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**Chemical modification of cellulose for electrospinning applications**

**Master Thesis**

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## **Declaration**

Hereby I declare that this master thesis, my original investigation and achievement, submitted for the master degree at Tallinn University of Technology has not been submitted for any degree or examination.

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**Tselluloosi keemiline modifitseerimine elektroketruse rakendusteks**

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<b>ACKNOWLEDGEMENTS .....</b>	<b>3</b>
<b>CONTENTS .....</b>	<b>4</b>
<b>ABBREVIATIONS AND ACRONYMS .....</b>	<b>7</b>
<b>INTRODUCTION .....</b>	<b>9</b>
<b>CHAPTER 1: OVERVIEW.....</b>	<b>11</b>
1. Important components involved in Cellulose Stearate obtention .....	11
1.1. Cellulose.....	11
1.1.1. Introduction .....	11
1.1.2. Molecular structure .....	12
1.1.3. Supramolecular structure.....	13
1.1.4. Degradation of cellulose.....	14
1.2. Cellulose Derivatives .....	14
1.2.1. Introduction .....	14
1.2.2. Derivatives .....	15
1.2.2.1. Esters .....	16
1.2.2.2. Ethers.....	17
1.3. Ionic liquid (IL) .....	18
1.3.1. Introduction and definition.....	18
1.3.1.1. Cations.....	18
1.3.1.2. Anions .....	19
1.3.2. Synthesis reaction .....	19
1.3.3. General properties .....	20
1.3.4. Impurities and consequences.....	20
1.3.5. IL as a reaction media .....	21
1.3.6. IL used: 1-butyl-3-methylimidazolium chloride ([C <sub>4</sub> min]Cl) .....	21
1.4. Stearoyl chloride .....	22
2. Techniques for polymer characterisation.....	23
2.1. Determination of phase transition: Calorimetry test.....	23
2.2. Determination of sample spectra: Fourier Transform Infrared (FTIR) spectroscopy with ATR .....	23
2.3. Determination of degree of substitution.....	24
3. Electrospinning .....	24

<b>OBJECTIVE .....</b>	<b>27</b>
<b>CHAPTER 2: LABORATORY PROCEDURES .....</b>	<b>28</b>
1. Synthesis of Cellulose Stearate .....	28
1.1. Introduction .....	28
1.2. Previous preparations for synthesis .....	29
1.2.1. Cellulose .....	29
1.2.2. Stearoyl chloride .....	29
1.2.3. Ionic liquid .....	29
1.3. Cellulose stearate synthesis itself .....	29
1.3.1. Dissolving cellulose .....	29
1.3.2. Reaction .....	30
1.3.2.1. Chemical compounds involved .....	30
1.3.2.2. Procedure .....	30
1.3.2.2.1. Without adding catalyst .....	30
1.3.2.2.2. With catalyst: tin(II) 2-ethylhexanoate .....	32
1.3.3. Washing and drying the polymer .....	32
2. Synthesis of IL .....	34
2.1. Introduction .....	34
2.2. Chemical compounds involved .....	35
2.3. Procedure .....	35
2.3.1. Reaction .....	35
2.3.2. IL wash .....	36
2.3.3. Remove solvents used in IL wash .....	37
3. Syntheses with high purity reagents .....	38
4. Determination of Degree of Substitution .....	39
4.1. Procedure .....	40
4.1.1. Samples preparation .....	40
4.1.2. Saponification reaction .....	40
4.1.3. Titration .....	41
4.2. Calculations .....	41
5. Calorimetry test .....	42
6. FTIR spectroscopy .....	43
<b>CHAPTER 3: RESULTS AND DISCUSSION .....</b>	<b>44</b>
1. IL preparation .....	44

2. Characterisation of samples .....	44
2.1. Degree of substitution results .....	45
2.2. Calorimetry test results .....	46
2.3. FTIR spectroscopy results .....	52
2.3.1. Peaks obtained and general comments .....	53
2.3.2. Comparison between derivative spectra obtained by reaction with and without catalyst .....	56
2.3.3. Comparison of esters spectra versus cellulose spectrum .....	58
2.3.4. Comparison between esters spectra .....	60
2.3.5. High purity reagents .....	61
3. Electrospinning .....	62
3.1. Results .....	63
3.1.1. Organic solvents tried for dissolving the polymers .....	64
3.1.2. Electrospinning attempts with cellulose stearate obtained from 1:3 synthesis without catalyst .....	65
3.1.2.1. Solubility .....	65
3.1.2.2. Solvent mixtures .....	66
3.1.2.3. Electrospinning experiments .....	68
<b>CONCLUSIONS .....</b>	<b>72</b>
<b>RÉSUMÉ IN ENGLISH .....</b>	<b>75</b>
<b>KOKKUVÕTE .....</b>	<b>77</b>
<b>REFERENCES .....</b>	<b>79</b>
<b>APPENDIX .....</b>	<b>84</b>

## Abbreviations and acronyms

[BF <sub>4</sub> ] <sup>-</sup>	Tetrafluorobromide
[C <sub>4</sub> min]Cl	1-butyl-3-methylimidazolium chloride
[CF <sub>3</sub> SO <sub>2</sub> ] <sup>-</sup>	Trifluoromethanesulfonyl anion
[N(CN) <sub>2</sub> ] <sup>-</sup>	Dicyanamide anion
[PF <sub>6</sub> ] <sup>-</sup>	Tetrafluorophosphide
ATR	Attenuated Total Reflectance
bp	boiling point
Br <sup>-</sup>	Bromide
Cl <sup>-</sup>	Chloride
cm <sup>3</sup>	cubic centimetre (unit of volume)
CO	Carbon monoxide
CO <sub>2</sub>	Carbon dioxide
cP	Centipoise
CS	Cellulose Stearate
DMAc	Dimetilacetone
DMF	N,N-dimetilfesamida
DMSO	Dimetilsulfoxide
DP	Degree of polymerization
DS	Degree of substitution
DSC	Differential Scanning Calorimetry
EA	Elemental Analysis
FTIR	Fourier Transform Infrared spectroscopy
g	gram (unit of weight)
HCl	Acid chloride
IL	Ionic liquid
ILs	Ionic liquids
MeOH	Methanol

ml	millilitre (unit of volume)
mp	melting point
NaOH	Sodium hydroxyde
NIR	Near Infrared spectroscopy
NMR	Nuclear Magnetic Resonance
°C	Degree Celsius
phph	phenolphthalein
THF	Tetrahydrofuran
µm	micrometre (unit of length)

## Introduction

Since few years ago electrospinning has become one of the main topics of research due to the possibility that it offers of obtaining nanoscale fibers. Nowadays this field is growing in research and more different polymers are tried to electrospin.

Cellulose is not an easy polymer for working with because of its crystalline structure, but on the other hand is the most abundant natural polymer in the biosphere. In order to process it, its derivatives are used instead of cellulose itself.

Some cellulose derivatives have been tried to electrospin before, such as cellulose acetate (the most famous one), ethyl cellulose [1], methylcellulose [1, 2], etc. A lot of papers have been published about cellulose acetate and some of them talk about cellulose esters that come from cellulose substituted with long aliphatic chains from fatty acids. And this is the topic that concerns this project, obtaining a fiber from a cellulose derivative that comes from a fatty ester, which is quite innovative.

In this thesis, the polymer which is studied is cellulose stearate, which can be abbreviated as CS. It is obtained by reaction between stearoyl chloride and cellulose using 1-butyl-3-methylimidazolium chloride (an ionic liquid) as a reaction media. The length of its side chains is 18 carbons and the product obtained is an ester. Before obtaining the polymer is necessary to prepare the reaction media.

For obtaining the fiber, the degree of substitution has to be tested after polymer obtention, as well as a calorimetry test and a FTIR spectrum have to be done. The degree of substitution (DS) should be as big as possible because the properties from the compound obtained are better than the ones with low DS. For electrospinning a high solubility in organic solvents is needed in order to prepare the mixtures. So, the DS has to be high.

Trying to achieve that is what is going to be done by synthesizing different polymers whose only difference is the reagents ratio used in the reaction. Purifying the polymer in a good way is really important for avoiding interferences in electrospinning. In addition, using high purity reagents is tested in order to see if that affects properties of CS obtained and increases DS.

Determining the suitable conditions of the mixtures for electrospinning as well as the ones for the electrospinning setup are two more goals. A lot of experiments have been done before about that but for each polymer the conditions are different, so the only way of finding the optimum parameters and characteristics for CS is carrying out a lot of experiments.

All in all is good to say that cellulose stearate fibers hardly ever have been tried to obtain by electrospinning. That confers to this work a wide range of opportunities of finding new information about CS behaviour in this technique. On the other hand it means that there is not that much information related to this topic.

## **Chapter 1: overview**

### **1. Important components involved in Cellulose Stearate obtention**

#### **1.1. Cellulose**

##### **1.1.1. Introduction**

Cellulose is the most abundant of all natural organic polymers and it has a huge production. [3] There is more cellulose in the biosphere than any other substance because [4] it is the main component or molecule in cell walls, for example, 40-60% in weight of dry wood, over 90% of raw cotton and linen. [4, 5] Cellulose biosynthesis is a phenomenon observed in bacteria and eukaryotes including plants and animals, between others. [6] Therefore, thousands of millions of tonnes are produced by photosynthesis annually all around the world. [3]

It was in 1838 that Anselme Payen established the name of cellulose for the fibrous component of cell wall membranes of plants. He realized that it is the unique chemical structure of them. Despite this discovery, it was not until 1930s that the macromolecular nature of cellulose was discovered. Its structure as a linear high molecular weight polymer of glucose units was determined. This molecule tends to form crystalline aggregates due to the chemical composition and conformation of its chains and their hydrogen bonding system. [3, 4, 5] Most cellulose is crystalline, but its long chains of glucose residues associate in crystallites that consist of 5000 to as many as 30000 glucose residues. [6] The degree of polymerization (DP) of cellulose is extremely variable, it comprise from 100 DP in cellulose powder to 20000 DP in cotton secondary wall. Even a DP up to 44000 can be found in some plant species. [4]

Because of these characteristics, and as a consequence especially of the extremely high interchain bonding between molecules, cellulose is insoluble and infusible. The second thing means that it thermally decomposes before it can be melted. A polymer like this cannot be processed easily so transforming it into a derivative makes its melting point be under its decomposition temperature (it is of a high interest). Therefore, the polymer can be processed. [7]

Cellulose microfibrils are remarkable in their structure, their mechanical properties and their mechanism of synthesis. Their diameter can vary from 3nm in the primary cell

walls of seed plants to 25 nm in some algae and its density-specific tensile strength relation is better than the one of many natural and manufactured fibers. [6] These fibers can normally contain absorbed water and its content depends on humidity and temperature where they are placed. [3]

### 1.1.2. Molecular structure

The cellulose molecule is a linear polymer of D-anhydroglucopyranose units linked together by  $\beta$ -1,4-glycosidic bonds. These bonds between them are created when water is eliminated by combining the hydrogen and the hydroxyl group. [8]

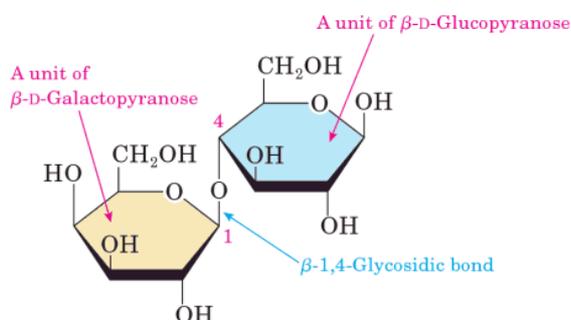


Figure 1.  $\beta$ -1,4-glycosidic bond between two units of D-anhydroglucopyranose. [9]

The most stable conformation of the rings is the chair conformation because it is the one that has the lowest level of energy. [4]

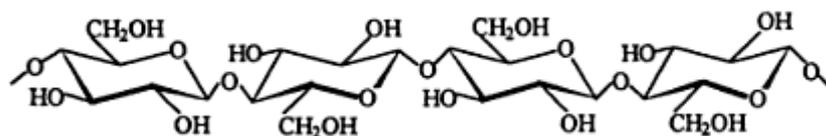


Figure 2. Steric configuration of cellulose. Chair formula. [10]

The common way of numbering the carbons of the structure is the following one:

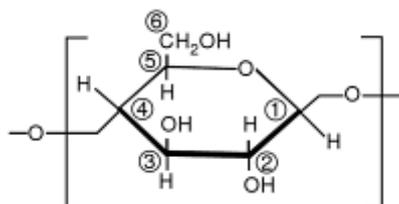


Figure 3. Glucopyranose unit of cellulose. Carbon numeration usually used. [5]

As it can be seen, carbon 1 (C1) has two oxygen atoms attached, C2 and C3 have an hydroxyl group, C4 has only one oxygen attached and the biggest substituent, a hydroxymethyl group, is attached to C5. [4] All the substituents, including the glucosidic bonds, are in the mean plane of the ring (equatorial) and not in the perpendicular to it (axial) where C-H bonds are placed. [3] These rings made of six carbons are called pyranoses. [8]

All  $\beta$ -1,4-linked glucans have a reducing end and a non-reducing end. The first one contains a cyclic unsubstituted hemiacetal and the second one an additional hydroxyl group at C4. [3, 4]

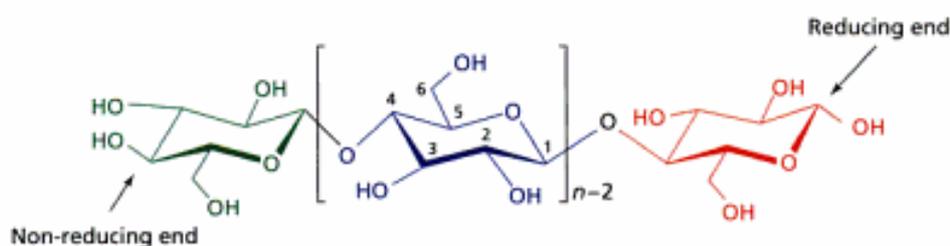


Figure 4. Reducing end and non-reducing end of cellulose. [4]

### 1.1.3. Supramolecular structure

Cellulose is a highly crystalline material but it does not form crystals like glucose, from where it is derived. Glucose is soluble in water but cellulose is not. It is said that water cannot penetrate the cellulose crystallites and if some traces of water goes inside, it is really difficult to remove them completely. [3]

Polysaccharides usually crystallize in numerous forms, or polymorphs, that depend on the history of the sample. Chains can be put together in different ways giving rise to different forms of cellulose. Four different diffraction patterns were found, therefore, four different polymorphs were registered. They were named “cellulose I-IV”. Despite similarities of patterns and molecular shape, there are important differences in chain-packaging within these groups. Many of these forms can be converted from one to the other form by chemical or physical treatments. [3, 6] The most common polymorphs are cellulose I and II. [4]

In nature, cellulose is generally found as the cellulose I crystalline form in which the glucan chains are aligned parallel to each other [6] and they are fully extended. [3]

Cellulose II, called “hydrate cellulose”, is the thermodynamically stable form produced when cellulose is regenerated (dissolved and precipitated) or subjected in the solid state to the process of mercerisation (treated with a concentrated alkaline solution and washed with water) [3, 4] In this case, chain molecules are placed antiparallel. [11]

The transformation from cellulose I to cellulose II is irreversible. [4]

#### **1.1.4. Degradation of cellulose**

The physical properties of cellulose can be affected only for a slightly change in its composition, even when it is reduced to powder. For these reasons, dealing with cellulose should be done carefully. One of the important things of this material is its chemical stability that permits holding degradation. Anyway, this little degradation makes tensile strength decrease as one of the consequences. [3]

Cellulose degradation is produced for different reasons but heat is an important one. There are two competing reactions, dehydration and depolymerisation, that provokes it.

Dehydration forms carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), water, aldehydes [12], etc. What is more, in the glucose unit an intra-ring scission could happen. [13]

In dry air at high temperatures depolymerisation takes place and a lot of substances can be formed, like carbonyl group, carboxyl group, CO and CO<sub>2</sub>. [3] As well a heavy oil fraction and a char fraction can be obtained. [13]

Heating cellulose over 120°C can provoke its degradation, but heating it under this temperature for prolonged time may not affect its properties. [13]

### **1.2. Cellulose Derivatives**

#### **1.2.1. Introduction**

Obtaining derivatives from a polymer preformed, what means doing a postpolymerization, is a good way of upgrading polymer properties. The reactions that permit its obtention have to be done on reactive sites dispersed in the polymer main chain or on reactive sites attached directly to the polymer backbone. [7]

In cellulose case, highly purified wood pulp composed of 92-98% cellulose is used for manufacturing cellulosic products derived from the chemical processing of cellulose. Some time ago, pure cellulosic products represented about 60% of the uses and derivatives of cellulose the rest. [4] The treatment of this polysaccharide is an illustrative example of how a polymer can be transformed from an intractable material to another that can be readily fabricated. [7]

### **1.2.2. Derivates**

Any macromolecular product of the reaction of cellulose with another substance may properly be described as a derivative. However, the term is usually used for esters, ethers and similar products. [3] The two named are of particular importance. [4]

The chemical reactivity of cellulose is determined by the supermolecular structure of its solid state. In the preparation of derivatives the main thing that has to be taken into account is the hydroxyl groups because chemical modification of cellulose involves them. They represent nearly the 32% by weight of cellulose. [10]

The three hydroxyl groups that the intermediate chain unit has are the ones that react undergoing addition, substitution and oxidation reactions. It is generally accepted that the primary hydroxyl group (placed in carbon number 6) is more reactive than the secondary ones (placed in carbons 2 and 3). This is like this due to the effects of neighbouring substituents. Their influence affects acidity and tendency for dissociation. [4, 5, 10]

Besides that, there is another fact that affects the reactivity of hydroxyl groups, the packaging. As it is known, cellulose has some parts that are crystalline and some parts that are amorphous. About the hydroxyls of the crystalline structure it has to be said that they are less reactive than the ones from amorphous part because they are linked with other cellulose units in inter and intramolecular level. That fact makes this hydroxyl groups less accessible to reactants, so hydroxyls of the amorphous part are attacked first. This different reactivity depending on the different parts of the same material provokes that if the reaction is stopped prematurely, just some parts will have the substituents attached. In order to avoid that, or just for trying to minimise it, swelling and decrystallization are needed. [10]

According to that, not all the derivatives have the same number of hydroxyl groups substituted. The way of express how many of them have reacted is the degree of substitution (DS), which is a number between 0 and 3. It shows the average or fraction of hydroxyl groups substituted by the substituents and is an easy way of comparing reactions and polymers. [3, 10]

The DS affects and conditions the properties of the derivatives obtained. At the same time, the type, the distribution and the uniformity of the substituents and the degree of polymerisation [3] do it too. Solubility and plasticity are the ones more affected.

Obtaining a high DS makes the derivative to be more soluble in organic solvents but less soluble in water. The water absorptivity is decreased what means that derivatives with low DS are more sensitive to water. [10]

Some of the industrial applications of derivatives don't need a high DS, so it is important to control it. A complete reaction is not needed because the hydroxyl groups should not be fully substituted. [5, 7]

Below are explained the two best known types of derivatives: esters and ethers.

#### 1.2.2.1. Esters

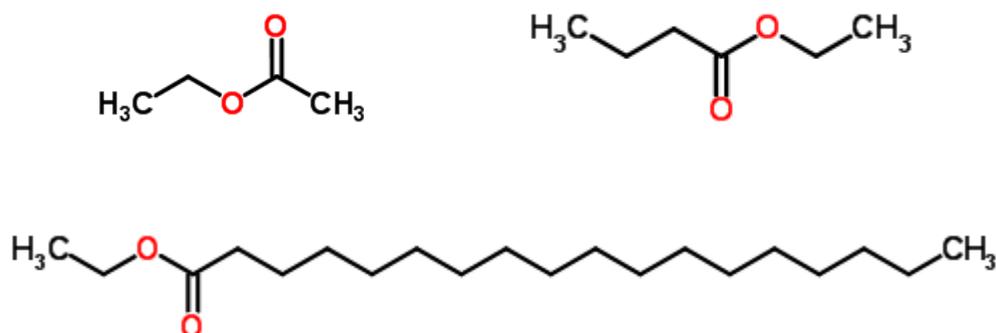
Cellulose esters are prepared by mixing activated cellulose with most organic and inorganic acids [3], by reaction with the corresponding carboxylic acid [7], by reaction with acid or acyl chlorides or by reaction with anhydrides. Esterifications are done in the presence of a dehydrating agent because water can make the reaction to go in the wrong direction. It is important to remark that these reactions are reversible. [4, 10]

Esterification reaction has some limitations such as the type and the size of acid residue and the degree of acid-catalyzed hydrolysis. The product obtained and the difficulty of reaction is associated directly to the number of carbons of the substituent. As much bigger is the number of carbons in the acid or anhydride, more difficult is to achieve a good substitution of the hydroxyl groups. It happens because the reactivity of cellulose with compounds diminishes rapidly as their number of carbons increases. [10]

The most important esters obtained are acetates, nitrates and xanthates. [3] There are others with less importance like sulfur-containing cellulose esters or phosphorus-containing esters. [10]

For long chain cellulose esters partially esterified the decomposition temperature is lower than cellulose and it has been proved that higher degree of substitution makes thermal stability improve. [12]

Some esters of higher aliphatic acids are prepared (like cellulose propionate or butyrate) similarly to acetates but an important difference is that they are less reactive and more expensive. Longer ones that come from fatty acids like stearic, lauric and palmitic are obtained by the reaction of cellulose with acyl chlorides. [4]



**Figure 5. Esters examples: ethyl acetate (up on the left), ethyl butyrate (up on the right) and ethyl stearate (down) [14]**

All these esters mentioned are formed by between 3 and 18 carbons in their side chains. This length is what makes some properties to be different from the esters formed with short substituent. Some changes observed, considering the increase of length, are that hydrophobic behaviour is increased, solubility in many organic solvents too, the melting point is lower and the tensile strength is lower too. [4]

#### 1.2.2.2. Ethers

Cellulose ethers are obtained by the reaction of cellulose with an alkaline hydroxide (converting cellulose in “alkali cellulose”) and then this product combined with the corresponding alkyl halide. [7, 10, 15] For obtaining a good reaction two main processes that cannot be avoided are swelling and decrystallization of cellulose because if not some areas can remain unreacted. The second one is achieved thanks to the alkali addition. [15]

Replacing hydroxyl groups with alkyl groups makes properties change (i.e. solubility, thermal stability, biodegradation). One example is as the ether has a higher degree of

substitution (DS), it becomes less soluble in polar organic solvents but more soluble in nonpolar ones. A classification of commercially ethers is water-soluble or organosoluble. [10]

The most important ether is ethyl cellulose due to its properties. It has heat stability, low flammability, high impact strength and high water absorption (lower than cellulose acetate). [7] Most of commercial cellulose ethers have a DS around 1,5. [3]

### **1.3.Ionic liquid (IL)**

#### **1.3.1. Introduction and definition**

Ionic liquids (ILs) are a new and remarkable class of solvents and the interest on them has experienced an enormous increase. Entries in Chemical abstracts have increased from 20 per year (1995) to more than 1500 (2005). This increasing interest is due to all applications that they have. They can be used for specialized electrochemical applications, as reaction media or as working fluids in mechanical applications. [16]

Ionic liquids are liquids that consist exclusively or almost exclusively of ions and for this reason they show ionic conductivity. This definition includes liquids that are known as molten salts or fused salts. They have melting points or glass-transition temperatures below 100°C and they typically are organic salts or mixtures of an organic and an inorganic salt. Those that are liquid at room temperature are often called “room-temperature ionic liquids”. [17]

A lot of complex compounds can be made synthetically due to the increasing interest and development of these products. A lot of cations and anions are known in this field [18] p. 2 with an estimated number of  $10^{18}$  of different ILs [19]. Aqueous solutions of salts are not classified as IL because they do not consist only of ions. [17]

##### **1.3.1.1. Cations [18]**

IL cation is generally an organic structure of low symmetry which has in the centre one positively charged nitrogen or phosphorus. Recent research talks about room temperature ionic liquids based on asymmetric dialkylimidazolium cations associated with a variety of anions.

The alkyl cations of many ammonium, imidazolium, pyridinium and phosphonium ionic liquids are prepared by alkylation of a suitable precursor, a nucleophile, using an alkylating agent that can be for example a halogenoalkane. [17]

ILs that are cations can be divided in different groups that are five-membered heterocyclic cations, six-membered and benzo-fused heterocyclic cations, ammonium, phosphonium and sulphonium based cations, functionalized imidazolium cations and chiral cations. [20]

### 1.3.1.2. Anions

Room temperature ionic liquids formed by anions usually correspond to inorganic or organic materials that have a negative charge. [18]

$\text{Cl}^-$ ,  $\text{Br}^-$ ,  $[\text{BF}_4]^-$ , and  $[\text{PF}_6]^-$  are the most common anions whereas  $[\text{CF}_3\text{SO}_2]^-$  or  $[\text{N}(\text{CN})_2]^-$  are not as extensively used as the first ones. [19]

### 1.3.2. Synthesis reaction [16, 21]

The ions that form ILs can be obtained by different forms. One of these forms is via protonation with a free acid and the other is by quaternization of an amine, phosphine or sulfide, using a haloalkane or dialkylsulfates.

In the protonation reaction, addition of nitric acid to an aqueous solution of ethylamine is needed. The amine is used in excess but it can be easily removed with the water by heating the mixture to  $60^\circ\text{C}$  in vacuum.

The quaternization of amines and phosphines is known for many years. This way of obtaining ions is simpler because the procedure consists just in mixing the desired alkylating agent with the amine while stir and heat is applied. On one side, chloroalkanes, bromoalkanes and iodoalkanes are the ones widely used for this kind of reaction and on the other side, 1-alkylimidazoles are the most common starting materials. These last ones provide access to a great number of cations and furthermore they are available at a reasonable cost. [16]

### 1.3.3. General properties [17]

ILs have a really wide liquid range because the distance between melting point or glass-transition temperature and boiling point or thermal decomposition temperature is around 380°C. Many IL form glasses at low temperatures and at high temperatures they normally do not evaporate due to negligible vapour pressure.

Viscosity of ILs is higher than the one of molecular solvents and it is presented in a range from 10 to 500 cP. There are some facts about the IL structure and composition that affect strongly viscosity. Generally for bigger cations viscosity is bigger too, so the size of it affects directly. The same happens with the length of alkyl chain, viscosity increases with chain length. Temperature produces big changes on viscosity, making it to decrease when IL is heated.

Generally, ILs are less dense than water, what means that its density is lower than 1g/cm<sup>3</sup>. As other properties, length chain and bulk cation affect density. The decrease of both makes density increase because the packaging is easier. That means that space between IL components is the minimum.

### 1.3.4. Impurities and consequences

Impurities that an ionic liquid could contain are organic starting materials, halides, water, among others. Some of the impurities make IL to have colour. [20]

The impurity which is generally presented with a largest concentration and which is the most difficult to eliminate is water and it is really important to keep away from ILs. Removing other reaction solvents is easier than removing water because they are more volatile, so applying heat and vacuum is enough for achieving that. According to this fact, it is highly recommended to heat IL over 70°C and with stirring for several hours just to achieve a low degree of water contamination. One of the problems with water is that even if the IL is not miscible with it, IL can absorb water from the air (because of humidity). [16] Imidazolium halide salts in particular are known to be extremely hygroscopic.

Only some applications of IL have problems with the presence of water because it reacts as a normal reactive (it is not inert). Moreover, water can affect physiochemical properties of IL, its stability and can decrease the power of a catalyst.

About IL colour must be said that is something totally unexpected while the reaction is being done. A colourless mixture is expected due to reagents mixed because all of them are transparent. Anyway, the product obtained is yellowish in colour [16]. Sometimes happens that IL has a yellow to brown discoloration [17]. Impurities nature that produces this phenomenon is still unclear but it is probably produced by presence of traces of raw materials or its thermal degradation and oxidation products. Pyridinium salts tends to form easily coloured impurities than imidazolium ones. [16]

Obtaining ionic liquid without colour requires a large inversion of money and special care during and after the procedure of synthesis. [16] p. 28 Some actions that can be done for minimize this effect are purify all the raw materials, make the reaction under a flow of inert gas such as nitrogen or kept the temperature as low as possible. [16]

### **1.3.5. IL as a reaction media**

For the polymer that concerns this project, cellulose stearate, dissolving the raw material, cellulose, is needed for developing the reaction. IL is used as a reaction media because it has been tested that is a good solvent for cellulose, especially alkylimidazolium chloride salts. Besides these ones, another potential solvent for cellulose is alkylimidazolium methylphosphonate. The ones that are not suitable at all are carboxylate-based ILs due to their low thermal stability.

A really important factor in the dissolution of cellulose is ILs polarity because if it is enough high, the dissolution can be done without applying heat. The two things that do not make it as comfortable to use as wanted are the high melting point and high viscosity. [22]

### **1.3.6. IL used: 1-butyl-3-methylimidazolium chloride ([C<sub>4</sub>min]Cl)**

Lots of simulations and experimental studies have been done about imidazolium based ILs. This kind of systems has polar and non-polar domains. Besides that, using this kind of IL has some risks because of their toxicity (they can contaminate soil and water). ILs can become persistent pollutants and generate environmental risks. [20]

Synthesis of 1-alkyl-3-alkylimidazolium chloride is well known. The reaction involves as reagents N-alkylimidazole and alkyl chloride and it is called quaternization reaction [21]. Usually high pressure is used. [23]

In order to obtain [C<sub>4</sub>min]Cl, the reagents that should be mixed are N-methylimidazole and chlorobutane.

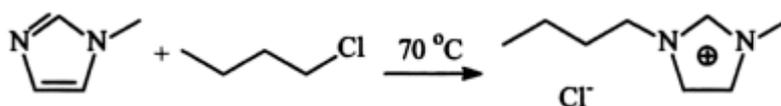


Figure 6. Reaction of [C<sub>4</sub>min]Cl obtention. [23] p. 219

#### 1.4. Stearoyl chloride

Generally, acid halides are obtained directly from the corresponding carboxylic acid with a variety of reagents. The two widely used reagents are thionyl chloride and oxalyl chloride. An important point is that the other halides (fluorides, bromides and iodides) are prepared with an exchange process between the acid chloride and another suitable source of halide.

Specifically, stearoyl chloride is a halide obtained from a carboxylic acid, stearic acid, which is included in the huge group of fatty acids. [24]

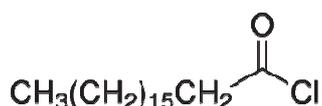


Figure 7. Molecular formula of stearoyl chloride. [25]

The acid from which it comes has 18 carbons so it is an octadecanoic acid and it is a saturated fatty acid [26]. The only functional group that stearic acid has is the carboxylic group at the end of its chain.

Referred to fatty acids, it is good to mention that there are known more than 1000 natural acids but only around 50 are important. They can be found in milk fats and in some vegetable oils. [27]

## **2. Techniques for polymer characterisation**

### **2.1.Determination of phase transition: Calorimetry test**

Nowadays this calorimetry test is called Differential Scanning Calorimetry (DSC) what means that the change of heat rate is measured compared to a reference sample and it is recorded with a temperature program.

DSC is widely used for investigations related with chemical reactions and physical transitions because it measures power (heat flow rates) and characteristic temperatures using just a small amount of product (milligrams). It is used too as quality guarantee. Especially for polymers it allows its characterisation but it has more uses such as purity determinations, kinetic investigations, determination of heat capacity, etc. [28]

In this research it is used with the purpose of determining the purity of the sample after its synthesis. It is useful for detecting the presence of impurities thanks to the absorption of heat during the phase transition, which takes place at different temperature for each compound.

### **2.2.Determination of sample spectra: Fourier Transform Infrared (FTIR) spectroscopy with ATR**

An infrared spectrometer bases its functional nature on the use of infrared radiation (wavelengths from 700nm to about 1mm [29]). A continuous source of this light is guided through the sample, where some part of it is selectively absorbed and the rest is reflected. The light remaining passes to the detector which detects the difference between the intensity of the light sent and the light received.

Thus, this technique is used for obtaining a sample absorption spectrum. It can be used as a quality control because quantitative analytical information can be found in this kind of graphs. It is widely used due to all advantages that it presents. It permits rapid and reproducible analyses, a minimum amount of sample is required (what makes the cost low), high resolution absorption bands can be obtained, it can scan the sample a large number of times in a really short time, it has high sensitivity, etc.

Using the accessory of Attenuated Total Reflectance (ATR) allows analysing, in addition to solid samples, liquid samples. [30, 31]

### 2.3. Determination of degree of substitution

In order to have an idea of how the reaction has been carried out, the degree of esterification of cellulose is determined. Actually, it is called degree of substitution (DS) (it is explained in *Chapter 1:overview 1.2.2. Derivatives*). There are multiple techniques and procedures for obtaining this value. Although some of them have limitations (for example they cannot be used with long side chains), they are still used.

One suitable technique for determining DS is Nuclear Magnetic Resonance spectrometry (NMR), which provides H-NMR spectra that can be easily integrated giving directly this value. [32, 33] Another kind of graphs that can be used is the one obtained with FTIR spectroscopy. With this technique and dissolving the polymer in IL is possible to determine DS too. [34]

Another one is by the aminolysis of the ester groups with pirrolidine followed by a chromatographic separation of the fragments.

Using Elemental Analysis (EA) for determining DS is suitable too. This method consists in finding out the percentage of C, H and O and then converting them to DS by mathematic correlations. [35]

Another possibility of determining DS is first finding the acetyl value. It can be done by using NIR (Near Infrared spectroscopy) or by saponification method. [36]

The one used in this research is the last mentioned, saponification method, which is a simple and cheap manual test. It involves a saponification reaction by adding NaOH to a mixture of polymer and alcohol and then a back titration with HCl (process explained in detail in *Chapter 2: laboratory procedures 3.Determination of degree of substitution*). [37 - 43]

### 3. Electrospinning

Nano and micro-fibers have really different properties compared to other fibers because of the high area on the surface related to the weight, the high pore volume, etc. So it makes them to be an important topic of nowadays research.

The obtention of nanofibers can be carried out by so many different techniques such as drawing, template assisted synthesis, phase separation, electrospinning, etc. But the one

that is better due to its simplicity of laboratory material requirement, low-cost, results obtained and versatility is the last one, electrospinning. It has a really different characteristic compared to the other techniques which is that it does not use mechanical forces for the fibers production, it uses electrical forces. What is more, the fiber is formed by repulsive electrostatic forces.

The interest and the research about electrospinning have incredibly increased since 2009. Before that year only around 20 papers were published about this topic but after that, it turned to more than 1500 papers per year. Besides that, a lot of conferences are held out around the world.

Electrospinning works applying charge to the fluid (molten polymer or polymer solution) in order to provide stretching force to a collector where there is a potential gradient. A polymer solution droplet will only appear if sufficient high voltage is applied. Another remarkable point is that the evaporation of the polymer solution is a determinant factor for forming the fiber.

This technique has a lot of parameters that should be controlled in order to obtain some result or just one result with specific properties. The diameter of the fibers obtained depend on polymer concentration, viscosity, net charge density of the solution, voltage applied, distance to the collector, type of collector, among others. Thus, it is easy to display the setup but controlling the technique requires so many experiments and time.

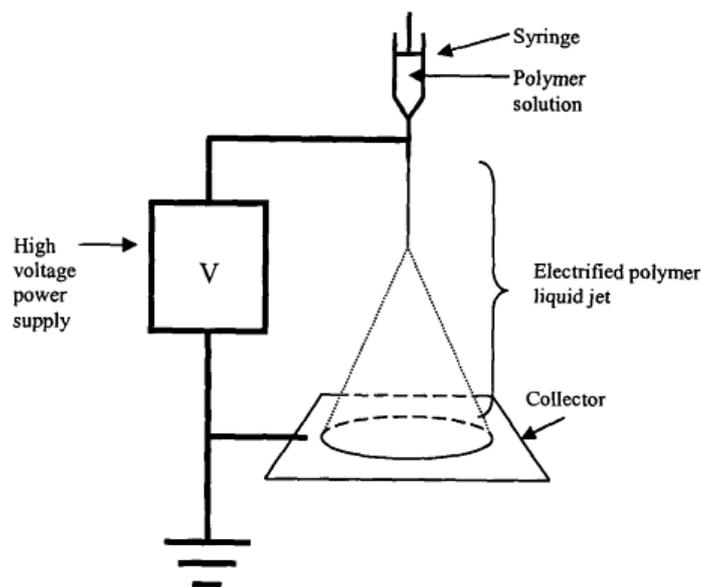


Figure 8. Schematic diagram of the electrospinning process. [44]

Cellulose esters are an easier way of electrospinning cellulose. For example, cellulose acetate is one of the most common cellulose esters tried with this technique. [44, 45, 46]

## Objective

The aims of the thesis and specifically of the experimental part carried out in the laboratory are the following ones:

- Synthesize cellulose stearate with different DS and find the conditions that provide the higher one.
- Synthesize IL in order to use it as a reaction media.
- Purify the polymers obtained. Make sure of its purity carrying out FTIR spectroscopy and calorimetry test.
- Test out the solubility of the polymers obtained in organic solvents.
- Find suitable conditions for electrospinning mixtures.
- Obtain CS fibers by means of electrospinning.

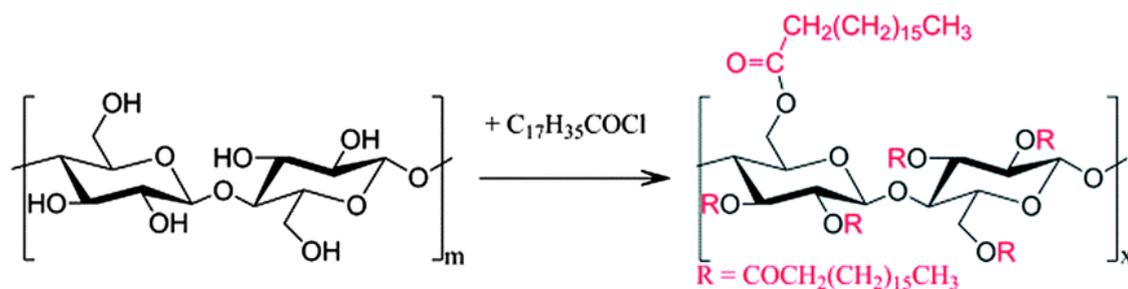
## Chapter 2: laboratory procedures

Some more pictures than the ones presented in this chapter (of laboratory procedures, machines and compounds obtained) can be found in *APPENDIX*.

### 1. Synthesis of Cellulose Stearate

#### 1.1. Introduction

Cellulose Stearate (CS) is obtained as a product of reaction between cellulose and stearoyl chloride and, in this study, with IL as a reaction media. The first reactant is a biopolymer which exists in the nature and it is the main structural component of plant cell walls [47]. About the second one, it comes from a fatty acid, stearic acid, which has an aliphatic chain of 18 carbons.



**Figure 9. Reaction of CS obtention. Cellulose reacts with stearoyl chloride in order to produce CS. [48]**

Five different syntheses have been carried out. The difference between them remains in the rate of cellulose-stearoyl chloride and the use or not of catalyst. Changing conditions and rates of reaction generates a variation in the polymer's degree of substitution.

One thing that all of them have in common is the media where the reaction is developed. It is an ionic liquid (IL) and the one used is 1-methyl-3-butyl imidazole which is also prepared in the laboratory.

Before starting the synthesis it is needed to have cellulose in powder, stearoyl chloride melted (not crystallized) and IL prepared.

## **1.2. Previous preparations for synthesis**

### **1.2.1. Cellulose**

Cellulose is purchased in sheets and with a breaker it should be made powder. The reason of transforming cellulose into powder is that it should be dissolved in IL and the best way of achieving a homogeneous mixture is having it divided in small particles.

### **1.2.2. Stearoyl chloride**

Stearoyl chloride is purchased from *Sigma Aldrich*® and sometimes it arrives crystallized. In order to use it, it should be melted and the easiest way of doing it is immersing the bottle in hot water during some minutes.

### **1.2.3. Ionic liquid**

Ionic liquid has to be synthesised in laboratory. The procedure is explained below in *Chapter 2: laboratory procedures, 2. Synthesis of IL.*

## **1.3. Cellulose stearate synthesis itself**

Obtaining the polymer could be divided in three parts. The first one consists of dissolving cellulose into IL, the second one of reaction between cellulose and stearyl chloride itself and the third one of washing and drying the polymer obtained.

### **1.3.1. Dissolving cellulose**

Drying cellulose is needed before using it for the synthesis because presence of water in this mixture decreases solubility of cellulose in IL and makes the second crystallize. In order to do it, cellulose is introduced in the oven at 105°C with vacuum applied during one day. After this procedure, cellulose is stored in a desiccator that contains silica gel. This gel is presented in small spheres and it is useful because it can control relative humidity of a place.

In order to dissolve cellulose, 100g of IL are placed in an Erlenmeyer flask. Afterwards, cellulose is added to it. It is important to add cellulose slowly because it can form balls that are impossible to dissolve. This new mixture should be stirred and heated under vacuum during one day or until it becomes transparent (a homogeneous media is needed for the esterification). Temperature required is between 85 °C and 100 °C.

## 1.3.2. Reaction

### 1.3.2.1. Chemical compounds involved

All the reagents and solvents involved in the synthesis of CS are presented in *Table 1*.

**Table 1. Reagents and solvents involved in CS synthesis.**

Compound	Supplier
Cellulose	
Stearoyl chloride	Sigma-Aldrich ( $\geq 90\%$ )
Methanol	Sigma-Aldrich
Tin(II) 2-ethylhexanoate (if needed)	Sigma-Aldrich

Methanol and tin(II) 2-ethylhexanoate are used directly as they are received. However, cellulose and stearoyl chloride need some pre-treatment (as explained in *Chapter 2: laboratory procedures, 1.2. Previous preparations for synthesis*).

### 1.3.2.2. Procedure

The reaction can be done with different rates of stearoyl chloride and cellulose. The ones planned for this research are (they are expressed in mols ratio *stearoyl chloride* : *cellulose*):

1. 1:1
2. 3:1
3. 3:1 (with catalyst)
4. 5:1
5. 5:1 (with catalyst)

The aim of that is to test out the degree of substitution obtained and which are the best conditions for obtaining a good polymer.

#### 1.3.2.2.1. Without adding catalyst

The second reactive, stearoyl chloride, is added to the mixture where cellulose is dissolved. It is added drop by drop to prevent reagents segregation and to ensure that all that this compound is reacting.



**Figure 10. Setup for Cellulose Stearate obtention.**

The reaction is carried out with magnetic stirring, heated at 85°C and with reflux. We need the last one because during the reaction some gases can be generated (HCl is evaporated while stearoyl chloride is reacting with cellulose) so they have to be condensed and returned to the mixture. The reaction time is 3 hours, but if catalyst is used, reaction time decreases.

All reactions are developed with 1g of cellulose while the amount of stearoyl chloride is what changes. It is determined as described below.

### ***Calculations***

The repeating unit of cellulose is the one presented in *Figure 3* and its molecular weight is 162 g/mol. The molecular weight of stearoyl chloride is 302,92 g/mol. This data are used in the calculations presented below.

It is necessary to calculate how many grams of stearoyl chloride are needed for 1g of cellulose. So first number of mols of cellulose added in the IL is determined:

$$1 \text{ g cellulose} \frac{1 \text{ mol cellulose}}{162 \text{ g cellulose}} = 0,0062 \text{ mols cellulose added to IL}$$

For these mols and considering that the reaction between cellulose and stearoyl chloride is 1:1, stearoyl chloride grams needed are:

$$0,0062 \text{ mols cellulose} \frac{1 \text{ mol stearoyl chloride}}{1 \text{ mol cellulose}} \frac{302,92 \text{ g stearoyl chloride}}{1 \text{ mol stearoyl chloride}} = 1,88 \text{ g stearoyl chloride}$$

But stearoyl chloride is liquid so with its density<sup>1</sup>, millilitres required can be calculated:

$$1,88 \text{ g stearoyl chloride} \frac{1 \text{ cm}^3}{0,897 \text{ g}} = 2,09 \text{ cm}^3 \text{ stearoyl chloride}$$

For reactions that use a different ratio the amount of stearoyl chloride used is just the one calculated multiplied for the ratio. Table below (*Table 2*) summarize quantities needed for reactions:

**Table 2. Quantities of reagents needed.**

<b>Ratio (stearoyl chloride :cellulose)</b>	<b>IL (g)</b>	<b>Cellulose (g)</b>	<b>Stearoyl chloride (cm<sup>3</sup>)</b>
1:1	100	1	2,09
3:1	100	1	6,27
5:1	100	1	10,45

#### 1.3.2.2.2. With catalyst: tin(II) 2-ethylhexanoate

The procedure and the calculus are exactly the same. The only different step is that before adding the second reactive, stearoyl chloride, catalyst should be added to the mixture composed of IL and cellulose.

In this case, time of reaction becomes 1 hour and a half (half of the reaction time in the synthesis without catalyst.). Therefore, adding catalyst makes the reaction faster but possibly the polymer obtained is different. In other words, adding an esterification catalyst enhances the reaction but can provoke severe degradation at high temperature.

[49] pag 297

### 1.3.3. Washing and drying the polymer

After reaction is completed, the mixture is not homogeneous anymore because the polymer, cellulose stearate, is not soluble in IL (it precipitates like powder). As it can be seen in the following pictures, at the end of the reaction the mixture becomes whiter (CS obtained is dispersed in the IL).

<sup>1</sup> Stearoyl chloride density data is taken from original bottle: 0,897 g/ml.



**Figure 11. On the left: mixture of IL, cellulose and stearoyl chloride. Start point of the reaction. On the right: polymer obtained after 3 hours of reaction.**

In order to separate it from IL, the mixture has to be washed and filtered more than once. Before filtering, it should be mixed with methanol and then stirred during one hour to ensure that all IL is removed from the polymer. The substance used is methanol because IL is soluble in it but the polymer is not. The polymer precipitates slowly if stirring is stopped, therefore, two phases segregates so they can be separated (IL mixed with methanol and the polymer). Filtering and washing it three times should be enough for purifying it and it is advisable to leave the polymer mixed overnight with methanol at least one time.

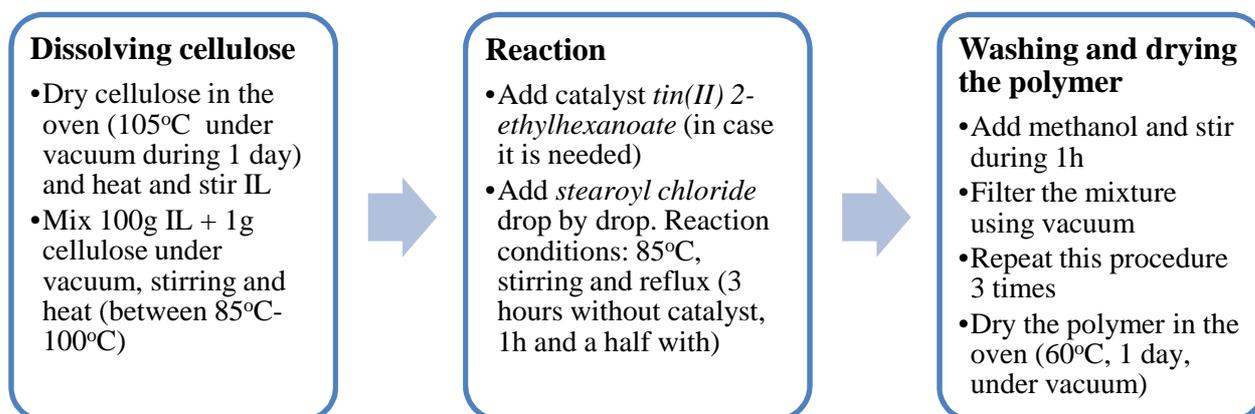
The filtration used is vacuum filtration because it makes the procedure faster and the polymer gets dry easily. During filtration, it could happen that the filter gets blocked. This is produced because the polymer particle is really small and because the filter diameter is so small too. For avoiding that is recommended to filter the mixture in small amounts and if it is totally blocked, the filter should be changed. Filters used has a pore's diameter of 0,45 or 0,5  $\mu\text{m}$ .



**Figure 12. Filtration under vacuum setup.**

After filtering, the methanol used should be transparent and the polymer obtained white. Yellow appearance of it may indicate that it contains impurities (it can be proved with calorimetry test and FTIR spectra). Used methanol is kept because it can be recovered and reused.

After that, the polymer is placed in a petri dish and introduced in the oven with vacuum connected. Drying process is carried out at 60°C as maximum and during 1 day. If after putting it there it is not white, impurities should be removed by washing it again.



## 2. Synthesis of IL

### 2.1. Introduction

As mentioned before, an ionic liquid can contain a lot of impurities that makes it be coloured. In order to minimize the presence of impurities and for increasing reaction output, IL has been prepared with technical reagents and with high purity reagents separately.

Obtaining the IL could be divided in three parts. The first one consists of the reaction itself (mixing the reagents), the second one of washing the IL and the third one of removing the solvents used in the previous step.

## 2.2. Chemical compounds involved

All the reagents and solvents involved in the synthesis of IL are presented in *Table 3*.

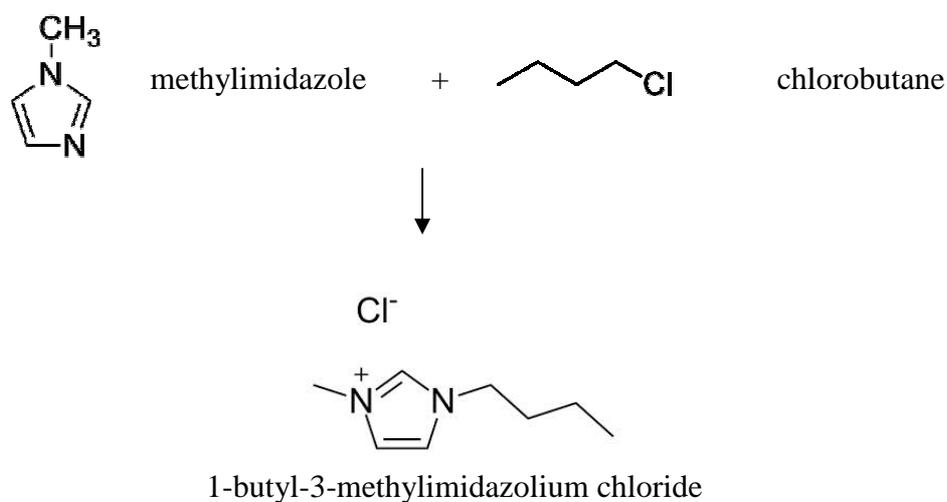
**Table 3. Reagents and solvents involved in IL synthesis.**

Compound	Supplier
Methylimidazole	Merck KGaA (<99%)
Chlorobutane	Merck KGaA
Ethyl acetate	Merck KGaA
Nitrogen	inline gas

## 2.3. Procedure

### 2.3.1. Reaction

Obtention of 1-butyl-3-methylimidazolium ( $[C_4min]Cl$ ) chloride needs as raw materials methylimidazole and chlorobutane. The reaction produced is the one presented below:



**Figure 13. Reaction produced for obtaining  $[C_4min]Cl$**

These two components react 1:1 what means that the same number of mols of each should be mixed. However, the procedure followed is to add slightly more quantity of chlorobutane in order to ensure that the reaction is completely developed (the ratio used is 1:1,5) (i.e. for obtaining 424g of IL, it is needed to mix 164 g of methylimidazole and 260 g of chlorobutane). This action is necessary because chlorobutane is highly volatile and it is unavoidable to lose some material while preparing the mixture. Afterwards unreacted material is removed from the mixture.

Conditions established for this reaction are: continuous stirring during 3 days, reflux, nitrogen atmosphere and high temperature.

Reflux is needed for keeping the volatile reagents in the mixture in order to not losing a large amount of material (especially chlorobutane due to its high volatility).

Nitrogen atmosphere is required to prevent humidity absorption from air because it causes a bad effect to the mixture. Hydrolysis of stearyl chloride can happen so it is important not giving advantage to it. Same reason justifies high temperature, which is fixed at 75°C.

For one synthesis the amount of IL used is around 100 g so the quantity prepared has to be large taking into account all synthesis planned.



**Figure 14. Setup for IL obtention.**

### **2.3.2. IL wash**

After reaction is completed (it takes 3 days), IL has to be washed. All the non reacted reagents and the impurities should be removed.

First of all stir is stopped because after waiting few seconds two immiscible phases appears. The upper one is chlorobutane not reacted (the excess added while preparing

the mixture) and the other one is the IL. This new compound obtained, [C<sub>4</sub>min]Cl, is more viscous than the mixture at the beginning and it is slightly orange.

Having two different and immiscible phases makes separation easier allowing it to be made by decantation. The upper phase is removed carefully in order to lose as less IL as possible.



**Figure 15. IL after the reaction is completed. Two phases can be observed.**

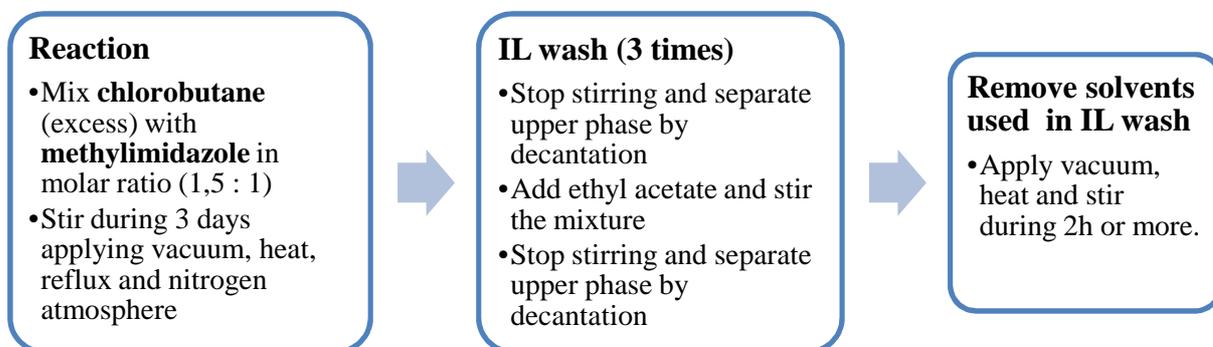
This method is only used to remove the visible part of the phase. After that, it is needed to add ethyl acetate for removing all methylimidazole that could be remaining mixed unreacted with IL. In fact, some more solvents can be used such as diethyl ether or dichloromethane. The high boiling point of methylimidazole (196°C) does not allow avoiding this step. [50] About removing chlorobutane, it can be done easily just heating the mixture because its boiling point is 78°C. [51]

After this addition, two phases are formed again because this product and IL are immiscible. It is needed to stir this new mixture (approximately 10 minutes) and then wait until the two phases are separated once more. The procedure is the same as the first one, thus upper phase should be decanted. To ensure that there is no methylimidazole remaining, this procedure is repeated three times (it takes around 1 hour).

### **2.3.3. Remove solvents used in IL wash**

Finally, removing the ethyl acetate added or any other solvent used can be easily done. This material is highly volatile so heating the mixture and applying vacuum is sufficient (that should be carried out with stirring during 2 hours). It is during this procedure when chlorobutane is eliminated too.

After all this procedure, the IL is ready to be used. Even so, every time before starting a new polymer synthesis it should be dried again applying vacuum, stir and heat. It is really important to avoid humidity because if not IL crystallizes quite fast.



### 3. Syntheses with high purity reagents

For producing the polymer, two more reactions have been done with 1:5 ratio. In these cases, high purity compounds were used.

The procedures for IL synthesis and cellulose stearate synthesis are the same as described in *Chapter 2, 1. Synthesis of Cellulose Stearate* and *Chapter 2, 2. Synthesis of IL*. The only things that change are the raw materials.

- One synthesis was done preparing IL with high purity reagent (methylimidazole) and using high purity stearoyl chloride. Compounds for cellulose stearate and IL syntheses are presented in *Table 4*.

**Table 4. Compounds for cellulose stearate and IL syntheses.**

	<b>Compound</b>	<b>Supplier</b>
<b>Cellulose stearate synthesis</b>	Cellulose	-
	Stearoyl chloride	Sigma-Aldrich (97%)
	Methanol	Sigma-Aldrich
	Tin(II) 2-ethylhexanoate (if needed)	Sigma-Aldrich
<b>IL synthesis</b>	Methylimidazole	Sigma-Aldrich (99%)
	Chlorobutane	Merck KGaA
	Ethyl acetate	Merck KGaA
	Nitrogen	-

- The other one was done preparing IL with technical purity (the same IL used for the other syntheses described in *Chapter 2, 1.3.2.2.Procedure*) and using high purity stearoyl chloride. Compounds for cellulose stearate and IL syntheses are presented in *Table 5*.

**Table 5. Compounds for cellulose stearate and IL syntheses.**

	Compound	Supplier
<b>Cellulose stearate synthesis</b>	Cellulose	-
	Stearoyl chloride	Sigma-Aldrich (97%)
	Methanol	Sigma-Aldrich
	Tin(II) 2-ethylhexanoate (if needed)	Sigma-Aldrich
<b>IL synthesis</b>	Methylimidazole	Merck KGaA (<99%)
	Chlorobutane	Merck KGaA
	Ethyl acetate	Merck KGaA
	Nitrogen	-

#### 4. Determination of Degree of Substitution

The degree of substitution (DS) is determined by a manual method that involves saponification followed by back titration. [36] The method used is based in Eberstadt method in which a preliminary swelling of esters in alcohol is applied in order to make easier the saponification reaction. [37]

This procedure permits to obtain the acyl group content in percentage and using this percentage, the DS can be calculated.

One disadvantage of this method is that takes at least 3 days for preparing the samples before they can be titrated. The procedure involves different reagents (described below in *Table 6*).

**Table 6. Reagents and solvents involved in saponification method.**

Compound	Characteristics
Ethanol	75 %
Sodium hydroxide solution	0,5N
Hydrochloric acid solution	0,5N
Phenolphthalein	-

The degree of substitution has to be tested in all the polymers synthesised and in the unreacted cellulose, so the procedure has to be repeated 6 times.

## 4.1. Procedure

This method can be divided in three parts. The first one is the preparation of the samples, the second one is the saponification reaction and the third one is the titration. All of them have the same importance because it is a highly sensitive method, so they should be carried out very carefully because a tiny mistake affects the final result.

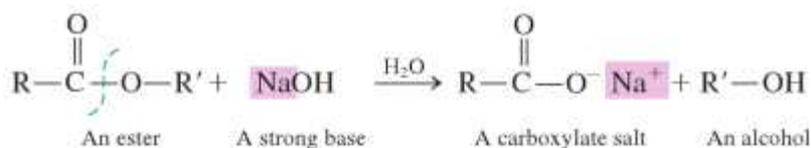
### 4.1.1. Samples preparation

It is needed to dry the samples that are going to be analysed. They are placed in weighing bottles, approximately 1 g of the sample, and introduced in the oven for 2h at 105°C. After that, the weighing bottles are stoppered and left inside a desiccator until they cool down.

When the samples are cold enough, they are transferred to Erlenmeyer flasks. It is really important to know exactly the amount of sample that is going to be titrated so the weighing bottles are weight before and after removing the polymer from inside.

### 4.1.2. Saponification reaction

Before starting the reaction, 40 ml of ethanol are added to each sample and in order to dissolve properly the polymer, this mixture is heated during 30 min at 55°C. After that time is passed, the reaction of saponification is going to take place by adding 40 ml of sodium hydroxide solution 0,5N. The mixture is heated again at the same temperature but during 15 min. What is happening in this process is the following reaction.



**Figure 16. Reaction of saponification. [40]**

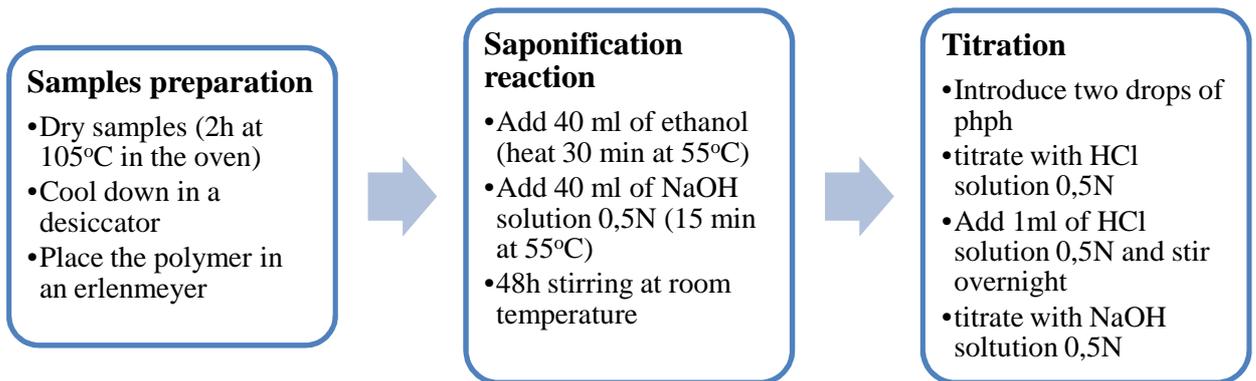
The Erlenmeyer flasks have to be kept at room temperature without heating but stirring during 48 hours. It is important to stopper them tightly.

### 4.1.3. Titration

After waiting two days, the excess of sodium hydroxide added is titrated with hydrochloric acid solution 0,5N. In order to detect when all the sodium hydroxide is neutralized, phenolphthalein (phph) is used as indicator. When this indicator is added to the alkaline mixture, it becomes pink (basic pH) and the titration should be carried on until the colour disappears (colourless). This is the end-point of the titration.

After that, 1ml of extra hydrochloric acid is added in order to neutralize the sodium hydroxide that can be remaining mixed with the polymer. This new mixture should be stirring overnight.

Finally, the excess of hydrochloric acid added is titrated with sodium hydroxide until the end-point that is when pink colour appears again.



### 4.2. Calculations [52, 53]

With all the data collected from the experimental procedure the acyl group content is calculated with the following formula (1).

$$\text{acyl group content (\%)} = \frac{((D-C) \cdot N_a + (A-B) \cdot N_b) \cdot \frac{M}{10}}{W} \quad (1)$$

Where:

A: volume of NaOH (ml) added to the sample

B: volume of NaOH (ml) added to the blank

C: volume of HCl (ml) added to the sample

D: volume of HCl (ml) added to the blank

W: weight of the sample (g)

Na: normality of HCl solution

Nb: normality of NaOH solution

M: molar mass of grafted acyl radical. In this case  $M=267,48$  g/mol.

As commented before, the DS can be calculated using this percentage according to the following formula (2).

$$DS = \frac{162 \cdot \% \text{ acyl group}}{100 \cdot M - (M-1) \cdot \% \text{ acyl group}} \quad (2)$$

Where:

M: molecular weight of ester group (g/mol). In this case  $M=267,48$  g/mol.

## 5. Calorimetry test

The calorimeter used is a Differential Scanning Calorimeter DSC7 supplied by *Perkin Elmer*.

The calorimeter can operate with different programmes that can be chosen by the user. The programme used is heating the sample from room temperature until 200°C with a speed of 20°C/min and cooling it down until 0°C at the same velocity. This way of working allows determining glass transition, melting point and crystallizing point of the sample (they should be the same temperature in cooling and heating curves because both characterize the same phase change).

## 6. FTIR spectroscopy

Analysing the sample with this technique is useful because it permits to confirm the product that is obtained with the reaction of esterification. In order to compare and be sure about the reaction has been successfully completed, cellulose is analysed too.

The infrared spectroscopic analysis was performed on a spectrometer FT-IR with an ATR (Attenuated Total Reflectance) accessory. The brand of the spectrometer is *Interspectrum*® and from the accessory is *Specac*. The range of wavelength used is from  $500\text{ cm}^{-1}$  to  $4500\text{ cm}^{-1}$  with spectral resolution of  $2\text{ cm}^{-1}$ . The scans taken from each sample are 8 and from the background are 8 too. Those are overlapped forming a unique graph for each sample.

Thanks to ATR accessory, not only samples that are transparent and solid can be analysed. Liquid, powder, films, etc samples could be tested directly because when a sample preparation is involved in between, some properties might change. So having this equipment makes the obtention of the spectra easier and it is a good way to ensure that the sample remains with the same composition and shape how it is synthesized.

## Chapter 3: results and discussion

### 1. IL preparation

Two different reactions were carried out, just being different in the reagents purity.

The one where high purity methylimidazole was used was the one carried out with more problems. The ionic liquid obtained was totally brown while the other was slightly yellow.

This result is totally the opposite of the expected one. Using the high purity reagent was tried two times and the result was exactly the same, a totally brown product. The second time that this reaction was performed the mixture was supervised after one day since the reaction started. Surprisingly, the mixture was already brown. Pictures presented below can give an idea of the different behaviour of the reagents.



**Figure 17. On the right side, IL prepared with technical purity methylimidazole. On the left side, IL prepared with high purity methylimidazole.**

This phenomenon perhaps happens because the time of reaction should be less compared with the one established for the technical purity reagents.

### 2. Characterisation of samples

The target of this study is to ensure that syntheses have been carried out properly, so the polymer is valid to be used in future electrospinning tests. What is going to be checked is thermal behaviour and infra-red spectra.

Besides these two checkups, the degree of substitution is determined in order to compare how different reaction conditions affect the polymer obtained.

First of all, some pictures of CS obtained are presented below.



**Figure 18. CS obtained. (Left image) Up on the left: *synthesis 1:5 with catalyst*, up on the right: *synthesis 1:3 with catalyst* and down: *synthesis 1:5 without catalyst*. (Right image) *synthesis 1:1*.**



**Figure 19. Polymers obtained by using high purity stearoyls chloride and technical purity IL (on the left) or high purity IL (on the right).**

As it can be seen in *Figure 19*, the polymers obtained were totally black. Perhaps they were burnt when staying in the oven at 60°C over night. Surprisingly, the polymers were melted in the oven and before analysing them they crystallized due to solvents evaporation.

## **2.1.Degree of substitution results**

As explained in *Chapter 1: overview, 2.3. Determination of degree of substitution* saponification method is used, what means that these results are just guidance. The method should be accurately carried out because is extremely sensitive. Another important point is that the formulas used are empirical, hence the results are approximations.

What is expected about the results is that increasing the ratio between cellulose and stearoyl chloride will increase the DS.

In the *Table 8* are presented the results of titration such as the amount of polymer used and millilitres of HCl and NaOH needed for titration.

**Table 7. Results of titration.**

Synthesis ratio (cellulose : stearoyl chloride)	Weighing bottle + polymer (g)	Weighing bottle (g)	Polymer (g)	HCl 0,5N (ml)	NaOH 0,5N (ml)
1:1	24,39	24,02	0,37	19,7	3,2
1:3	24,38	23,92	0,46	19,1	3
1:3 with catalyst	25,00	24,02	0,98	36,1	1,4
1:5	24,98	24,00	0,98	39,2	1,5
1:5 with catalyst	24,82	23,85	0,97	38,7	1,6
Blank 1*	24,47	23,95	0,52	19,1	3
Blank 2*	25,01	24,01	1	42	0,8

\* Blank1 is used for 1:1 and 1:3 calculations and Blank 2 for the rest.

After doing calculations using the data from *Table 6* and equations (1) and (2) from *Chapter 2: laboratory procedures, 3.2. Calculations*, the content of acyl group and the DS obtained are summarized in the table below (*Table 9*). The important result is the DS.

**Table 8. Results of acyl content and DS.**

Synthesis ratio (cellulose : stearoyl chloride)	% acyl group	DS
1:1	43,4	<b>0,46</b>
1:3	46,5	<b>0,53</b>
<b>1:3 with catalyst</b>	<b>88,7</b>	<b>4,62 *</b>
1:5	47,8	<b>0,55</b>
1:5 with catalyst	56,5	<b>0,78</b>

\*This result is not correct because the degree of substitution can be only between 0 and 3. During the procedure for determining it something went wrong.

Although DS obtained are not as big as expected, they follow the correlation expected. When the ratio between cellulose and stearoyl chloride increases, DS increases too. There is just a slightly difference between them so in general the properties of them should be the same, referring mainly to solubility. These low results may be because of the media where the reaction is carried out (IL) or due to long aliphatic chain of the substituent.

## 2.2. Calorimetry test results

As DSC is used to study phase transitions of a polymer during heating, it is expected to obtain only one melting temperature. If more than one are detected is because the polymer contains impurities. For this reason, this technique is useful for knowing which impurities the polymer has. Therefore, for using this cellulose stearate afterwards they should be removed by washing it again with organic solvents.

The following three compounds can be found in the sample. Thus, its melting temperatures and its boiling point (only mentioned if it is under 200°C, the maximum temperature achieved in this experiment) are presented:

Stearic acid: melting point (mp) 69,8°C [54]

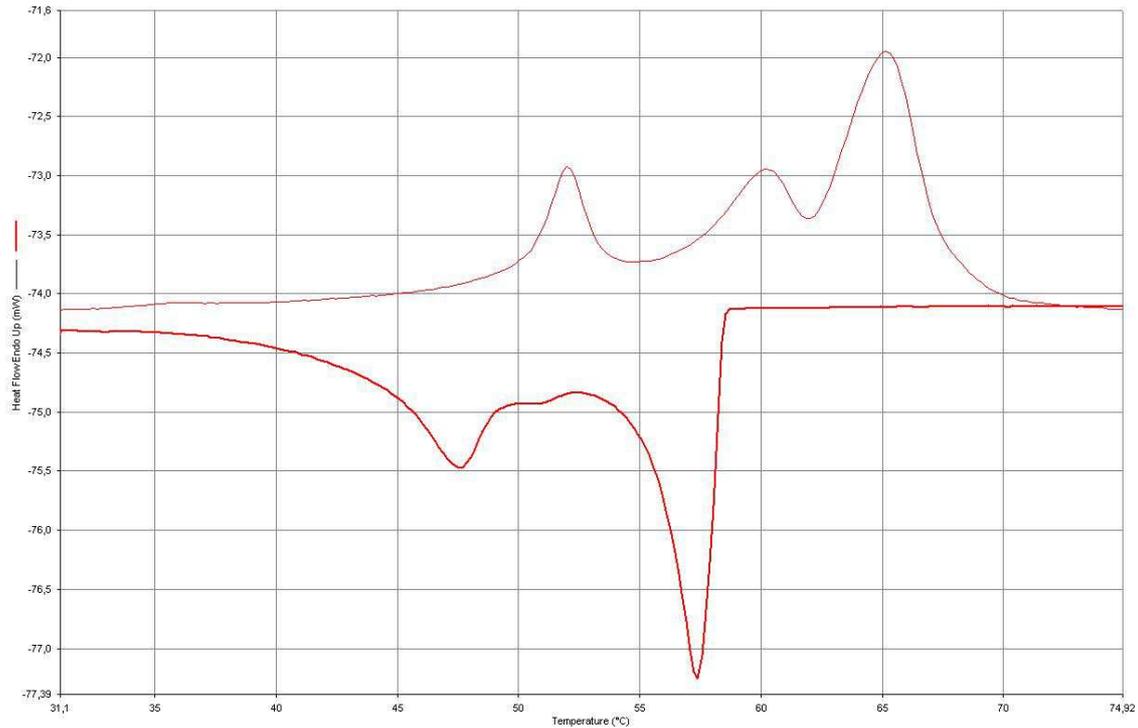
Stearoyl chloride: mp 21-22°C and boiling point (bp) 174-178°C [25]

Water: mp 0°C and bp 100°C

All graphs are presented below, separated due to reaction conditions used for polymer obtention. In all of them, two curves are presented, the one referred to the process of heat up the sample (upper one) and the one referred to cool down the sample (lower one).

The first graph presented (*Figure 20*) is from the polymer obtained by synthesis 1:1 without catalyst, which has a DS of 0,46.

As it can be seen, it presents two huge peaks: one around 50°C and the other around 65°C.

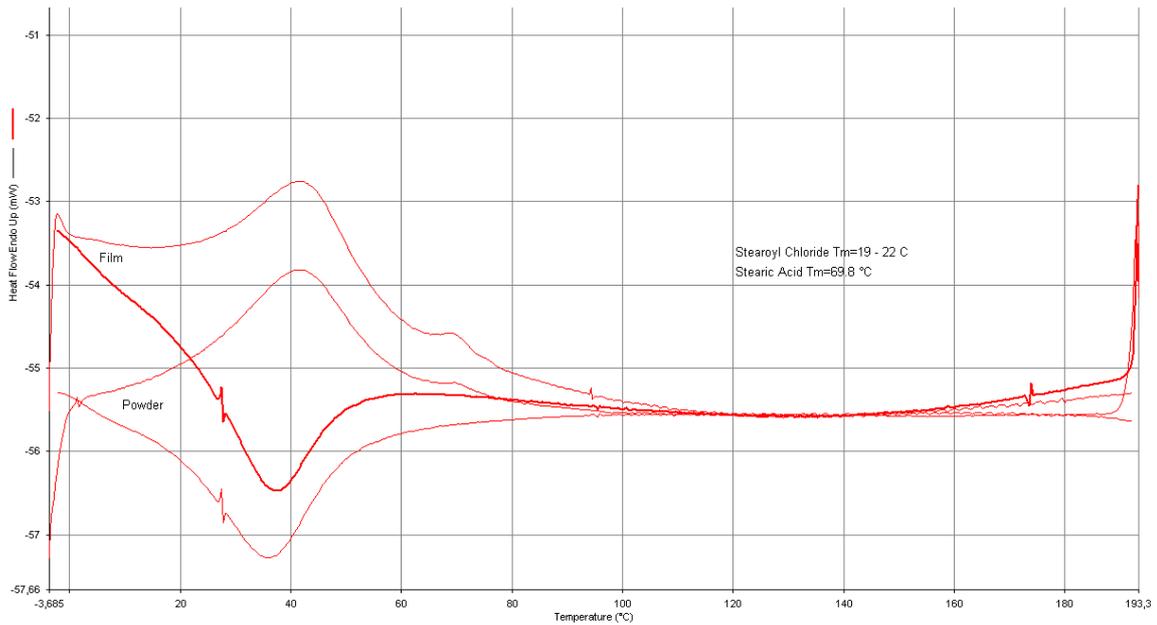


**Figure 20. Calorimetry graph of cellulose stearate with 0,46 DS ( synthesis 1:1 without catalyst).**

The two next graphs correspond to polymers obtained by syntheses 1:3 without (*Figure 21*) and with catalyst (*Figure 22*). The first one has a DS of 0,53.

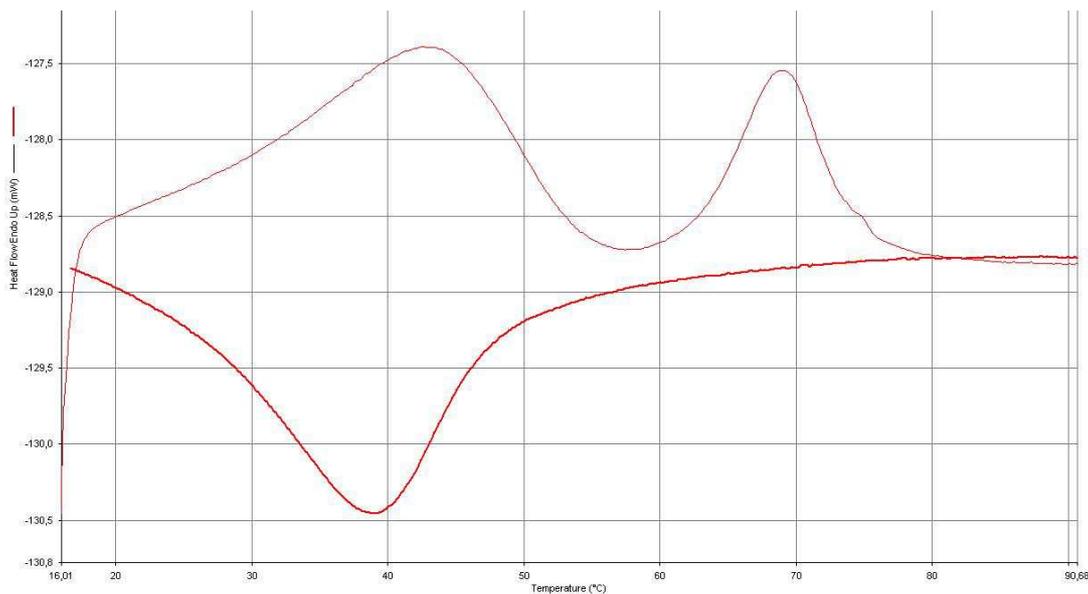
It is good to mention that for polymer obtained with ratio 1:3 without catalyst two shapes of it were tried (as powder and as a film) (*Figure 21*).

About the first graph (*Figure 21*), it can be seen that it presents one huge peak around 40°C and a small, nearly inappreciable, at 70°C. They are the same ones presented in the previous graph, but the fact that the second peak mentioned is smaller means that it contains less impurities. Analysing the graph can be seen that the shape of the sample does not change the result.



**Figure 21. Calorimetry graph of cellulose stearate with 0,53 DS (synthesis 1:3 without catalyst).**

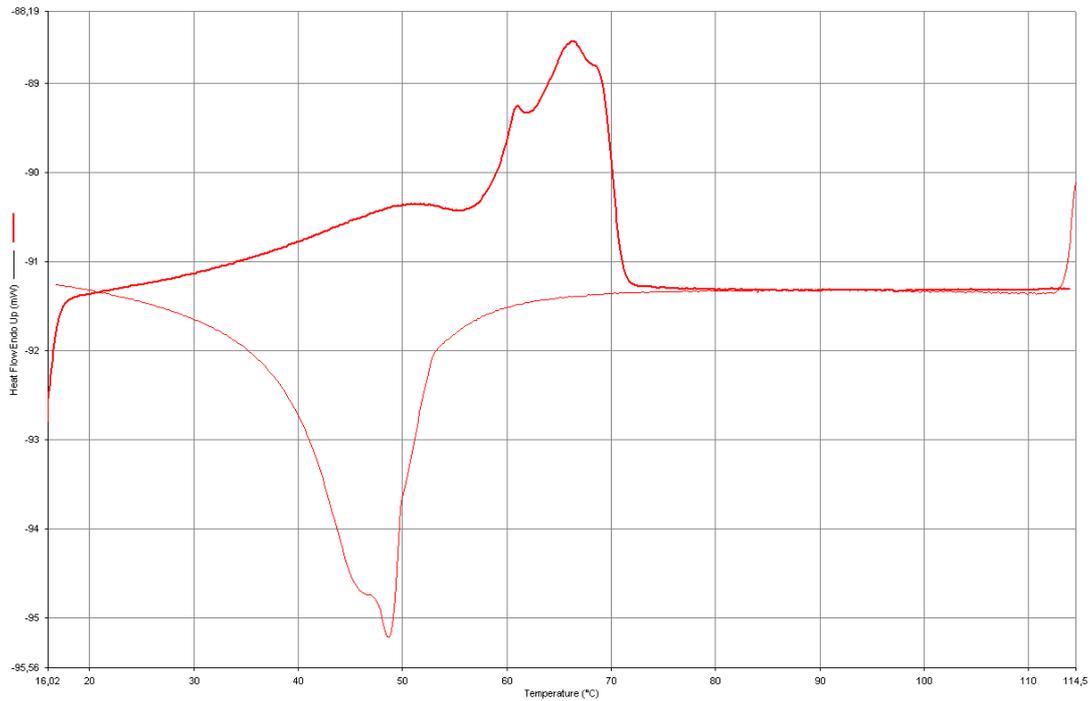
In the second calorimetry result (*Figure 22*) two peaks are obtained. This time, one appears around 40°C and the other one around 70°C. It can only be seen in the heat up curve, not in the cool down one. It sometimes happens in this kind of graphs because of the cooling and heating velocity. It is a general behaviour in calorimetry graphs.



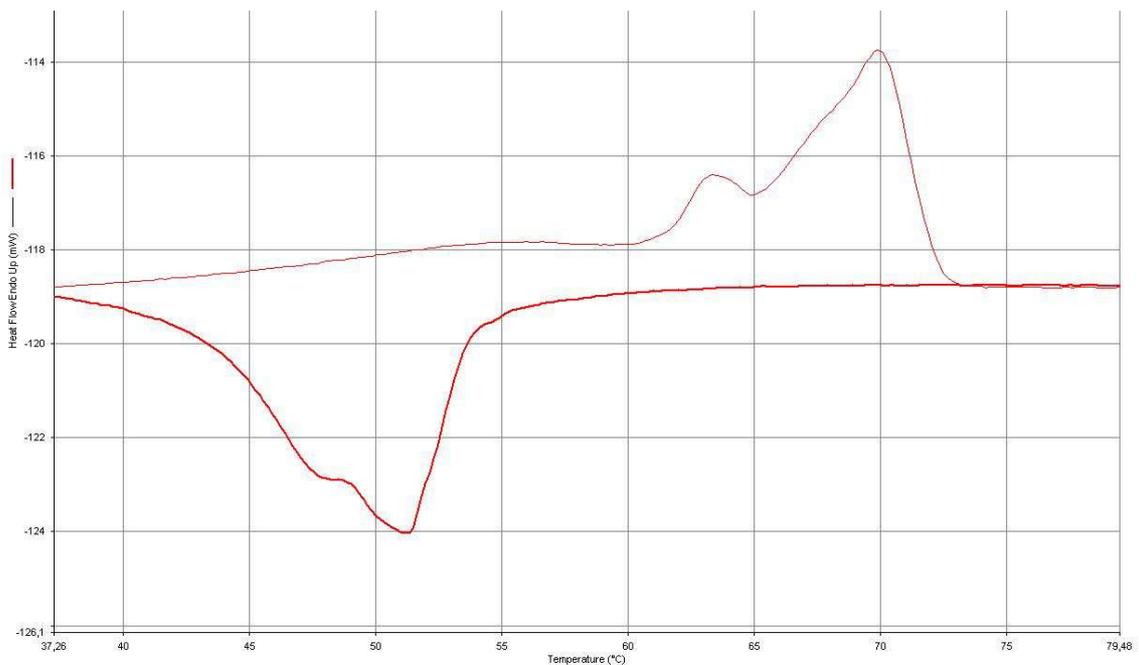
**Figure 22. Calorimetry graph of cellulose stearate obtained from synthesis 1:3 with catalyst.**

### Chapter 3: results and discussion

The following graphs belongs to CS with 0,55 (Figure 23) and 0,78 (Figure 24) DS. The first one corresponds to synthesis 1:5 without catalyst and the second to synthesis 1:5 with catalyst.



**Figure 23. Calorimetry graph of cellulose stearate with 0,55 DS (synthesis 1:5 without catalyst).**

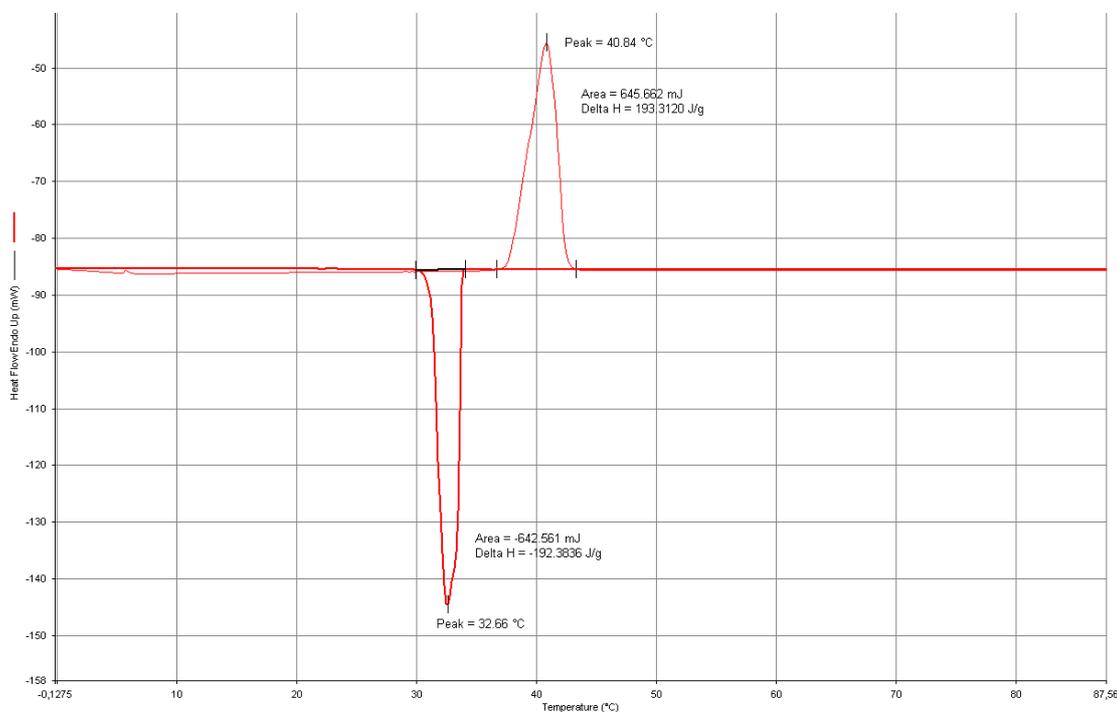


**Figure 24. Calorimetry graph of cellulose stearate with 0,78 DS (synthesis 1:5 with catalyst).**

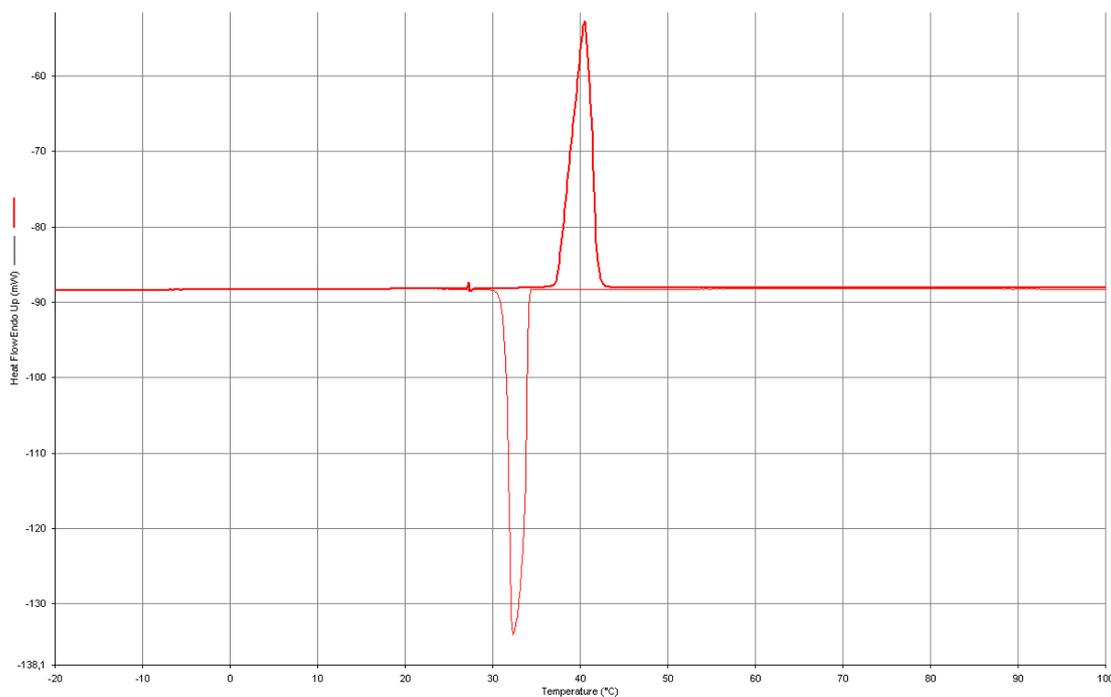
In both cases, the graph presents the main peak around 70°C (talking only about the heating curve) what means that these polymers has a lot of stearic acid remaining.

Finally, the two graphs for the CS obtained with high purity reagents are presented. The first one (*Figure 25*) corresponds to CS obtained with IL and stearoyl chloride of high purity and the second one (*Figure 26*) to CS with only stearoyl chloride of high purity.

Both graphs only show one peak at the same temperature. It is present around 40°C so it corresponds to the melting temperature of the polymer. There are no peaks that shows that these CS present impurities.



**Figure 25. Calorimetry graph of cellulose stearate obtained from synthesis 1:5 without catalyst and carried out with high purity reagents.**



**Figure 26. Calorimetry graph of cellulose stearate obtained from synthesis 1:5 without catalyst and carried out with high purity stearoyl chloride.**

Summarising, taking a quick view to all graphs, it can be seen that the polymers more purified are the ones produced with high purity reagents (*Figure 25* and *Figure 26*). In all the other graphs at least two peaks can be appreciated what means that besides the polymer there are impurities. The main impurity that can be detected is stearic acid due to the peak that appears around 65-70°C. There is no stearoyl chloride remaining in the samples and water neither.

The polymer melting temperature is imprecise to determine and it varies slightly from one ratio to the other. As a general comment, the range obtained is from 40 to 50°C.

### 2.3.FTIR spectroscopy results

Six spectra have been obtained (one for each synthesis and one for cellulose). All of them are presented below.

The results obtained from FTIR spectroscopy are presented in graphs (spectra). They are obtained directly from the laboratory device used for examining the samples and they show the absorbance in front of wavenumber ( $\text{cm}^{-1}$ ).

All peaks presented are referred to the bonds between the different atoms that shape cellulose stearate and other possible compounds that are remaining as impurities inside the polymer. Thus, it is really useful for detecting these impurities.

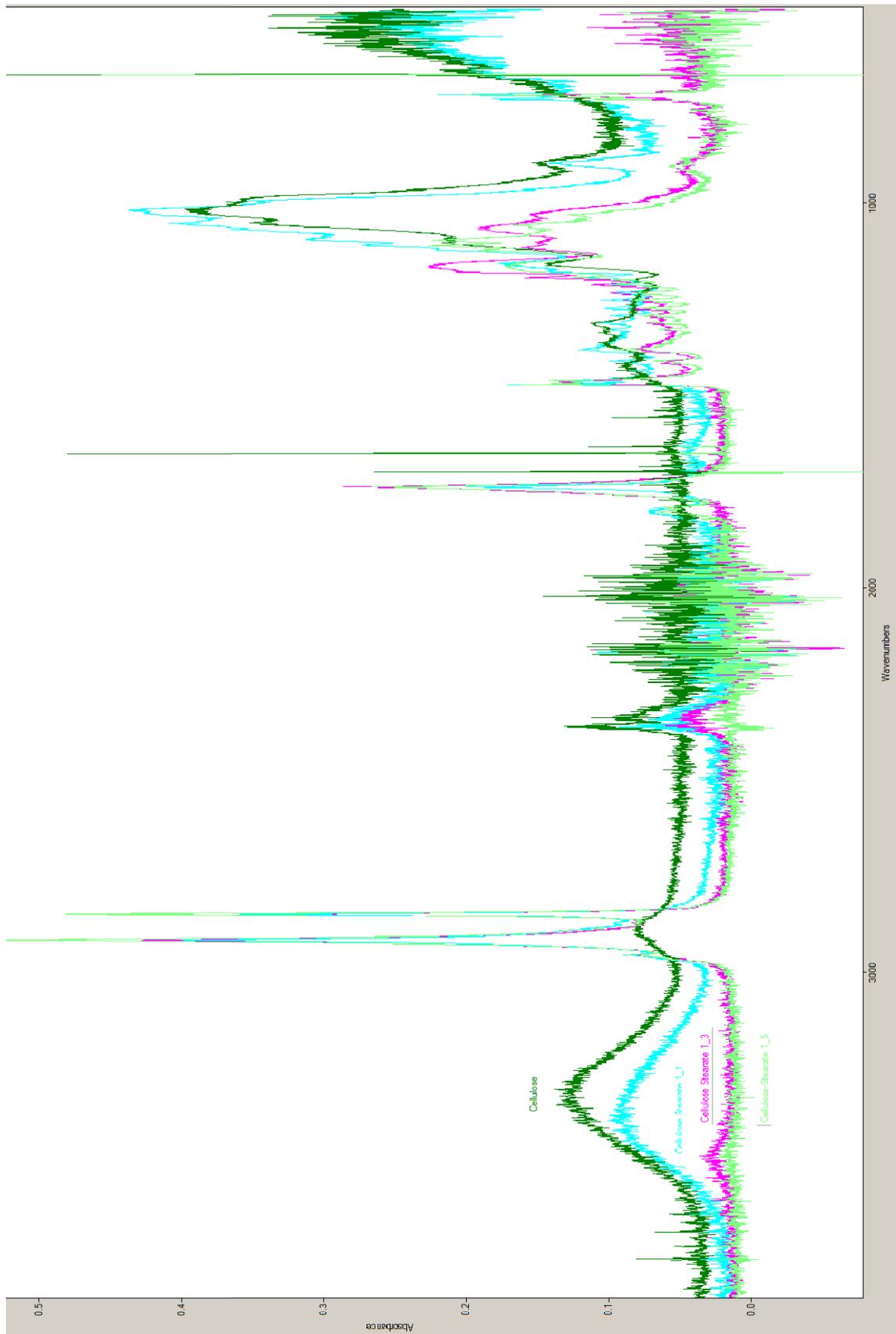
### 2.3.1. Peaks obtained and general comments

Apparently, by taking a quick look to all graphs of cellulose stearate they seem to be the same. This is a good point because it means that all reactions have been carried out in a similar way. Moreover, it means that there are no different products obtained depending on the ratio of the reaction, all the reactions have produced the ester, and there are not strange impurities remaining. The one that is different is cellulose spectrum because it is not an ester, so it does not present all the picks that the rest have. In order to appreciate these slight differences, all graphs are overlapped in one (*Figure 27*).

First of all, main peaks that appear in the spectra are summarized in *Table 7* and also its meaning is explained. [55, 56, 57, 58, 59]

**Table 9. Main peaks from the spectra and their meaning.**

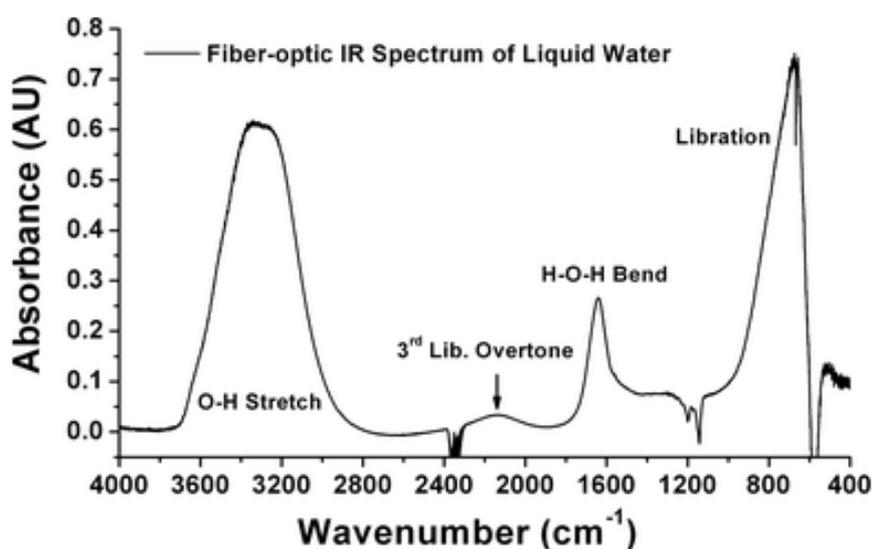
Wavenumber (cm <sup>-1</sup> )	Corresponding bond or group movement	Related compounds
3400	O-H stretch	Water [55, 56 pag 74] cellulose OH [58]
1600	H-O-H bend	
2800	C-H aliphatic	Aliphatic chain of 18 carbons [58]
2900		
1744 [57]	C=O	Ester
1237 [57]	C-O-C	
1000-1100 [57]	C-O	Ester and cellulose C-OH
722 [58]	CH <sub>2</sub> rocking	at least -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -
1400 [57]	CH <sub>3</sub>	Last carbon from aliphatic chain



**Figure 27. Cellulose (dark green), Cellulose stearate 1:1 (blue), 1:3 (pink) and 1:5 (light green) spectra overlapped.**

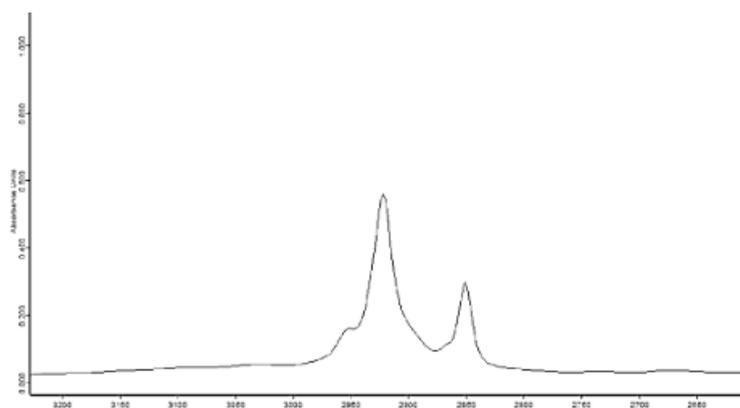
Secondly, besides detecting the peaks, there are two other spectra that are extremely useful for interpreting the ones obtained. These are the liquid water (*Figure 28*) and the stearic acid (*Figure 29*) spectra.

The first one is important because it allows explaining the shape of the polymer spectra in the highest (over  $3000\text{ cm}^{-1}$ ) and in the lowest (under  $1000\text{ cm}^{-1}$ ) wavelengths. If water spectrum and obtained spectra (cellulose and stearates) are compared carefully, it can be seen that they are truly similar, especially in these areas mentioned. Hence, it can be said that there is water remaining in the samples analyzed.



**Figure 28. IR spectrum of liquid water [55]**

The second one (*Figure 29*) confirms the presence of carbon chains that come from stearoyl chloride, the reagent that provides the side chains in CS. They are formed for eighteen carbons and there are a lot of them so the intensity of the signal is sufficiently important for taking it into account. The problem with these peaks is that they can be referred to the presence of stearic acid in the mixture, not only to the aliphatic chains that are substituting cellulose hydroxyls.

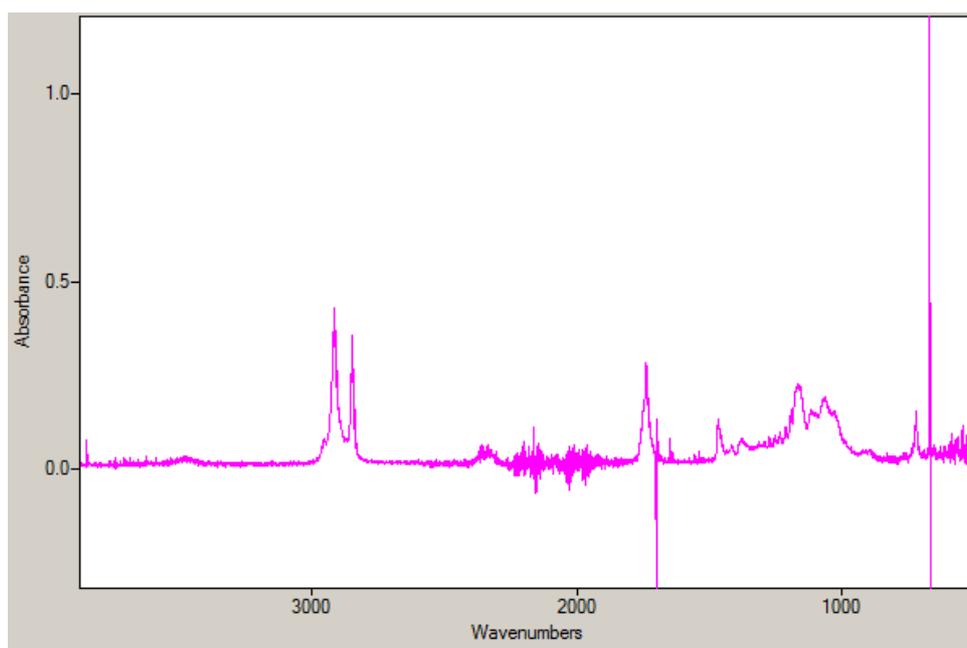


**Figure 29.** IR spectrum of stearic acid (peaks at 2900 and 2800  $\text{cm}^{-1}$ ). [60]

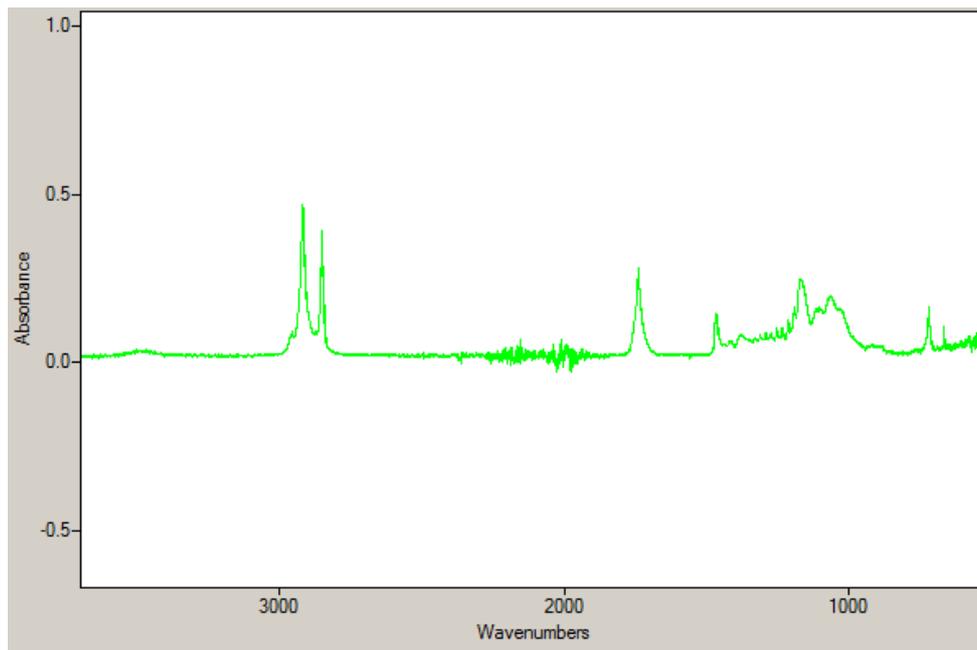
### **2.3.2. Comparison between derivative spectra obtained by reaction with and without catalyst**

The syntheses that are carried out with a ratio of 1:3 and 1:5 were tested with and without catalyst in order to see if something changes and if it is possible to obtain the same product, cellulose stearate.

Comparing the two spectra of ratio 1:3, nothing seems to change. Both of them have the same peaks, what means that the products, the raw materials remaining and the impurities are the same. Therefore, it is better to use catalyst because reaction time becomes half. The spectra are presented below.



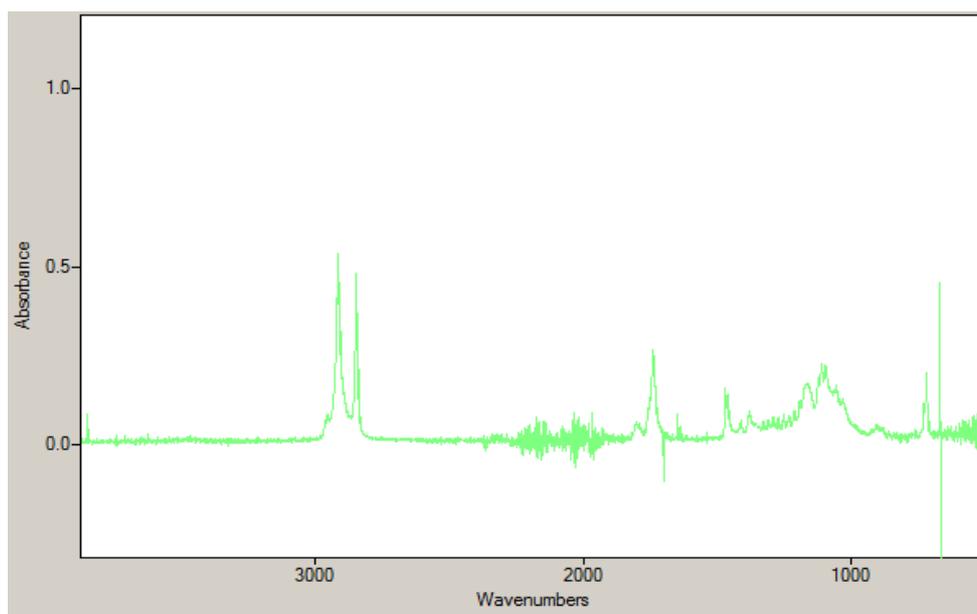
**Figure 30.** Cellulose stearate spectrum. Synthesis 1:3.



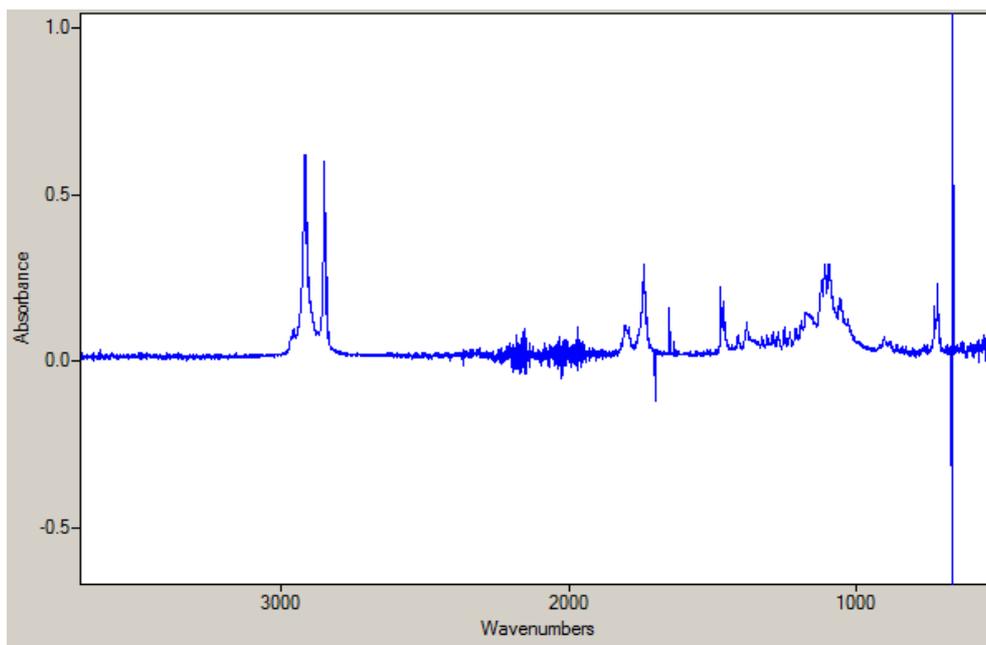
**Figure 31. Cellulose stearate spectrum. Synthesis 1:3 with catalyst.**

The same results were obtained with the 1:5 reactions. The differences between using or not using catalyst does not modify the spectra. The spectra are presented in *Figure 32* and *Figure 33*.

As in both synthesis ratios the same conclusion is found out, definitely can be proved that using catalyst does not affect CS obtained and moreover it reduces reaction time.



**Figure 32. Cellulose stearate spectrum. Synthesis 1:5.**



**Figure 33. Cellulose stearate spectrum. Synthesis 1:5 with catalyst.**

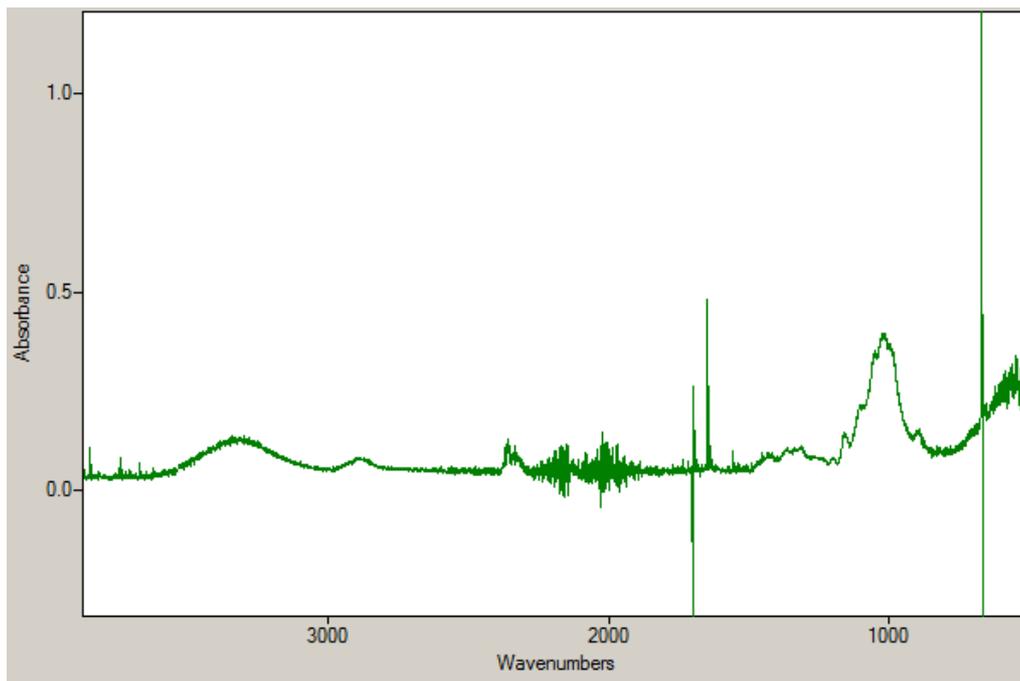
### 2.3.3. Comparison of esters spectra versus cellulose spectrum

As it was supposed to be, cellulose spectrum and derivatives spectra have a lot of differences. This fact proves that the reaction has taken place and the product obtained (derivative) is different from the raw material. All comments are based on *Figure 27*.

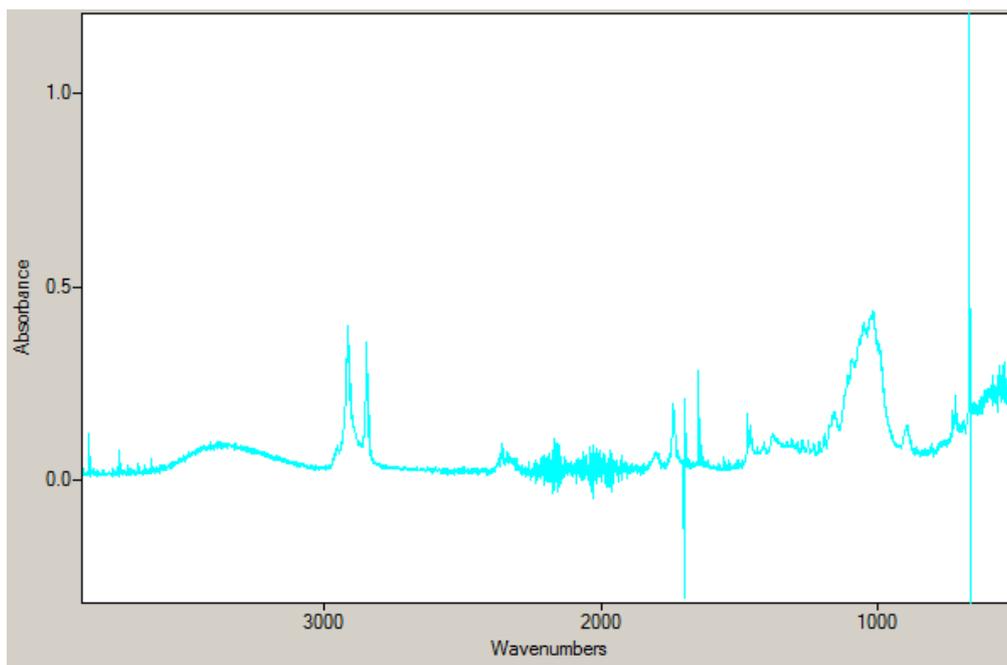
One surprising thing about spectra is that the 1:1 synthesis spectrum is really similar to cellulose spectrum but, on the other hand, it also presents the characteristic peaks of esters. The others two ratio spectra are definitely different from cellulose spectrum.

The main difference that shows that the reaction was accomplished is the spectra shape around  $1000\text{ cm}^{-1}$ . This wavelength corresponds to C-O bond which is presented in cellulose in the hydroxyl groups (-C-OH). These groups are the ones that react with the substituent, so the hydrogen is replaced for an acyl group (R-CO-). Due to this fact, a new bond is formed, -C-O-C- ( $1237\text{ cm}^{-1}$ ), and the first bond mentioned becomes less in number. This is the reason because the peak at  $1000\text{ cm}^{-1}$  becomes smaller while the peak at  $1237\text{ cm}^{-1}$  becomes bigger. As much bigger is DS, easier is to appreciate this change in the spectrum.

Cellulose spectrum and CS obtained from synthesis 1:1 are presented below (*Figure 34* and *Figure 35*).



**Figure 34. Cellulose spectrum.**



**Figure 35. Cellulose stearate spectrum. Synthesis 1:1.**

In addition, around  $1740\text{ cm}^{-1}$  a new peak appears in derivatives spectra. The bond that absorbs at this wavelength is C=O which is one of the most characteristics bonds of an ester. Detecting that peak reaffirms that cellulose stearate has been obtained.

Another two peaks that should be mentioned are the ones that appear in 2800 and 2900  $\text{cm}^{-1}$ . The presence of long aliphatic chains that belong to the cellulose substituent generates them. So they do not appear to the cellulose spectra.

Finally, comparing the water peaks of the spectra can be seen that cellulose stearate is more hydrophobic than cellulose. Only the product obtained by the reaction with ratio 1:1 is nearly as hydrophilic as cellulose (see *Figure 27*).

#### **2.3.4. Comparison between esters spectra**

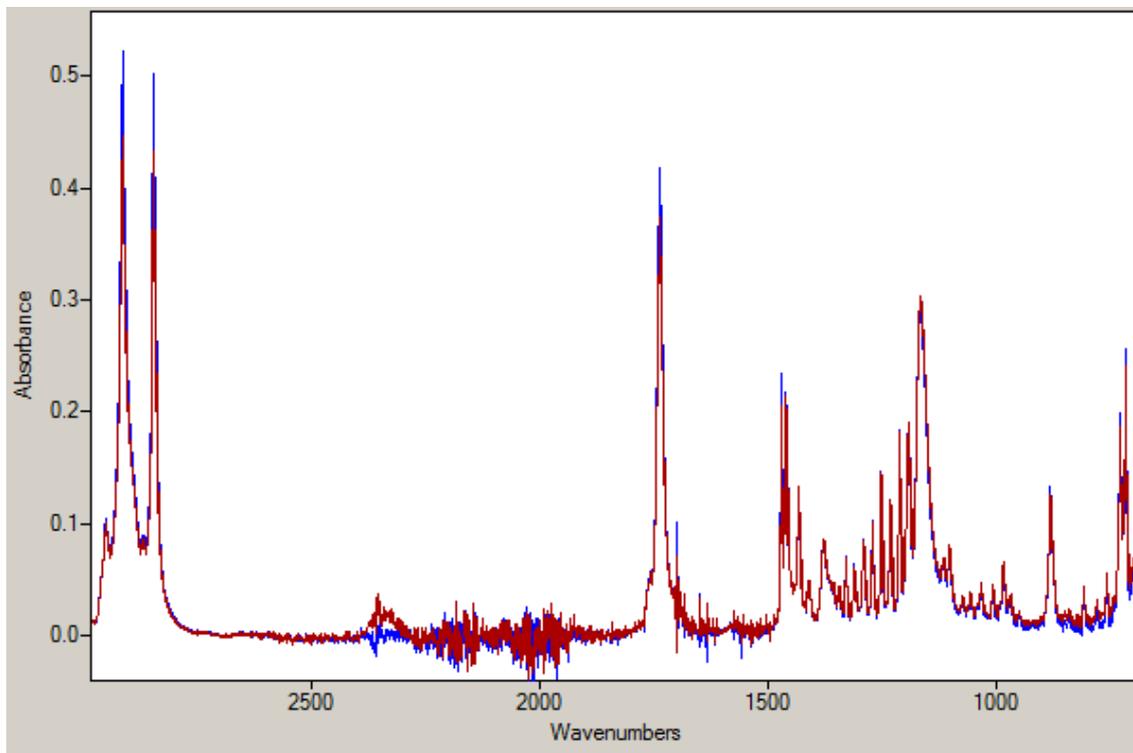
The comparison between spectra of the three synthesis that have different ratio *cellulose* : *stearoyl chloride* leads to think that the reaction in the case of 1:3 and 1:5 is better than in 1:1 ratio. In fact, there are some areas where spectra show significant differences (see *Figure 27*).

Over 3000  $\text{cm}^{-1}$  and under 1000  $\text{cm}^{-1}$  the strongest peak is presented by the synthesis 1:1 while the other two reactions are similar and the peak is nearly inappreciable. As it has been said before, this peak is one part of water spectrum so it provides enough information to ensure that when ratio of the reaction increases, water absorption decreases. In other words, the polymer obtained in the reaction with ratio 1:5 and 1:3 are more hydrophobic than the one obtained with the ratio 1:1. Comparing ratios 1:5 and 1:3, they do not present differences related with water absorption.

Another remarkable difference is on the peaks that appear around 1000  $\text{cm}^{-1}$ . The product obtained by 1:1 synthesis still presents an enormous amount of C-O bonds instead of a majority of C-O-C ester bonds (1237  $\text{cm}^{-1}$ ). With the other two ratios happens the other way round, C-O bonds are changed for C-O-C bonds and for this reason this peak become smaller. Because of this observation, carrying out the reaction of cellulose esterification with 1:1 as ratio leads to think that the ester obtained has a low degree of substitution.

### 2.3.5. High purity reagents

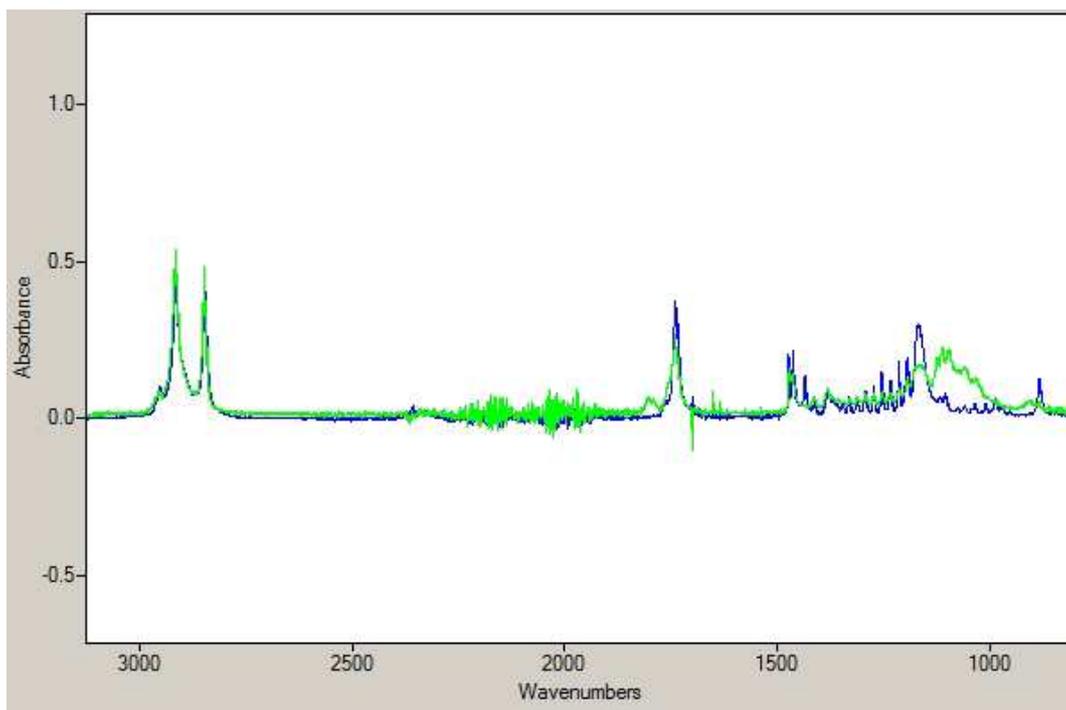
The results obtained using high purity reagents are summarized in one graph. Both reactions are carried out with a ratio 1:5 and without catalyst.



**Figure 36. FTIR spectra of 1:5 synthesis done with high purity IL (blue line) and technical purity IL (red). In both cases high purity stearoyl chloride is used.**

As it can be seen, there is no big difference between using or not pure IL. This fact does not affect to CS obtained. Just one small peak around  $2400\text{ cm}^{-1}$  appears when technical purity IL is used instead of high purity one (may be because of the large quantity of impurities that the first contains due to its colour).

Another interesting comparison is the one made between one of this CS obtained from high purity compounds and CS obtained from all technical purity reagents. The graph is presented below.



**Figure 37. FTIR spectra of 1:5 synthesis done with all compounds of technical purity (green line) and technical purity IL but high purity stearoyl chloride (blue line).**

Between the use of high purity stearoyl chloride or not, more differences can be observed. One of the main peaks of an ester is the one that appears around  $1250\text{ cm}^{-1}$ , referred to C-O-C bonds and it is by far bigger when high purity stearoyl chloride is used. This means that the majority of C-O bonds from cellulose (peaks around  $1000\text{--}1100\text{ cm}^{-1}$  nearly cannot be seen) have reacted forming the ester. Thus, using high purity reagent (stearoyl chloride) allows obtaining higher DS.

### 3. Electrospinning

In order to produce fibers with this technique, the polymer has to be dissolved because it is obtained as powder from the synthesis. The mixture has to be homogeneous and enough viscous and the most important thing is that there cannot be precipitated polymer.

For dissolving the polymer, cellulose stearate (CS), organic solvents were tried. First of all, a small portion of polymer was mixed with a lot of solvents separately and the ones

where the polymer was soluble were chosen as the main components for the electrospinning solutions.

Indeed, the best solutions for using in electrospinning are the ones that contain a mixture of solvents. It is usual that the mixture contains one solvent and one non-solvent, referred to the polymer solubility. Thus, the organic solvents found that cannot dissolve CS were added in a small fraction to the ones where is soluble.

Another important thing to take into account is the concentration of the polymer in the solvents mixture. The range of concentrations tried was from 8% to 17 % by mass.

After finding a good mixture of solvents and a suitable polymer concentration, the mixtures were tried in the electrospinning device and later checked in the microscope (some pictures are presented below).

All in all, it can be said that there are three steps required to produce fibers by electrospinning. The first one is finding suitable solvents for the polymer studied, the second one is prepare a mixture of solvents for dissolving the polymer and find the right concentration of it and finally, the third one is electrospin that mixture.

### **3.1. Results**

Even though five different reactions were performed only one product was electrospinned. The only polymer tried was the one obtained from the synthesis with 1:3 ratio and without catalyst. The only reason for paying attention just to one derivative obtained was the lack of time. Finding the suitable conditions and solvents requires a lot of time, resources and experiments. Until the moment, any of the mixtures tried was successful in obtaining fibers.

Anyway, all polymers obtained where dissolved in the same solvents in order to see if the reaction ratio and the degree of substitution really affect CS solubility.

### 3.1.1. Organic solvents tried for dissolving the polymers

With the aim of obtaining a visual, quick and easy comparison between the solubility of the polymers, solubility results are presented in the table below (*Table 10*).

**Table 10. Solubility results for polymers synthesized.**

Solvent	Synthesis ratio (cellulose : stearyl chloride)	1:3	1:3 cat	1:5	1:5 cat	1:5 IL and stearyl chloride high purity	1:5 technical purity IL + stearyl chloride high purity
DMSO	Soluble						
	Turbulence						X
	No soluble	X	X	X	X	X	
DMF	Soluble					X	X
	Turbulence	X	X	X	X		
	No soluble						
DMAc	Soluble					X	
	Turbulence	X	X	X	X		X
	No soluble						
Chloroform	Soluble	X	X	X	X	X	X
	Turbulence						
	No soluble						
Toluene	Soluble	X		X		X	X
	Turbulence		X		X		
	No soluble						
methanol	Soluble						
	Turbulence		X	X	X	X	X
	No soluble	X					
acetone	Soluble					X	
	Turbulence		X	X	X		X
	No soluble	X					
ethyl acetate	Soluble					X	X
	Turbulence	X	X	X	X		
	No soluble						
water	Soluble						
	Turbulence						
	No soluble	X	X	X	X	X	X
formic acid	Soluble						
	Turbulence					X	X
	No soluble	X	X	X	X		
ethanol	Soluble						
	Turbulence	X				X	X
	No soluble		X	X	X		

The polymers obtained with technical purity do not present a lot of differences in solubility at all. Just some changes were produced when dissolving them in toluene, methanol, acetone and ethanol. The changes in solubility are not bigger because the degree of substitution of all the polymers is more or less the same (presented in *Chapter*

3: results and discussion, 2.3. Degree of substitution) and this is the main parameter related with solubility.

As it can be seen in *Table 10*, the only solvent for all of them is chloroform and the common non solvents are DMSO, water and formic acid.

In toluene, surprisingly, are soluble just the polymers that were synthesized without catalyst. The solubility in ethanol is decreased when the ratio of the synthesis is increased and the contrary happens with methanol and acetone.

About using high purity reagents it should be said that solubility in organic solvents is increased. In this case, this new polymer is soluble in DMF, DMAc, acetone and ethyl acetate while the other ones are not. Due to this observation, it can be said that CS obtained with reagents of higher purity has higher degree of substitution.

### 3.1.2. Electrospinning attempts with cellulose stearate obtained from 1:3 synthesis without catalyst

#### 3.1.2.1. Solubility

Focusing on the polymer obtained from 1:3 synthesis without catalyst, it has to be said that just two suitable solvents were found, chloroform and toluene. For this reason, all the rest tried were considered as possible candidates of being non-solvent in the mixture for electrospinning. In *Table 11* is summarized the solubility of this polymer.

**Table 11. Solubility for polymer obtained in 1:3 synthesis without catalyst.**

Solvent	Soluble	Turbulence	No soluble
DMSO			X
DMF		X	
DMAc		X	
Chloroform	X		
Toluene	X		
methanol			X
acetone			X
ethyl acetate		X	
water			X
formic acid			X
ethanol		X	

Usually, for electrospinning, the most common solvents used are dimethylacetone (DMAc), N,N-dimethylformamide (DMF) and dimethylsulfoxide (DMSO). They were the first tried but they are not suitable for CS. Consequently, other options were considered. Chloroform and toluene are solvents that have never been used for electrospinning because of their fast volatility. However, as they can dissolve CS they were used as the main solvent in the solvent mixture.

### **3.1.2.2. Solvent mixtures**

As said before, chloroform and toluene are the main solvents for CS in the mixtures prepared. The target of adding a non solvent is to decrease mixture's volatility. Anyway, the amount of non solvent added should be tiny because it can provoke polymer precipitation.

The best procedure for finding good conditions for the mixture is the following one.

First of all, the mixture of solvents should be prepared in the ratio chosen. After that, a high concentration of polymer should be chosen and the polymer and the solvent mixture amount placed in a weighing bottle. Then, the concentration of polymer can be corrected if it is wrong just adding solvents mixture.

This way of working (starting with a high concentration) is better because it is easier adding more solvents to the mixture than adding polymer if the concentration is wrong.

For expressing the relation between solvents in the mixture, mass ratios are used instead of molar ratios.

Some of the combinations used and tried are summarized in *Table 12*.

**Table 12. Solvent mixtures tried.**

	Solvent mixture (antisolvent : solvent)	% polymer	Ratio OK	Ratio NOT OK	Remark
<b>Chloroform</b>	1 acetone : 4 chloroform	10		X	Jelly
	1 DMSO : 4 chloroform	10		X	too viscous and precipitation
	1 DMSO : 4 chloroform (recalculate)	10	X		-
	1 DMSO : 10 chloroform	15		X	jelly
	1 MeOH : 4 chloroform	10		X	precipitation
	1 MeOH : 8 chloroform	10		X	not enough viscous
	1 MeOH : 8 chloroform	12	X		-
	1 DMF : 10 chloroform	15		X	jelly
	1 Ethanol : 10 chloroform	15		X	jelly
	1 THF : 10 chloroform	15		X	jelly
	1 THF : 10 chloroform	11	X		-
1 THF : 10 chloroform	13	X		-	
<b>Toluene</b>	1 acetone : 3 toluene	17		X	Jelly
	1 acetone : 5 toluene	12		X	Jelly
	3 acetone : 5 toluene	9,3		X	Jelly
	1 MeOH : 8 Toluene	10		X	too viscous
	1 MeOH : 8 Toluene	9	X		-
	1 DMSO : 8 Toluene	10	X		-
	1 THF : 8 toluene	10		X	too viscous
	1 THF : 8 toluene	9		X	too viscous

The following picture can illustrate how these mixtures look like.



**Figure 38. Examples of electrospinning mixtures. The one on the left is suitable for electrospinning, the one in the middle is too viscous and the one on the right, the polymer is precipitated.**

As it can be seen, the mixtures tried were not successful at all. Particularly, the worst non-solvent used was acetone. It provokes polymer precipitation very easily (with few millilitres) and it is highly volatile.

Mixtures obtained with suitable conditions were tried in the electrospinning device. Anyway, some of the other mixtures were tried too but without expecting any positive result.

### 3.1.2.3. Electrospinning experiments

Electrospinning device is showed in the following picture. It consists of an automatic dispenser, a rotary cylinder and a high voltage supplier.



**Figure 39. Electrospinning setup.**

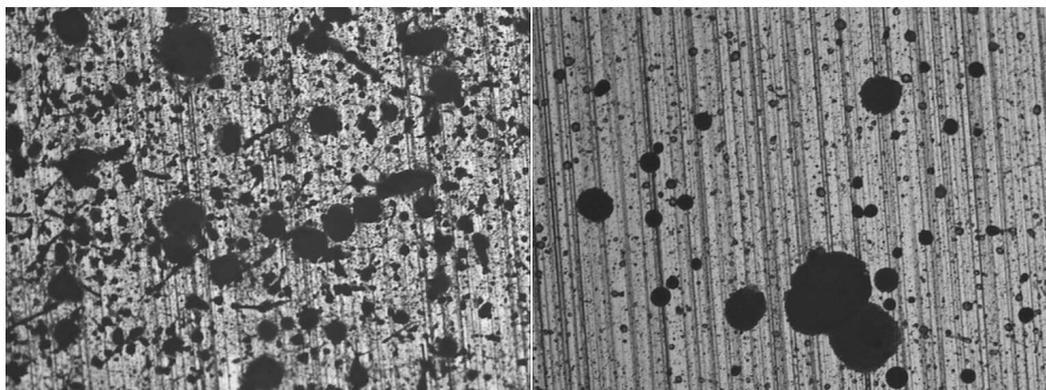
Some of its parameters (explained in *Chapter 1: overview, 3. Electrospinning*) can be changed in order to obtain different results. The ones modified for achieving CS fibers were the voltage and velocity rate (millilitres of product electrospinned per hour).

In order to electrospin the mixture, it has to be placed in a syringe and afterwards introduced in the machine. The syringes used are of 1ml and the needle diameter is 0,4mm. Some results of electrospinning attempts are presented in *Table 13*.

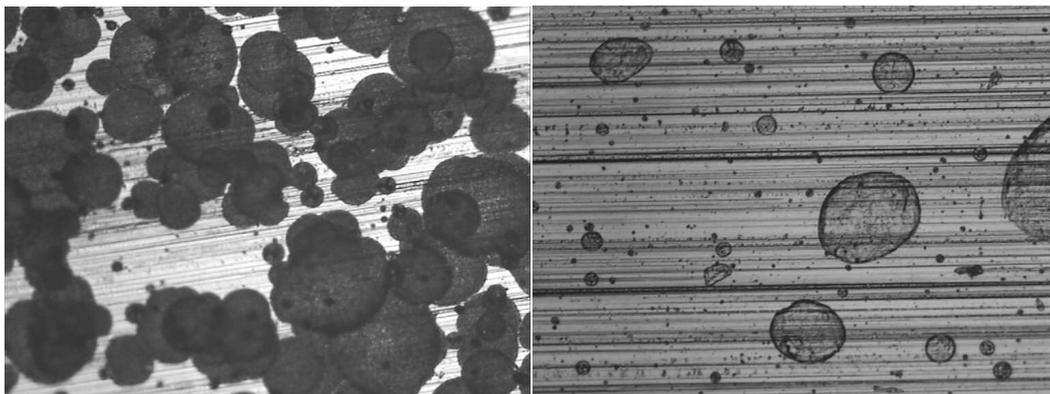
**Table 13. Different mixtures tried to electrospin.**

	<b>Solvent mixture</b>	<b>Electrospinning conditions</b>	<b>Fibers</b>	<b>Observations</b>
<b>Chloroform</b>	pure chloroform (10% polymer)	15 kV; 3,5 mL/h	NO	drops
	1 MeOH : 8 chloroform (12% polymer)	18 kV; 1,5 mL/h 15 kV; 1,5 mL/h 15 kV; 0,5 mL/h 18 kV; 0,5 mL/h 15 kV; 3,5 mL/h	NO	no drops, it evaporates so fast
	1 MeOH : 8 chloroform (10% polymer)	15 kV; 2,5 mL/h 15 kV; 1,5 mL/h	NO	drops, evaporation so fast
	1 DMSO : 4 chloroform (10% polymer)	15 kV; 2,5 mL/h	NO	drops, spray
<b>Toluene</b>	pure toluene (10% polymer)	15 kV; 2 mL/h 15 kV; 1,5 mL/h	NO	drops
	1 MeOH : 8 Toluene (10% polymer)	15 kV; 3,5 mL/h	NO	drops
	1 DMSO : 8 Toluene (10% polymer)	15 kV; 2,5 mL/h	NO	drops, spray
	1 THF : 8 toluene (9% polymer)	15 kV; 2,5 mL/h	NO	drops

Some pictures made with a microscope of these results are presented below.



**Figure 40. Microscope images. On the left 4 chloroform : 1 DMSO and 10 and on the right 8 chloroform : 1 DMSO and 10%.**



**Figure 41. Microscope images. On the left 8 toluene : 1 DMSO and 10% and on the right 8 toluene : 1 methanol and 10%.**

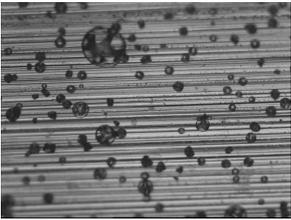
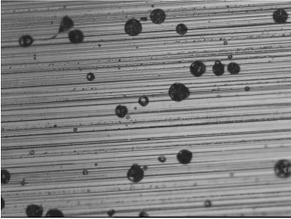
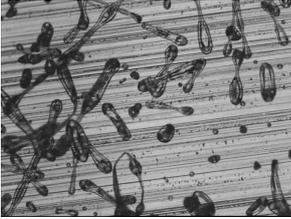
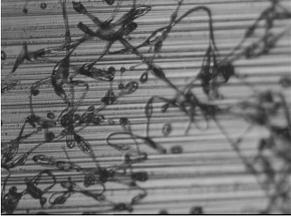
After all these trials done without any success, a different strategy was tried. Using as solvent only pure chloroform, different mixtures were prepared with different polymer concentrations (7%, 9%, 11%, 13%). Using a concentration of 15% was tried but the mixture was totally jellied. Electrospinning all of them was the good way for finding optimum polymer concentration. After that, the ones with best results (11%, 13%) were tried with the same concentration but adding another solvent to the mixture, THF. The mixtures and the results are summarized in *Table 14*.

Thus, the appropriate concentration of polymer is between 11% and 13% for obtaining some kind of small fibres. What is obtained has the shape of a mesh. The entire surface where the fibre is collected is covered with these small fibres mentioned.

Lower and higher concentrations should not be used. Lower concentrations leads the results to drops and higher concentrations make the solution become jelly making it impossible to electrospin.

Adding a non-solvent to the mixture apparently does not change anything. Comparing the results where the same polymer concentration is used, the extended drops (or short fibres) look more or less the same.

**Table 14. Results obtained with electrospinning just varying polymer concentration.**

<b>Solvent</b>	<b>Polymer concentration</b>	<b>Microscope image</b>
<b>Chloroform</b>	7%	
	9%	
	11%	
	13%	
<b>Chloroform + THF</b>	11%	
	13 %	

## Conclusions

### *Goals achievement*

The synthesis of CS has been carried out successfully with all ratios. All the polymers precipitated correctly as powder except the one obtained with 1:1 synthesis. While washing it with methanol its behaviour was gelatinous, but its later characterisation showed that the ester was achieved.

Obtaining the DS by saponification method is quite imprecise due to its sensitiveness. It would be a good idea to try one of the other mentioned methods that are based in spectra obtention.

Increasing the ratio between cellulose and stearyl chloride has made DS to increase (as expected). Anyway, the difference determined is not enough significant for noticing changes in CS properties. The maximum DS obtained is 0,78 in 1:5 synthesis with catalyst.

For CS obtained by reactions carried out with high purity reagents was not possible to determine DS. But owing to the increased solubility in organic solvents that these CS present (compared to all the other polymers obtained) it can be said that DS is high. At least it can be ensured that DS is much more higher than 0,78 because if there is only a tinny difference, the solubility properties are not modified.

The fact that the substituent has really long aliphatic chains may be a reason for the low DS value obtained. As longer is the substituent aliphatic chain, reactivity decreases a lot.

Using IL is the simplest way for achieving cellulose modification and it can be recovered easily, compared to the conventional cellulose modification carried out with poisoning and non-recoverable reagents. Surprisingly, synthesizing it with high purity reagents produced a extremely dark (brown) IL. The IL obtained with the normal products was nearly transparent, what means that the first one is full of impurities. It leads to think that high purity reagent is more sensitive to temperature and impurities. Anyway, using it for producing CS was tried and the results show that the purity of ionic liquid does not affect the reaction process at all (FTIR spectra of CS obtained in technical purity IL and high purity IL have the same shape).

Using FTIR spectra is useful because comparing the spectrum of raw cellulose and the spectra from the derivatives can be seen how the reaction has progressed. Is an easy way to ensure that the reaction has taken place because ester peaks and aliphatic chain peaks appear in derivatives spectra and not in cellulose one. Thanks to this graphs it has been seen that using catalyst does not affect the result. So using it leads to decrease until half the reaction time without changing properties (1,5h instead of 3h).

By means of calorimetry test the presence of impurities can be detected in all the samples. All of them present stearic acid as the main impurity. Hence, its presence shows that the cleaning process done is not enough (methanol is used).

The solvents found that can dissolve CS with a degree of substitution around 0,5 (all ratios tried) are chloroform and toluene. For the polymers obtained with high purity reagents was found that DMF, DMAc, acetone and ethyl acetate are suitable solvents too.

Using chloroform and toluene for electrospinning is a problem because they have high volatility. Its use makes the mixture to dry really fast while it is being electrospinned. This may be one of the reasons of obtaining drops instead of fibers.

For these reasons, attempts for electrospin CS have not been successful, but it does not mean that the polymer is not suitable for electrospinning. The conditions of the mixtures (like polymer concentration, solvents...) and from the setup (like voltage, distance from the syringe to the collector...) should be changed and tried more times. The range of concentration obtained as the most suitable is between 11% and 13% in mass because the mixtures have enough viscosity but they do not become jelly.

#### *Further experiments*

As example for trying in the future, the mixtures for electrospinning can be heated up (but always below solvent boiling point) for dissolving CS easily and for avoiding that they become jelly. Applying heat will allow increasing the percentage of polymer in the mixture, even arriving to 20% by weight. Not only heating the mixture is enough, the syringe and the needle should be heated up too. Is the only way of preventing jellification of the mixture while electrospinning it.

What could also be tested is a more careful way of removing water from the IL and from the cellulose, as well as using purged nitrogen. The one used during this synthesis is inline gas, so it can be replaced for high purity gas from balloons. Trying to add an organic base could also work for improving the reaction because the by-product is HCl.

Finally, CS should be cleaned with an organic solvent where stearic acid is more soluble than in methanol but at the same time cellulose stearate is not.

## Résumé in English

The aim of the thesis is to develop technology for producing cellulose fatty acid esters that later will be used to produce fibrous materials by means of electrospinning. Main material of the study is cellulose-stearate which is a polymer synthesised by reaction between stearyl chloride and cellulose. The experimental part consists of synthesis of it by chemical modification of cellulose using ionic liquid as a reaction media. In addition, ionic liquid is also synthesised from the beginning.

Various syntheses are carried out in order to obtain polymers with different degree of substitution because it is known that it affects solubility a lot. Three ratios cellulose: stearyl chloride are tested as well as the use of catalyst or not. Those tested are 1:1, 1:3 with and without catalyst and 1:5 with and without catalyst too. Moreover, high purity reagents for producing IL and CS are purchased (methylimidazole and stearyl chloride) in order to compare its use in CS obtention. The synthesis chosen for repeating is 1:5 without catalyst.

All samples are characterized by means of differential scanning calorimetry (DSC), infra-red spectroscopy (FTIR) with ATR accessory and saponification method for determining the degree of substitution.

As expected, as bigger the ratio is, bigger is the DS obtained but one important point is that the results found are all under 1 what means that the DS is really low. Using catalyst or not does not affect to DS and it does not modify the properties so it is better to use it because reaction time becomes half (1,5h). The method for determining that is a manual test based in a saponification reaction and a back titration.

From the calorimetry test it is observed that the main impurity remaining in the samples after washing them with methanol is stearic acid. Separate it from CS is difficult because this compound may not be enough soluble in this organic solvent.

The FTIR spectra are a useful technique to control if the reaction is being done or not. In the cellulose stearate graphs obtained, the typical peaks from ester ( $1740\text{ cm}^{-1}$  for C=O and  $1240\text{ cm}^{-1}$  for C-O-C) can be found but they cannot be found in cellulose spectra, as expected. Comparing cellulose spectrum and a derivative one it can be seen that the peak corresponding to bond C-O from the hydroxyl groups ( $1000\text{-}1100\text{ cm}^{-1}$ )

decreases while the other ones from ester mentioned before increases. With these observations it can be said that the reaction has taken place, thus the polymer has been obtained.

Another important point is to find appropriate solvent or solvent mixture and spinning conditions for obtaining the fibrous materials with controllable parameters. The technique used for producing fibres, called electrospinning, is nowadays an important field of research and it is being developed for future applications related with nanoscale fibers diameter. It is based in the obtention of fibers by applying a difference of voltage between mixture supplier (syringe) and the collector.

The attempts with this method have not been successful at all so no fibers have been obtained (some more experiments are required for finding the optimum electrospinning conditions). Anyway, while doing these tests two suitable solvents for the polymer have been found, toluene and chloroform. The fact that they are highly volatile makes electrospinning more difficult. The range of polymer concentration in the mixtures has to be between 11-13%, more than that makes the mixture become jelly and less makes it not enough viscous.

Definitely, using high purity reagents (especially pure stearoyl chloride) makes DS increase a lot. Testing the solubility of the polymers obtained with these conditions showed that are highly soluble in a lot of organic solvents. This result leads to think that DS is much more bigger in polymer obtained with high purity reagents than in technical ones. It is more important that stearoyl chloride is high purity one than the IL reagents.

All in all, this polymer, as well as electrospinning technique, should be further studied in order to obtain the fibers expected.

## Kokkuvõte

Magistritöö eesmärgiks oli arendada tselluloosi rasvhapete estreid, mis sobiksid elektroketruse teel kiudude valmistamiseks. Peamine uuritav materjal oli tselluloosstearaat, polümeer, mis sünteesitakse stearoüülkloriidi ja tselluloosi vahelisel reaktsioonil. Töö eksperimentaalne osa koosnes peamiselt tselluloosstearaadi sünteesist, modifitseerides tselluloosi ioonvedeliku keskkonnas. Töö käigus sünteesiti ka sobiv ioonvedelik.

Töö käigus sünteesiti erineva asendusastmega tselluloosi derivaate, kuna on teada, et asendusaste mõjutab oluliselt nende polümeeride lahustuvust. Katsetati kolme tselluloosi : stearoüülkloriidi suhet ja reaktsiooni toimumist katalüsaatoriga või ilma selleta. Katsetatud suhted olid 1:1, 1:3 ja 1:5 koos katalüsaatoriga ja ilma selleta. Sünteesi suhtega 1:5 korral kasutades kõrgendatud puhtusastmega ioonvedelikku ja stearoüülkloriidi, et kontrollida puhtusastme mõju reaktsiooni tulemustele.

Kõiki proove analüüsiti diferentsiaalse skaneeriva kalorimeetria, ATR Fourier infrapunaspektroskoopia ja asendusastme määramiseks seebistusmeetodiga. Eeldatult kasvas asendusaste stearoüülkloriidid sisalduse kasvades kuid jäi siiski madalaks, väärtusega alla ühe. Katalüsaator ei mõjutanud asendusastet ja materjali omadusi kuid seda on mõistlik kasutada kuna reaktsiooni aeg lüheneb poole võrra.

Kalorimeetria abil leiti, et peamine jääk (ebapuhtus) materjalis peale pesemist metanooliga on steariinhape. Selle eraldamine tselluloosstearaadist on komplitseeritud piiratud lahustuvuse tõttu metanoolis.

Infrapunaspektroskoopia on kasulik meetod kontrollimaks soovitud reaktsiooni toimumist. Tselluloosstearaadi spektritest leiti estrile iseloomulikud piigid ( $1740\text{ cm}^{-1}$  iseloomustamiaks C=O rühma ja  $1240\text{ cm}^{-1}$  iseloomustamiaks C-O-C rühma), mis oodatult puudusid tselluloosi spektris. Leiti, et C-O sidemele vastav piik ( $1000\text{--}1100\text{ cm}^{-1}$ ) vähenes ja eelnevalt mainitud estrile iseloomulikud piigid kasvasid võrreldes tselluloosi spektrit selle derivaadi spektriga. Nende vaatluste põhjal saab järeldada, et tselluloosi derivaadi tekkimise reaktsioon on toimunud.

Töö teiseks oluliseks ülesandeks oli leida kontrollitud parameetritega kiulise materjali valmistamiseks sobiv lahusti või lahustite segu ja elektroketruse tingimused.

Elektroketrus on kaasajal oluline uurimisvaldkond, mille eesmärgiks on välja arendada nanomõõtmetes diameetriga kiududest tulevikumaterjale. Kiude saadakse rakendades suurt pinget erinevust polümeerilahust edastava süstlanõela ja (maandatud) kollektori vahel.

Käesoleva töö raames ei õnnestunud siiski täielikult elektroketruse teel tselluloosstearaadist kiude valmistada, kuna selle maht jäi sobivate ketrusparameetrite leidmiseks piiratuks ning tööd tuleb kindlasti jätkata. Siiski leiti katsetuste käigus kaks sobivat lahustit, toluen ja kloroform. nende lahustite suur lenduvus muutis ketruse siiski komplitseerituks. Optimaalne polümeeri kontsentratsioon nendes lahustites oli 11 – 13%. Suurem kontsentratsioon muutis lahuse geelisarnaseks ja väiksema kontsentratsiooni korral oli lahuse viskoossus ketramiseks liiga väike.

Kõrge puhtusastmega reagentide (eriti stearüülkloriidi) kasutamine suurendas asendusastet märgatavalt. Ka paranes selle tulemusena saadud tselluloosi derivaadi lahustuvus erinevates orgaanilistes lahustites. Sellest järeldub, et suure asendusastmega derivaatide saamiseks tuleb tehnilise puhtusastmega reagentide asemel kasutada kõrge puhtusastmega reagente.

Tselluloosstearaadi funktsionaliseerimise ja elektroketruse tingimuste alaseid uuringuid on vajalik jätkata, et oleks võimalik valmistada uudseid tselluloosipõhiseid nanomõõtmetes diameetriga kiude.

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## APPENDIX

Some extra pictures that show laboratory procedures, devices used and compounds obtained.



IL crystallized.



Desiccator.



Cellulose that has not been dissolved correctly in the IL.



Polymer mixed with methanol. Two phases can be observed.



IL used for polymerization 1:1.



Titration setup.



Starting point of the IL synthesis.



Mixture after titration with HCl.



Mixture after titration with NaOH.



Synthesis 1:5. Polymer obtained after drying it in the oven.



Synthesis 1:5 with catalyst. Polymer obtained after drying it in the oven.



Synthesis 1:1. Polymer obtained.



Synthesis 1:3 with catalyst. Polymer obtained after drying it in the oven.



Microscope used for evaluation of electrospinning results.



FTIR spectrometer with ATR accessory.



Differential Scanning Calorimeter.