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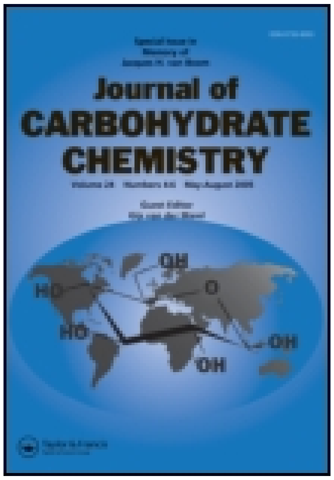

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Crosslinking of Cellulose by Olefin Metathesis

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ABSTRACT

New crosslinked microcrystalline cellulose plastic films were made by olefin metathesis. Cellulose was first acylated under microwave irradiation by 10-undecenoyl chloride in lithium chloride/*N*,*N*-dimethylacetamide homogeneous solution to yield unsaturated fatty acid cellulose esters with a degree of substitution (DS) varying from 1 to 2. After studying the variation of cellulose DS vs. microwave irradiation time, the unsaturated fatty acid cellulose esters were subjected to olefin metathesis using Grubbs's catalyst. Crosslinking ratio T ($0\% < T < 90\%$) and gel formation during cross metathesis of cellulose esters with different DS are discussed. Structure elucidation was mainly achieved from IR and ^{1}H NMR spectroscopic data.

Key Words: Cellulose; Crosslinking; Metathesis; Microwave; Plastic films.

INTRODUCTION

Because cellulose is considered to be the most abundant renewable polymer on earth, numerous studies have been carried out targeting the use of cellulose as an alternative to non-renewable petroleum based chemicals for the synthesis of potentially biodegradable materials. Cellulose modifications, often achieved by fatty acid

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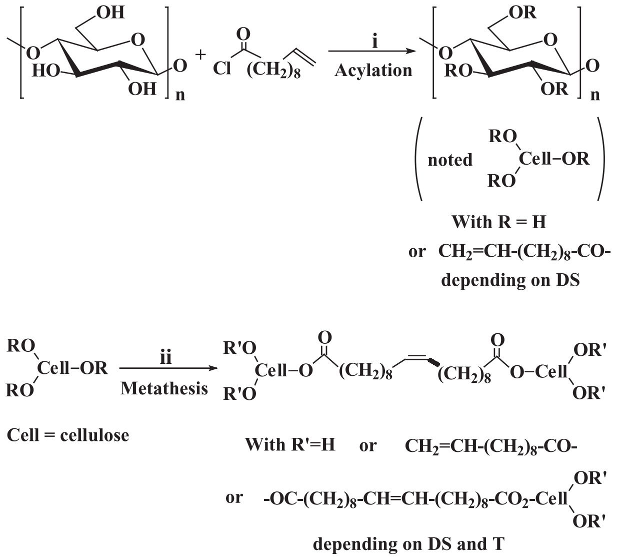

Scheme 1. Reaction sequences for cellulose crosslinking. i—DMAP in LiCl/DMAc, microwave irradiation; ii—Grubbs's catalyst $[RuCl_2(PCy_3)_2{=}CH{-}Ph]/CH_2Cl_2$ under argon, 2h.

acylation,[1−3] have attracted strong interest since the discovery of solvents allowing dissolution and homogeneous derivatization of cellulose.[4,5] More recently, our laboratory has elaborated plastic films by acylation of cellulose in a lithium chloride/*N*,*N*-dimethylacetamide (LiCl/DMAc) solvent system under microwave irradiation conditions.[6] Another transformation, crosslinking of cellulose, has great importance in textile[7] and paper research for studies on paper wet performance[8] and swelling behavior[9] of crosslinked cellulose derivatives.

The use of the olefin metathesis reaction has grown in organic synthesis since the discovery by Grubbs and co-workers of a new type of catalyst based on ruthenium;[10] this catalyst presents a low sensitivity to polar functions such as hydroxyl or carbonyl groups. For example, sugar derivatives[11−14] or nucleoside analogues[15] have been successfully synthesized with the help of this method.

The aim of this work is to obtain of new hydrophobic plastic films using olefin cross metathesis of unsaturated fatty acid esters of microcrystalline cellulose dissolved in LiCl/DMAc. These reactions are depicted in Scheme 1.

RESULTS AND DISCUSSION

The first step consists of cellulose acylation with 10-undecenoyl chloride by microwave irradiation under homogeneous conditions. Then in a second step, we performed olefin metathesis of the cellulose ester groups using Grubbs's catalyst.

Table 1. Irradiation times, DS and molar yields for reaction with 6 equiv of 10-undecenoyl chloride and 1 equiv of DMAP.

Entry	Microwave irradiation time (min)	DS[a]	Molar yield[b] (%)
1	1.5	1.0	90%
2	2	1.4	93%
3	2.5	1.7	95%
4	3	1.9	96%
5	3.5	2.0	92%
6	4	2.0	94%

[a] DS is the degree of substitution per glucose unit ($DS_{max} = 3$, standard error = 0.2).

[b] Quotient (×100) of amount of polymer isolated to the theoretical weight of cellulose ester according to DS (standard error = 5%). Every data entry represents the average of three independent experiments.

Acylation

In order to study the variation of DS as a function of microwave irradiation time, the reaction was carried out with 6 equiv of 10-undecenoyl chloride per anhydroglucose unit (73.8 mmol, 16 mL). Reaction times, DS and molar yields are presented in Table 1. Molar yields, close to 100% for each experiment, strongly support that on average acylation takes place on almost every anhydroglucose unit of cellulose. It can be observed, in Figure 1, that DS values rise linearly from 0 to 1.9 for

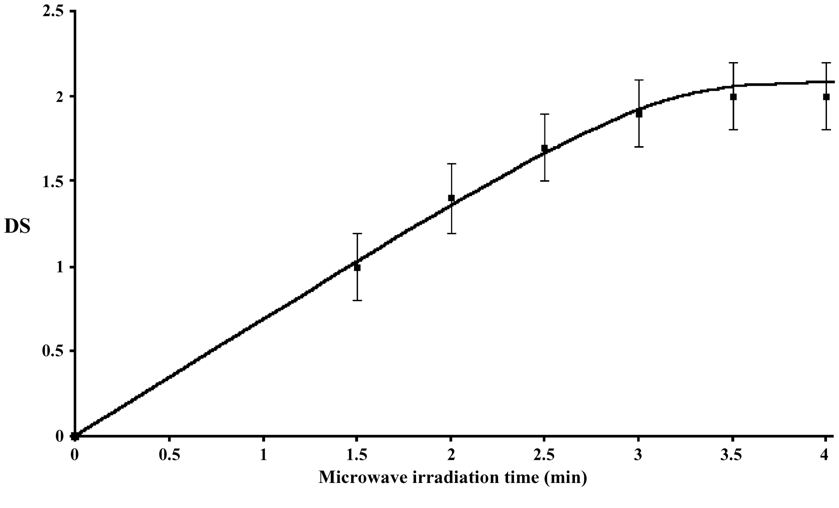

Figure 1. DS variation versus microwave irradiation (1 equiv of DMAP, 6 equiv of 10-undecenoyl chloride).

irradiation times varying from 0 to 3 minutes and then reach a plateau (DS $\approx$ 2.0) after 3.5 minutes or longer. According to the literature,[16] OH groups in position C-6 and C-2 are favored for acylation to an equal degree over those in C-3, although we never observed trisubstitution.

Cellulose esters were converted into plastic films by casting procedures as described in the experimental section. These films have the same aspect and the similar mechanical behavior as commercial plastics such as polypropylene or polyethylene: they are transparent and non brittle either by torsion or folding. Concerning their thermal behavior, it can be noted that they have a tendency to soften from 110°C to 250°C without turning black.

Olefin Cross Metathesis of Unsaturated Fatty Acid Cellulose Esters

In all experiments, the ester solution concentration was 1 g/100 mL in CH_2Cl_2, whatever the DS value might be. Too high concentration of C=C double bonds (above 1 g of cellulose ester per 75 mL CH_2Cl_2) resulted in gel formation, even if the catalyst ratio was very low ($<0.5\%$). In every case, the increase in crosslinking ratio goes with an increase of solution viscosity until gel formation. This rise in viscosity of the solution proves that cellulose underwent substantial crosslinking during the metathesis reaction. For the same experimental conditions, we chose 2 hours reaction time, as it was observed that the crosslinking ratio did not change even for reaction times from 2 to 24 hours.

For each cellulose crosslinking, casting was directly done after reaction by slow evaporation of CH_2Cl_2 at room temperature under atmospheric pressure. Plastic films were obtained in every case presented below. It should be noted that these films cannot

Table 2. Metathesis results and solutions appearance for different esters.

Entry	Ester DS	Catalyst ratio (% mol.)	T[a] (%)	Aspect[b]
1	1.4	0.1%	19%	LIQUID
2		0.2%	38%	LIQUID
3		0.4%	67%	GEL
4		0.4%	63%	GEL
5	1.7	0.25%	47%	LIQUID
6		0.25%	51%	LIQUID
7		0.4%	83%	GEL
8		0.4%	78%	GEL
9	1.9	0.2%	44%	LIQUID
10		0.2%	42%	LIQUID
11		0.3%	63%	GEL
12	2.0	0.1%	21%	LIQUID
13		0.15%	35%	LIQUID
14		0.2%	55%	VISCOUS
15		0.4%	91%	GEL
16		0.6%	89%	GEL

[a] Crosslinking ratio (standard error = 5%).
[b] Before casting.

be dissolved in any organic solvent nor in water. Their thermal behavior is similar to that of the starting cellulose ester except that they soften from 180°C to 250°C.

Results reported in Table 2 show that the metathesis reaction can be reproduced with the same percentage of catalyst and leads to the same crosslinking ratio (compare entries 3 and 4, 5 and 6, 7 and 8, 9 and 10). Whatever the DS of starting cellulose ester, gels appear as soon as the crosslinking ratio T reaches 60%.

We studied the influence of catalyst percentage on the crosslinking ratio for a sample with DS = 2.0. Reaction conditions were the same as those of the previous experiments, and the catalyst molar ratio ranged from 0.1% to 0.6%. Results are reported in Table 2 (entries 12 to 16). Very high values of crosslinking ratios were obtained even in presence of a very low amount of catalyst. The corresponding graph (Figure 2) representing T vs. metathesis catalyst ratio shows a linear increase in crosslinking ratio (from 0 to 70%) when the Grubbs's catalyst ratio increased from 0 to 0.3%. This rise is attenuated and T becomes constant (90%) for catalyst ratios up to 0.4%. It should be noticed that a viscous solution was obtained when T = 55%, and that a gel appeared when metathesis was conducted in presence of 0.4% catalyst.

Spectrometric Analysis

Cellulose esters and crosslinked products were characterized by IR spectral analysis. The IR spectra (Figure 3) of cellulose 10-undecenoate with DS = 2 (Figure 3a) and the corresponding crosslinked product with T = 50% (Figure 3b) display the features of both products and more especially characteristic of ester function bands at 1748 cm^{-1}, remaining hydroxyl groups of cellulose (3486 cm^{-1}), alkene functions from the aglycone moieties (3076 cm^{-1}, 1640 cm^{-1}, 909 cm^{-1} and 723 cm^{-1}), and alkyl chains (2926 cm^{-1}, 2855 cm^{-1}, 1463 cm^{-1}, 1417 cm^{-1}). Both alkyl and carbonyl stretching bands of the crosslinked product displayed an increased width compared to the corresponding bands of the starting cellulose ester; in addition,

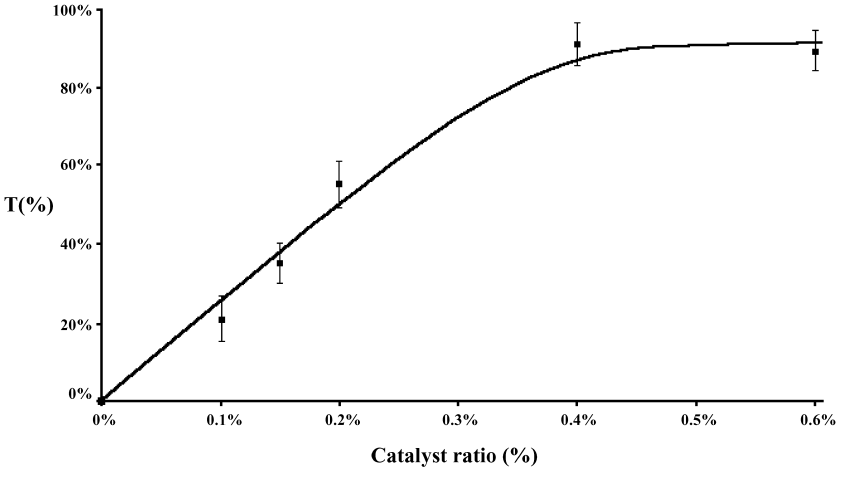

Figure 2. Variation of crosslinking ratio (T) versus to Grubbs's catalyst ratio (%mol) for a DS = 2 ester. Experimental conditions: see Table 2.

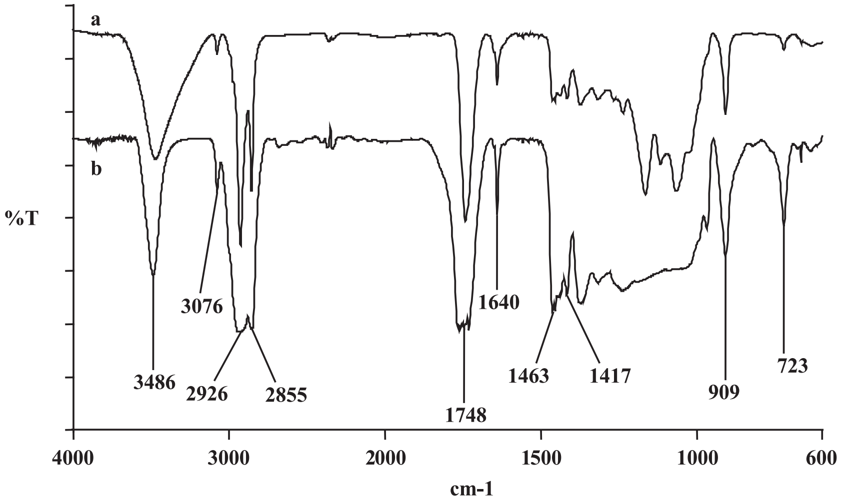

Figure 3. IR spectra of plastic films. a. cellulose ester with DS = 2; b. the corresponding crosslinked cellulose ester with T = 50%.

crosslinking resulted in an increase of intensity of the 723 cm^{-1} band, characteristic of the *cis*-alkene isomer.

Concerning ^{1}H NMR data, only starting cellulose esters can be analyzed due to the insolubility of casted crosslinked products in organic solvents. The ^{1}H NMR spectrum of cellulose ester displays peaks at 5.80 ppm and 4.97 ppm corresponding to ethylenic protons, peaks from 3.2 ppm to 5.5 ppm of anhydroglucose units and peaks representing protons α to the carbonyl group (2.32 ppm), α to the C=C double bond (2.02 ppm), β to the carbonyl group (1.60 ppm), and the remaining aliphatic methylene protons at 1.29 ppm. For the crosslinked products, we analyzed, after saponificationn and TLC, the diacid by ^{1}H NMR spectroscopy. We observed the same peaks representing aliphatic protons but the ethylenic protons are seen as two close peaks at 5.38 ppm and 5.34 ppm corresponding to protons from *E* and *Z* isomers of the diacid, respectively. It can be noted that olefin metathesis of cellulose esters is not selective for any of the two isomers because the *E*/*Z* molar ratio is very close to 1 in every case, as was reported in other studies.[15]

EXPERIMENTAL

Materials

Microcrystalline cellulose (20 µ), 4-dimethylaminopyridine (DMAP, Acros 99%), bis(tricyclohexylphosphine)benzylidene ruthenium(IV) dichloride (Grubbs's catalyst, Strem), 10-undecenoyl chloride (Fluka ≥97%), and solvents were distillated under conventional methods. Grubbs's catalyst was stored under inert atmosphere at 4°C. LiCl (Merck Eurolab 99%) was stored under vacuum.

Cellulose Dissolution

A stock solution of microcrystalline cellulose in LiCl/DMAc was prepared by adaptation of a method used elsewhere.[17] To remove trapped water, cellulose was subjected to a solvent exchange: after storage in vacuum, the polymer was first dipped into methanol (30 min) and then into DMAc (30 min). A solution of 6.7% (w/v) LiCl in DMAc was prepared by stirring for 1 h at 60°C. Then cellulose was added and stirred at 70°C until complete dissolution (approximately 3 h). The stock solution concentration is 33 g/L LiCl/DMAc.

Acylation of Cellulose

DMAP was firstly dissolved at room temperature in cellulose solution before adding 10-undecenoyl chloride, and the mixture was subjected to activation in a domestic microwave oven for 1.5 to 4 min (power output = 180 W).

In a typical experiment, 2 g of cellulose (60 mL of the stock solution, 12.3 mmol of anhydroglucose unit) was stirred with 1.5 g of DMAP (12.3 mmol, 1 equiv) until complete dissolution. Then, 5 or 6 equiv of 10-undecenoyl chloride were added. After microwave irradiation, the esterified product was precipitated by addition of water and twice purified by dissolution in chloroform followed by precipitation with methanol.

Casting, Characterization and Degree of Substitution

Every product was cast and gave plastic films. Cellulose ester (white powder) was dissolved in 30 mL chloroform and then the solvent was evaporated at room temperature under atmospheric pressure.

All products were characterized by FT-IR spectroscopy using an FT-IR Perkin–Elmer Spectrum 1000 apparatus and by ^{1}H NMR in $CDCl_3$ using a Bruker DRX-400 spectrometer (operating at 400 MHz). Chemical shift was measured in ppm with TMS as the internal standard.

The degree of substitution (DS) was determined by pHmetric titration after saponification of esters in 0.25 M NaOH at 50°C during 17 h or by ^{1}H NMR spectrometry, depending on the solubility of cellulose esters in chloroform as described in one of our preceding papers.[18]

Crosslinking Reaction

The reaction took place under inert atmosphere. The unsaturated cellulose ester was dissolved in dichloromethane with bubbling argon. Grubbs's catalyst was removed and stored under an inert atmosphere before its introduction into the ester solution.

Cellulose ester (1 g/100 mL CH_2Cl_2) was mixed with 0.1% to 0.6% of catalyst per mole of alkene unit and stirred for 2 h. After reaction, the crosslinked products were converted into plastic films by direct casting.

Experiments were carried out to study the reproducibility of olefin metathesis applied to cellulose esters. For esters of identical DS, the same ratio of catalyst was introduced in ester solution and the reaction mixture was stirred during 2 h under inert atmosphere.

Determination of the Crosslinking Ratio

The crosslinking ratio (T) was determined by saponification of the metathesis product using a 0.5 M NaOH solution at 80°C during 24 h. After acidification with HCl (pH 2) and extraction of the mixture of 10-undecenoic and 10-eicosendioic acids with chloroform, these two compounds were separated by TLC (eluent $CHCl_3$/EtOH 93/7) and T was calculated according to the following formula:

$$T = \frac{n_d}{n_t} \times 100$$

T is the quotient (× 100) of mole number of diacid isolated after saponification (n_d) to the theoretical one (n_t) for a complete reaction. T values can be related to undecylenic acid metathesis yields.

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