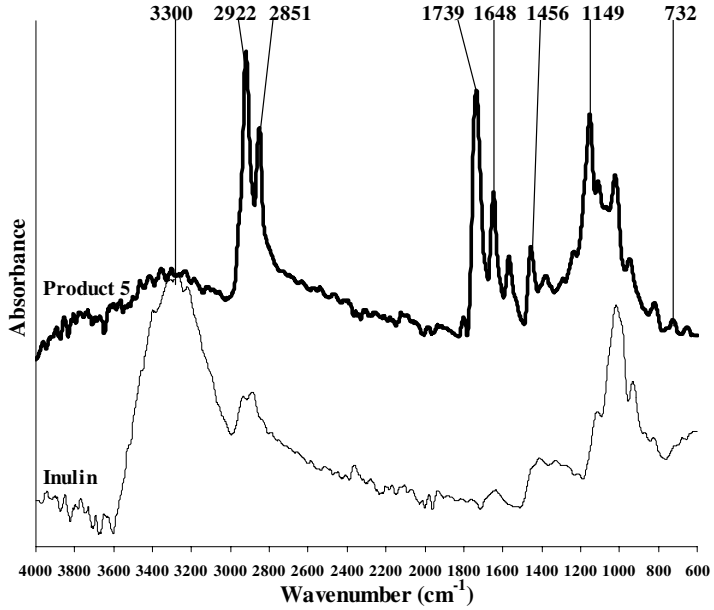


Figure 2. FT-IR spectra of inulin and inulin-based plastic film 5.

These spectra clearly show the efficiency of acylation with the decrease in intensity of the characteristic band of hydroxyl group, this decrease in intensity occurred with the appearance of a band around 1740 cm^{-1} characteristic of carbonyl ester functions. The apparition of the double bond characteristic band (1650 cm^{-1}) gives the evidence of the grafting of methacrylic groups onto inulin, and the signal around 730 cm^{-1} point out the presence of lauroyl chains, showing characteristic vibrations of at least four linearly branched CH_2 groups. A band at 1150 cm^{-1}, which is characteristic for C-O ester stretching vibrations, also appeared in inulin ester. We noticed a widening of the band around 2900 cm^{-1} corresponding to C–H stretching of methacryloyl and lauroyl chains.

A preliminary study of inulin-based plastic thermal properties was performed. The degradation temperature (T_d) of these films was determined by thermogravimetric analysis. The first results we obtained have shown that the degradation of these plastics occurred between 160°C and 170°C (these temperatures were measured for a plastic weight loss of 0.5%). Unfortunately, DSC analysis did not show any glass transition temperature or other phase transition temperature.

Conclusion

We found a new method for the valorization of chicory root inulin by converting it into plastic films by classical acylation reactions. Products obtained by these methods have either adhesive or plastic properties and are very promising materials for the substitution of petroleum-based plastics. In a near future, we will apply this strategy to native inulin.

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