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Master's Programme in MSc. Polymer Technology

Bio-based polyamides from 2,5-furandicarboxylic acid

Synthesis and characterization of bio-based furan-containing polyamides

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Abstract

Biobased polymers is one of the pathways to achieve more sustainable plastics and products. Polyamides (PA) are commodity polymers, having versatile applications from fibers in clothes to car parts. The most produced polyamides (PA6 and PA66) account for yearly fossil-fuel consumption of almost 10 million tonnes. The detrimental effects do not only concern the production phase, but also the consumption and end-of-life aspects. Hence, there is a crucial need to develop bio-based polyamides that are chemically recyclable to reduce the environmental impact of these materials.

In this work, furan-based polyamides (FPAs) were synthesized through a polycondensation reaction between hexamethylenediamine (HMDA) and a bio-based diacid, 2,5-furandicarboxylic acid (FDCA). In addition, copolymers were made by using different ratios of C6 and C10 diamines (HMDA and 1,10-decanediamine). The structure and chemical composition of the synthesized polymers and copolymers were confirmed using Fourier-transform infrared spectroscopy, and proton nuclear magnetic resonance. The highest molecular weight attained was 9900 g/mol, mainly due to limitations from the reactor setup (absence of a vacuum system and lack of adequate mixing). Adding to this, the degradation of FDCA and the evaporation of HMDA were identified as potential factors inhibiting the increase in molecular weight. Based on the thermal analyses, the FPAs were found to be amorphous, with an average glass transition temperature of 102°C. Further, the synthesized polyamides showed high thermal stability, having an initial degradation temperature (corresponding to 5% weight loss) of 340°C.

Keywords Bio-based, 2,5-furandicarboxylic acid, polyamides.

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Preface and acknowledgements

This thesis represents my final work in the joint Master programme of Polymer Technology. Coming from the other part of the world, studying at KTH and Aalto University was a very enjoyable, challenging, and self-discovering journey. During my study, I recognized that there are areas, be it theoretical or practical, in which I find myself capable of using my potentials in an efficient way, more than in other areas. Bearing knowledge and putting the latter into practice are two sides of the same coin. Indeed, I perceive learning and taking knowledge from my Master studies as a responsibility to apply it in ways that benefit societies, within the scope of my capabilities.

I would like to thank with all gratitude my supervisors prof. Jukka Niskanen and prof. Karin Odelius, as well as my advisor Lauri Välinen, for their insights, helpful remarks, advice, and support.
I want to thank as well my family, especially my dear father, who encouraged me and was constantly checking on me if I am doing well, and who without him, I would not have been able to pursue my studies. As for my lovely and caring sister, she knows that I cannot thank her enough for her support, and comprehensiveness, and for being there when I need it, although she is very busy.

Otaniemi, May 2024
Onsi Hanafi

Symbols and abbreviations

Đ	Dispersity
DSC	Diffraction scanning calorimetry
DMFDC	Dimethyl-furandicarboxylate
FTIR	Fourier transform infrared spectroscopy
HDMA	1,6-hexamethylenediamine
FDCA	2,5-furandicarboxylic acid
FPA	Furan-based polyamide
NMR	Nuclear magnetic resonance
PA	Polyamide
PE	Polyester
ROP	Ring-opening polymerization
SEC	Size exclusion chromatography
TGA	Thermogravimetric analysis

1 Introduction

Polymers and fibres form a significant part of the materials used in various economic sectors and aspects of our life. An increasing amount of attention has been focused on polyamides (PAs), which are produced in large volumes, and their market size is estimated to reach 10.9 million tonnes (Mt) in 2025 (compared to 8.2 Mt in 2018)[1]. The most produced polyamides (PA6 and PA66) account for fossil-fuel yearly consumption of almost 10 Mt[2]. In fact, the production of the majority of these products rely on fossil-fuels and they have significant environmental, human health and social negative impacts[3–6]. The detrimental effects do not only concern the production phase, but also the consumption and end-of-life aspects[4]. As a way to mitigate these drawbacks, shifting to a bioeconomy is a major umbrella under which research in polymer chemistry and technology is currently being performed. To provide alternatives with lower carbon footprint, the production of bio-based PAs is expected to grow, with an estimated demand of roughly 396 thousand tonnes per year by 2027.[1]

The benefits on the environment and on society obtained from producing bio-sourced materials closely depend on the resources involved and on the way they are managed. One of the main reasons for shifting towards a bioeconomy is to gradually substitute fossil-based materials with bio-based ones. This contributes to the reduction of the carbon footprint associated with the use and extraction of fossil-fuels, as well as to make use of a renewable resource. Nevertheless, it is important to note that the overall carbon footprint of a bio-based material is not necessarily lower than the one of its fossil-based counterpart. Another point to pay attention to is the performance of the bio-based material for its intended application(s). Changing the raw materials of a polymer or fibre does not affect only the synthesis process but also often the properties of the product, especially if the structure is altered. Therefore, the goal of achieving efficient synthesis of bio-based materials needs to be coupled with efforts in obtaining adequate material properties, considering a functionally equivalent material.

Goals of thesis

The main objectives of this master thesis project are to work on the efficient synthesis of polyamides (PAs) based on 2,5-furandicarboxylic acid (FDCA) and to evaluate their properties. For this purpose, fossil-based and bio-sourced diamines will be used, implying that both partially and fully bio-based PAs will be obtained. The properties of these different polymer products will then be compared to each other. PAs are strong and thermally stable polymers that are used in diverse applications, including textiles, construction and packaging applications[7]. Obtaining effective synthesis routes to bio-based polyamides is therefore an important contribution to the reduction of the

carbon footprint of multiple industrial sectors. The bio-based production pathway in this thesis work starts from FDCA (fig. 1), being an indirect product of lignocellulosic materials. In fact, a common intermediate compound is hydroxy-methyl-furfural (HMF), which can be attained from wood by chemical modification of cellulose[8]. Then, FDCA can be obtained from HMF in diverse ways, including through a chemical catalytic reaction or bio-catalytic reaction, followed by an oxidation step[9]. In addition, other methods and intermediate compounds have also been used[10].

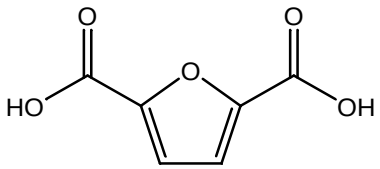


Figure 1: *Chemical structure of FDCA.*

Structure of the study

The experimental work of the thesis consists of a series of synthesis experiments, using FDCA and different diamine compounds, and by varying the reaction conditions and other materials used (such as solvent and catalyst), accordingly. Then, the composition and chemical structure of the synthesized PAs will be characterized using chemical methods, mainly size exclusion chromatography (SEC), fourier-transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR) analysis. In addition, the thermal properties will be investigated, using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Conclusions on the effectiveness of the polymerization process as well as on the properties of the polymers will be drawn based on these analyses and based on the comparison between the PAs produced.

Following the introduction (Ch. 1), the second chapter is on the literature review performed in the first phase of the thesis work. An overview of the state-of-art and production pathways of bio-based diacids and diamines will be provided. The categorization of PAs and the synthesis methods relevant to the thesis topic will also be discussed. The next chapter (Ch. 3) presents the experimental methods employed for the synthesis and characterization processes, as well as the materials used for that. Then, Ch. 4 concerns the presentation and discussion of the results. The chapter will be divided based on the different polyamides synthesized and on the types of characterization and properties analysis. The final chapter (Ch. 5) discusses the conclusions of the work, in addition to proposed recommendations and further scopes of study.

2 Literature review

Polyamides (PAs) have versatile applications, due to their advantageous mechanical and thermal properties[7]. PAs possess high strength at elevated temperatures, good toughness and thermal stability, in addition to being chemically resistant to many solvents[11]. Hence, it is desirable to produce functionally equivalent bio-based alternatives to high-performance polyamides and to enhance the understanding of their properties. Fully bio-based polyamides with competitive properties (compared to fossil-based ones) are being increasingly researched[7]. Additionally, there is a research gap in the investigation of the properties of furan ring-containing polyamides. Few studies exist on the synthesis and characterization of polyamides using FDCA[7,12–15]. Difficulties faced in the production process concern molar mass, reactivity and thermal stability[12]. One common synthesis route of polyamide is through the reaction of a diacid, having two carboxylic acid groups, and a diamine, with two amine groups. Being a polycondensation reaction, water is formed as a byproduct (fig. *2*).

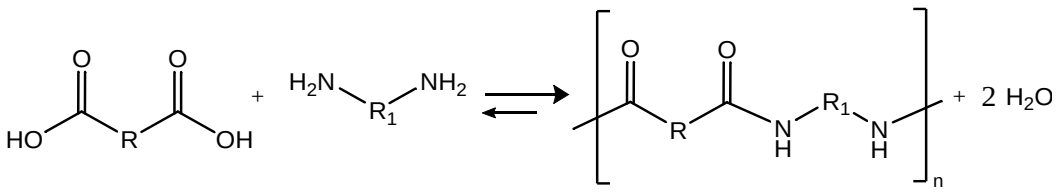


***Figure 2*:** *General reaction scheme of polyamide synthesis, with R and R_1 represent hydrocarbon groups.*

It constitutes a polycondensation reaction that leads to the production of water. Variations in the carbon number and structure (aliphatic vs. aromatic) of the R and R1 groups give rise to different polyamides. In the case of aliphatic PAs, the conventional nomenclature is as follows[2,16]:

PAxy or PAx,y ; where x and y are the number of carbon atoms present in the diamine (R1) and in the diacid (R), respectively.

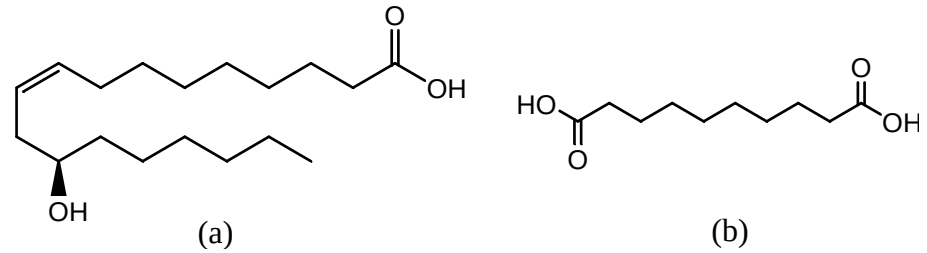
Other reaction pathways exist, in which the precursors can be cyclic amides (lactams) or amino acids. The most common catalysts mentioned in literature and the main synthesis routes of polyamides are discussed in section 2.3 ‘Types of bio-based polyamides and synthesis methods”.

This chapter provides a theoretical background to the state-of-art and development of bio-sourced diacids and diamines, based on recent research studies. To complement the picture, the last section gives a brief overview of the types of bio-based polyamides and their relevant synthesis methods.

2.1 Bio-based diacids

Different routes exist for the production of bio-based diacids. One of them that falls within the category of biological conversion is through the fermentation of biomass[17]. This requires the determination of the suitable bio-sourced sugars feedstock and the selection of micro-organisms capable of giving the desired product(s) in an efficient way. Advances in this field are continuously being made by improving and optimizing microbial stains and by applying various "metabolic engineering" techniques[17,18]. This includes strategies based on synthetic biology (chromosome engineering, "gene expression modulation", DNA assembly...), enzyme engineering and systems biology[17,19,20]. One of the advantages of microbial fermentation is the possibility of producing aminocarboxylic acids (or synthetic amino acids), such as 5-aminovaleric acid, γ-aminobutyric acid and 6-aminocaproic acid. Since amino acids contain both a carboxylic acid group and an amine group, they have the potential to be converted into cyclic amides, also called lactams, which can be utilized in ring-opening polymerization reactions. Examples mentioned in literature include ε-caprolactam, obtained from 6-aminocaproic acid, and δ-valerolactam[17].
A wide variety of "microbial production hosts" used for the synthesis of diacids, diamines and aminocarboxylic acids, are cited in literature, based on the work of various research teams[17]. These hosts are identified by the micro-organism itself, the specific genes involved, as well as crucial production variables, such as the cultivation conditions (whole cell, fed-batch, flask culture...) and the type of carbon source employed (glucose, L-lysine, monosodium glutamate). Prominent examples of diacids produced through fermentation are adipic acid[21], succinic acid[22,23] and glutaric acid[24,25].

Another way to obtain precursors for bio-based monomers of polyamides is by cracking vegetable oils. In this regard, oils rich in linoleic acid and castor oil are commonly used[2]. Each of these methods have their own pre-treatment and extraction steps prior to the main biological/chemical conversion process[16]. Castor oil presents several advantages due to its significant oil content (up to 60%), which is composed majorly of ricinoleic acid -$C_{18}H_{34}O_3$- (around 85-90%) and small amounts of linoleic acid (4-5%)[26]. Both fatty acids have a crucial role as intermediate compounds in the production of bio-PAs. For example, ricinoleic acid can be converted into sebacic acid -a diacid- (structure in fig. *3*). In addition, other polyamide precursors can be derived from castor oil, such as 11-aminoundecanoic acid[16].



(a) (b)

Figure 3: *Chemical structures of (a) ricinoleic acid and (b) sebacic acid*[2].

Furthermore, an important distinct production route is the chemical modification of lignocellulosic material constituents, through which can be derived a variety of chemical building blocks and monomers for bio-based polyamides. Theoretically and globally speaking, there are sufficient resources of plant biomass that contains around 75-80 wt% of cellulose and hemicelluloses [27] for the production of precursors for bio-based polymers. Nevertheless, it is crucial to consider that some of these resources are less suitable for chemical conversion to polyamide monomers than others, and to consider as well the competition with other economic sectors. An example of a diacid produced via the chemical catalytic modification method is adipic acid, obtained by reducing glucaric acid, which is an oxidation product of glucose[16].

2.1.1 2,5-furandicarboxylic acid

Considering the main topic of the thesis, further focus on the theoretical background of 2,5-furandicarboxylic acid (FDCA). In order to obtain the chemical precursors of FDCA, cellulose needs to be degraded through hydrolysis or depolymerized into its constitutive unit, namely glucose. The latter can then be modified to different compounds, including lactic acid, levulinic acid and 5-hydroxymethylfurfural (HMF)[28]. In each of these steps, there exist multiple reaction pathways[9].
The major production routes of FDCA from biomass are[9]:

1. Chemical/biological catalytic oxidation of HMF,
2. Dehydration of substances derived from hexose (C6 sugars) compounds,
3. Conversion of furan derivatives.

Simplified reaction schemes (intermediate steps omitted) of the first two routes can be seen on fig. *4*. The intermediate compound resulting from the oxidation of HMF is 5-formyl-2-furancarboxylic acid[9].

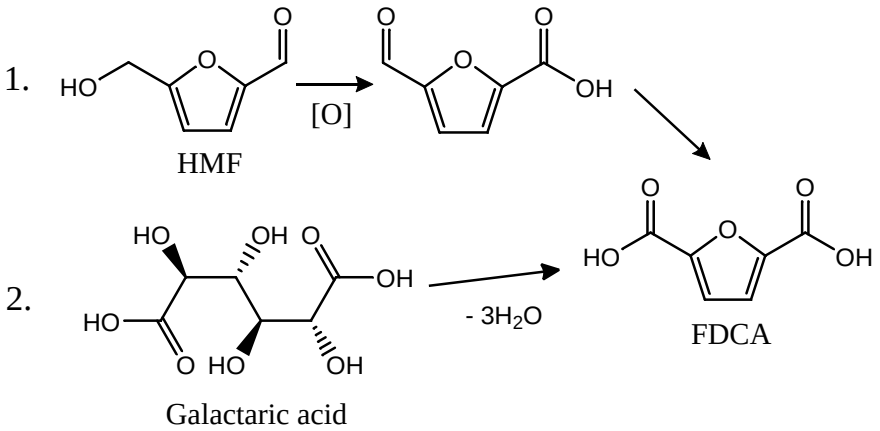


Figure 4: *Reaction schemes of the production routes 1 and 2. [O] symbolises oxidation and – $3H_2O$ indicates the dehydration process*[9,10].

Regarding the production route nº1, the chemical conversion occurs through a two-step process: dehydration followed by oxidation. In the context of this route, heterogeneous catalysis has proved to be more advantageous than the homogeneous one because of the drawbacks associated with the latter. In fact, lower purity (due to the presence of byproducts) and lower yield are obtained when using homogeneous catalysts[29]. Moreover, easier separation between the product and catalyst and better recyclability are achieved when using heterogeneous catalysts, of which the most prominent are "noble metal oxide" catalysts[7,30]. Furthermore, multiple synthesis pathways have been reported in literature within the production route nº2. One way consists of oxidizing C6 sugars (glucose and fructose) into aldaric acids, which can in turn be converted to FDCA via dehydration[9,10]. Alternatively, FDCA compounds were successfully produced in "bench scale experiments" through the esterification and subsequent dehydration of galactaric acid, which can be derived from pectin (found in agricultural waste such as citrus peel and sugar beet pulp)[10].

FDCA is recognized as an important building block in the bioeconomy chemical industry[28]. In addition to the production of polymers, FDCA has versatile applications, such as pharmaceuticals, composite materials and corrosion inhibition[9]. Its structure (fig. *1*) comprises of many advantages, since it has multiple functional groups and contains an aromatic ring (furan group). In fact, different monomers can be derived from FDCA, such as bis(2-hydroxyethyl) furan-2,5-dicarboxylate (BHEFDC) and dimethyl furan-2,5-dicarboxylate (DMFDC)[9,31]. Considering this, FDCA and its derivatives are very useful for the synthesis of bio-based polyamides and polyphthalamides. Another applications of FDCA in the polymer industry is for the production of polyethylene 2,5-furandicarboxylate (PEF), being the bio-based counterpart of polyethylene terephthalate (PET)[32,33].

2.2 Bio-based diamines

Aliphatic bio-based diamines can be produced via bio-processes, such as enzymes- or microorganisms-mediated reactions and fermentation. Since the microbial route common to diacids and diamines has been discussed, further information specific to diamines will be mentioned in this section.
Pyruvate can be made from glucose and xylose present in biomass, and in turn be modified to amino acids (L-arginine, L-lysine...). These amino acids are then converted to diamines, such as 1,3-diaminopropane, 1,4-diaminobutane and 1,6-diaminohexane (C3, C4 and C6 diamines respectively) through different biological pathways, using micro-organisms (*C. glutamicum*, *E. coli*...) and through metabolic engineering approaches[17,34]. Moreover, butanediamine can also be obtained by chemically converting succinic acid[16]. Another prominent example of bio-sourced diamines is decanediamine, also termed 1,10-diaminodecane, with the structure showed in fig. 5.[2] This compound can be synthesized from castor oil[16].

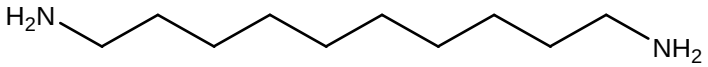


Figure 5: *Chemical structure of decanediamine.*

Adding to this, bio-based aromatic diamines have been synthesized as well from biomass, including lignin, terpenoids, cashew nutshells[34]. In fact lignin-based vanillin can be converted to different amine-containing (aromatic) compounds[35]. Similarly, divanillin is also beneficial for aromatic diamine synthesis. For instance, Llevot *et al.* worked on the production of 3,4-dimethoxydianiline and methylated divanillylamine structures from divanillin[36].

2.3 Types of bio-based polyamides and synthesis methods

Types of polyamides

Polyamides can be categorized or differentiated in several ways, including based on the types of monomers and polymerization technique involved. In fact, the synthesis routes can either be polycondensation (in its various forms) or ring-opening polymerization (ROP)[2]. These different production pathways are summarized in fig. *6*. Amino acids are compounds that consist of a chain of hydrocarbons with an amine functional group at one end and one carboxylic acid group at the other end. Different types of polycondensation techniques are used for the production of bio-based polyamides from either diacid-diamine monomers or amino acid precursors. This includes melt/direct/solution/interfacial polycondensations[37]. While solution

polycondensation occurs through the activation of carboxylic acid groups in mild conditions, the melt method generally avoids the use of solvents but requires higher temperatures. Moreover, the interfacial technique has the advantages of yielding high molecular weight polyamides and of being able to control product purity[37]. Cyclic amides can either be directly produced through biological routes (via fermentation) or derived from amino acid compounds[16,17]. Since lactams contain an amide group (NH-C=O), they can be converted to PAs through ring-opening polymerization. ROP is feasible under the condition of being thermodynamically favorable, within a specific temperature range. The main mechanisms of ROP are cationic, anionic, coordinative (coordination-insertion), and to a lower extent enzymatic mechanisms[38].

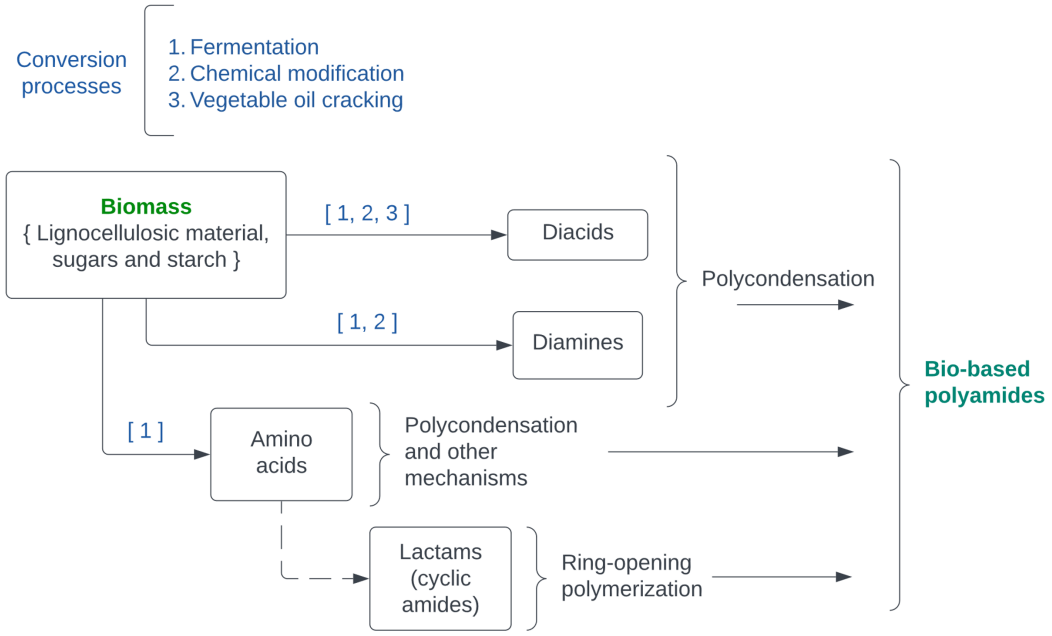


Figure 6: *Summary of synthesis routes of bio-based polyamides.*
The conversion processes from biomass to the monomer compounds are indicated with their respective numbers between brackets.

While semi-aromatic PAs are named polyphthalamides (PPAs), aramids are fully aromatic and have superior mechanical and thermal properties. The advantage of PPAs over aramids is that they can be reprocessed through thermal treatment[31]. Another point of distinction relates to the initial resources used for the production process. If all the raw materials used are bio-sourced, the polyamide can be considered as fully bio-based. Most importantly, this includes the monomers and potentially the catalyst(s) used. Amongst the different types of polyamides (PAs), some have been successfully synthesized from bio-based sources and reached the industrial scale. One

example is PA10,10 obtained by reacting bio-sourced decanediamine and sebacic acid (which can both be synthesized from castor oil) through polycondensation [11,26,39]. Another important one is PA11, produced by using 11-aminoundecanoic acid, derived as well from castor oil[12].

Synthesis methods

The synthesis methods mentioned in this section were described in literature for the production of different polyamides, with the commonality of using FDCA as the diacid monomer. Fig. *7* shows the polymerization reaction scheme of FDCA with 1,6-hexamethylenediamine (HMDA).

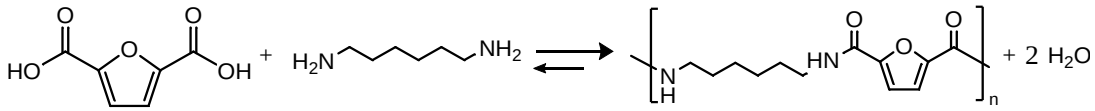


Figure 7: *Polymerization reaction scheme of FDCA and HMDA.*

One of the ways to synthesize polyamides from FDCA is 'polymerization through nylon salt formation', consisting of two steps[7,40]. In the first step, the diacid compound (in this case, FDCA) is dissolved in a solvent (such as ethanol or water) while heating (at 60°C) and mixing. Then, the diamine (in excess) is dissolved and is gradually added. This is typically done in a three-neck glass vessel. The formed nylon salts are then cooled down, filtered and washed. The second step is called "salt melt polycondensation" and is performed in a reactor that can withstand high temperatures (above 200°C), and in which the polymer can be easily removed[40]. Several parameters are important to consider when dealing with polycondensation reactions, such as temperature, reaction time, the degree of mixing, the catalyst(s) used and the type of solvent, when applicable. Common catalysts that were proved to be efficient for synthesizing furan-containing polyamides are sodium hypophosphite monohydrate[11,40], 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD)[41,42], titanium (IV) isopropoxide[31] and Ti(IV) citrate[31]. Except for TBD, these catalytic compounds are either an inorganic salt or a compound obtained by reacting a metal ore (in this case titanium) with inorganic and organic chemicals. Hence, generally speaking, in terms of sustainability, it is more relevant to consider how environmentally friendly these catalysts are, rather than the bio-based criterion.

Further, another common synthesis method is to perform the polycondensation reaction in two or multiple stages in one reactor. According to the method employed by H. Baniasadi *et al.* the amino acid, diamine, and diacid monomers were first mixed and heated to 200°C. Then, the reactor temperature was raised up to 240-260°C so that the monomers were melted

under an inert gas purge[43]. The reaction time depends on the polyamide to be produced. In another technique used by Cousin *et al.* the synthesis consisted of four stages, starting with the creation of "polyamide salt solution", using an aqueous solution of diamine and two diacids (in the context of producing co-polyphthalamides)[12]. The PA salt is also termed in literature "aqueous ammonium salt solution"[31]. While this phase was performed at 140°C and low pressures, the subsequent steps were at incremental temperatures and pressures, followed by depressurization. Finally, the reaction was allowed to proceed under vacuum at constant temperature.

One of the challenges of this method is the decarboxylation of furan compounds (in this case FDCA) at high temperatures, which causes the end capping of chain ends and leads to the shortening of the polymer chains[12]. The removal of the carboxyl groups (i.e. decarboxylation) happens through multiple steps. First, one carboxyl gets deprotonated, then carbon dioxide (CO_2) is formed after the cleavage of C-O and C-C bonds, detaching the group from the furan ring[14,44,45]. This leads to the formation of 2-furoic acid and furan[14], as shown in fig. *8*.

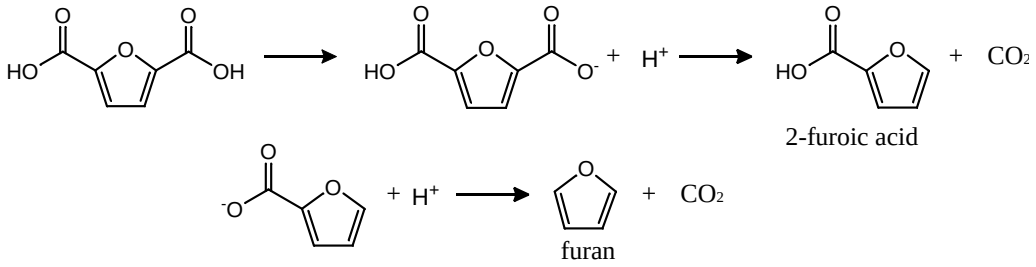


Figure 8: *Decarboxylation of FDCA.*

The synthesis of polyamide from the FDCA-derivative dimethyl furan-2,5-dicarboxylate (DMFDC) was also investigated in literature. Kamran *et al.* used a two-stage procedure, after converting FDCA to DMFDC through esterification using methanol, in an acidic medium. The first stage consisted of reacting DMFDC with HMDA in an inert environment at 65°C to yield oligomers. Then, the polycondensation step followed, performed at 230°C under vacuum and using two titanium (Ti)-based catalysts (for both stages), "ultra-pure Ti(IV) citrate" and Ti(IV) isopropoxide[31]. PA6F with a weight-average molecular weight M_w of 43 000 g/mol was obtained, when having the monomers in stoichiometric amounts[31]. Furthermore, other methods for the production of furan-containing polyamides mentioned in literature are interfacial polymerization[15] and enzymatic polymerization[46,47].

3 Research material and methods

3.1 Materials

The materials used in the syntheses are:
1,10-decanediamine [>98%, CAS: 646-25-3, Tokyo Chemical Industry -TCI-, Belgium]; dimethyl furan-2,5-dicarboxylate (DMFDC) [98%, CAS: 4282-32-0, AA Blocks Inc., California, USA]; ethyl alcohol [CAS: 64-17-5, Nalgene]; 2,5-furandicarboxylic acid (FDCA) [98%, CAS: 3238-40-2, AA Blocks Inc., California, USA]; 1,6-hexamethylenediamine (HMDA) [98%, CAS: 124-09-4, Aldrich, France]; methanol [≥99.9%, CAS: 67-56-1, Honeywell, Germany]; sodium hypophosphite monohydrate [≥ 99%, CAS: 10039-56-2, Sigma Aldrich Chemic, Switzerland]; titanium (IV) isopropoxide (TTIP) [97%, CAS: 546-68-9, Sigma Aldrich, India].

3.2 Synthesis of furan-based polyamides

The experimental work consisted of a series of experiments aiming at synthesizing different types of bio-based polyamides. Two different synthesis techniques were employed. Starting with diacid and diamine monomers, the first technique of PA6F synthesis process was generally composed of two phases:

1) Salt formation: The monomers were dissolved separately in an organic solvent (ethanol or methanol). The amount of diamine was determined as being 5 mol% in excess, inferring that the carboxylic acid of the diacid monomer is the limiting functional group. The monomers were mixed in a three-neck glass reactor, by adding HMDA to FDCA (or DMFDC) drop by drop, at a temperature of 60°C, with continuous stirring (no catalyst used in this step).
   Following 3 hours of mixing, the solution was vacuum filtrated, and washed three times with ethanol to eliminate unreacted monomers (especially excess HMDA). Fig. *19* in Appendix A shows a sample of nylon salt obtained from FDCA and HMDA.

2) Polycondensation: The formed nylon salts were then put to polymerize in the reactor vessel at higher temperatures (240-260°C), with nitrogen purging. The temperature was selected such that the nylon salt can melt, which facilitates the diffusion of the monomers. Having proper stirring is important to homogenize the distribution of the catalyst in the vessel and to enhance the reaction between the monomers. The polymerization reaction is described as a "salt melt polycondensation"[40].

In the second technique, the monomers were added along with the catalyst, and the reactor was directly or gradually set to the reaction temperature, without the formation of nylon salt. In both methods, the stirring rate was within the range of 250-350 rpm.

Several experiments were conducted, with varying amounts of FDCA and HDMA. The solvent used for salt formation and the reaction time of the polycondensation were varied as well. The values of these parameters are presented in table *1*. For experiments 1 to 10, 5 mol% excess diamine (i.e. in excess to the diacid monomer) was applied. Moreover, two different catalysts were used separately during the synthesis experiments. The first one is sodium hypophosphite monohydrate ($NaPO_2H_2 \cdot H_2O$), in the form of a powder, and the second one is titanium (IV) isopropoxide (TTIP), which is liquid at room temperature. The catalyst loading was increasing from 2 mol% (% of diacid monomer) to 4 mol% starting from experiment 5. For nomenclature, the name of the synthesized polyamide is based on the monomers and on the experiment number. As the monomers consist of C6 diamine and FDCA (F), the resulting polyamide is labelled PA6F. Considering the experiment number, PA6F-1 is the product of experiment 1, PA6F-2 of experiment 2 etc... Since dimethyl-furandicarboxylate (DMFDC) is a derivative of FDCA, polyamide obtained from any of these two diacid monomers was named PA6F for simplicity. Copolymers using C6 and C10 diamines (HMDA and 1,10-decanediamine) with varying C6:C10 diamines molar ratio were synthesized as well and named PA6:10F (table *2*). These will be discussed at the end of this sub-section.

Table 1: *Monomers weight (g) and parameters for the synthesis experiments of PA6F. Sodium hypophosphite ($NaPO_2H_2$) or titanium (IV) isopropoxide (TTIP) were used as catalysts.*

Experiment #	Polyamide	Diacid (g)	HMDA (g)	Solvent [step 1]	Reaction time (h) [step 2]	Catalyst
1	PA6F-1	21.5[a]	16.9	Ethanol	4	TTIP[1]
2	PA6F-2	10.0[a]	7.87	Methanol	6	TTIP[1]
3	PA6F-3	60.0[a]	47.1	Ethanol	6	TTIP[1]
4	PA6F-4	20.3[a]	15.9	-	24h	TTIP[1]
5	PA6F-5	18.3[a]	14.6	Ethanol	24h	$NaPO_2H_2$ [2]
6	PA6F-6	10.1[a]	8.02	-	> 24h	$NaPO_2H_2$ [2]
7	PA6F-7	12.5[b]	8.53	Methanol	> 24h	TTIP[2]
8	PA6F-8	12.1[b]	8.06	-	> 20h	TTIP[2]

The diacid used was [a] FDCA, [b] DMFDC.
The catalyst loading (mol% of diacid) was [1] 2 mol%, [2] 4 mol%.

All PA6:10F copolymers (table *2*) were obtained using the one-step synthesis method and were left to run overnight (reaction time > 20h). In the last copolymer synthesis experiment (11), three times more diamine (molar basis) was added compared FDCA, as a strategy to potentially get furan-based polyamides with higher molecular weight than in previous experiments.

Table 2: *Monomer quantities and C6:C10 diamines molar ratio of synthesized copolymers. The catalyst loading was 4 mol%.*

Experiment #	Polyamide	FDCA (g)	HMDA (g)	C6:C10 diamines ratio	Catalyst
9	PA6:10F-1	13.0	8.17	80:20	$NaPO_2H_2$
10	PA6:10F-2	12.1	7.11	75:25	$NaPO_2H_2$
11	PA6:10F-3	9.83	18.8	90:10	TTIP

3.3 Characterization methods

Size exclusion chromatography (SEC) is a commonly used technique for determining the number and weight average molecular weights (M_n and M_w respectively) of a polymer. This technique was applied to the synthesized furan-containing polyamides, using an Agilent Technologies – 1100 Series machine. For calibration, a solution of poly(methyl methacrylate) was used as a standard. The samples were prepared by dissolving 2 mg of powdered PA in 1 mL of hexafluoro-isopropanol (HFIP) solvent mixed with potassium trifluoroacetate (K-TFA) salt with a dosage of 3 g_{salt}/L (0.02 mol_{salt}/L).

The identification of the major functional groups present in the synthesized polyamides was performed through Fourier-transform infrared spectroscopy (FTIR) using Berker FTIR spectrometer. The number of scans and resolution were set to 50 scans and 4 cm^{-1} respectively, and the wavenumber range of the spectra was from 4000 to 400 cm^{-1}. In addition, further analysis of their chemical composition was done via proton nuclear magnetic resonance (^1H NMR) on a Bruker AVIII400 (400 MHz) spectrometer. The dissolution of the obtained polyamides was attempted with two solvents, at a concentration of 10 mg/mL. The process was facilitated with the help of a stirring machine set at 40°C using deuterated DMSO as solvent.

The thermal analysis of the polyamides using differential scanning calorimetry (DSC) is important to be able to determine the presence of first and second order phase transitions, in terms of heat flow as a function of temperature. DSC measurements were made on a TA Instruments Discovery DSC 250 machine. The method included two heating and cooling cycles under

nitrogen flow of 50 mL/min, and the weight of the samples ranged from 5 to 10 mg. The heating was to 300ºC and the cooling to 0ºC, both at a rate of 10ºC/min. Based on the thermic responses of a material under the cycles, DSC allows to measure the amount of heat released (exothermic process: crystallization) or absorbed (endothermic process: glass transition or melting)[48]. The y-axis of a DSC graph shows the heat flow (either in exothermic or endothermic direction), against temperature (x-axis). In this way, the thermomechanical performance of the polymers can be assessed. Moreover, it is possible as well to estimate if the polymer is crystalline, semi-crystalline or amorphous, based on the type of thermic responses.

Further, thermogravimetric analysis (TGA) allows to study the thermal stability of the samples, by measuring the sample weight and by extension the percentage of the initial sample weight (wt%), as the temperature increases. In this way, it is possible to determine the temperatures at which 5% and 10% of the polymer weight is lost. These are known as 5 wt% loss temperature (T_5) and 10 wt% loss temperature (T_{10}). TGA was performed on a TA Instruments TGA 5500 machine. The samples weighted 5 to 15 mg and were heated to 700ºC in a nitrogen atmosphere (25 mL/min).

4 Results and discussion

In this chapter, the results from the experimental work are presented and discussed. The synthesized bio-based polyamides (or polyphthalamides) were characterized using different methods. The characterization included chemical and thermal analyses.

4.1 Synthesis experiments

As previously mentioned in section 3.2, polyamides obtained using FDCA or DMFDC as the diacid monomer and HMDA as the diamine were named PA6F- (followed by the experiment number). The copolymers resulting from different ratios of C6 and C10 diamines were named PA6:10F-. To facilitate tracking the experiment number and its corresponding polyamide, a list of the polymers with name and description is provided in table *3*. For PA6Fs, their descriptions include the synthesis method and the diacid monomer used. For copolymers, only the C6:C10 diamines molar ratio is indicated since they were synthesized through the same technique (one-step synth.).

Table 3: *Summary of PA6F and copolymer samples and their description.*

Experiment #	Polyamide name	Description
1	PA6F-1	Nylon salt synth., FDCA – 1
2	PA6F-2	Nylon salt synth., FDCA – 2
3	PA6F-3	Nylon salt synth., FDCA - 3
4	PA6F-4	One-step synth., FDCA - 1
5	PA6F-5	Nylon salt synth., FDCA - 4
6	PA6F-6	One-step synth., FDCA - 2
7	PA6F-7	Nylon salt synth., DMFDC
8	PA6F-8	One-step synth., DMFDC
9	PA6:10F-1	Copolymer 80:20
10	PA6:10F-2	Copolymer 75:25
11	PA6:10F-3	Copolymer 90:10, with three times more diamine

In all the experiments except the third, the reactor was a three-neck flask glass reactor, put on a magnetic and heating plate (fig. *20* in Appendix A). As for the third one, it consisted of a cylindrical stainless-steel vessel equipped with a mechanical (overhead) stirrer and a heating jacket. Due to the size of the stainless-steel reactor, the experiment was performed at a larger scale, with around 100g of monomers. In order to assess the effect of higher temperatures, the reaction was run at 270°C. Although the third synthesis

experiment was done having better mixing, a specific issue arose that undermined the performance of the polymerization reaction and prevented from further using this reactor. A significant amount of HMDA evaporated from the reactor, which led to PA6F with very low molecular weight (M_w of 5600 g/mol, discussed in chapter 4.2). Without altering the way the experiment was performed, this issue was difficult to avoid for many reasons. In order to have proper mixing of the monomers or nylon salt, the polycondensation temperature needs to be close to the melting point of FDCA (>310°C), which is significantly higher than the one of HMDA (42-45°C). Adding to this, since the initial boiling point of HMDA is around 205°C, it evaporates at the reaction temperature. The presence of nitrogen flow exacerbated this, leading to higher monomer loss.
Hence, alternative synthesis experiments were conducted as an attempt to obtain high molecular weight PA6F. To minimize the amount of HMDA lost in subsequent experiments, the nitrogen flow was turned off after an initial phase of purging (~10min) to remove oxygen in the reactor flask. After 4-5 hours of heating with no nitrogen flow (at 250-260°C), nitrogen flow was then continued while the reaction proceeds overnight.

One of the challenges faced in the experimental work was the removal of the synthesized polymer out of the reactor, especially when using a glass round-bottom flask. In the case of a stainless-steel vessel, the most efficient method for this was found to be pouring liquid nitrogen on the polymer directly after ending the experiment to induce rapid crystallization. As soon the heat is turned off, PA6F starts to solidify and becomes very rigid and hard, due to slow crystallization, adhering to the surface of the vessel. To avoid this, the polymer solution needs to be quickly cooled down, resulting in small crystals that are easily removable from the reactor. However, a glass flask cannot withstand large differences in temperature when liquid nitrogen is used. Hence, an alternative technique was needed to extract the polymer from the reactor. One plausible way to achieve this was to dissolve PA6F, followed by precipitation and drying. It is a challenge to find a suitable solvent for the polyamide PA6F. While some researchers proposed a mixture of hexafluoro-isopropanol (HFIP) and chloroform ($CHCl_3$) as a solvent at room temperature[12,14] or $CHCl_3$ with trifluoroacetic anhydride[11], others performed solubility tests on multiple solvents and pointed out those in which furan-based polyamides (FPAs) are soluble[15,49,50]. A list of these adequate solvents is provided in table *4*.

Table 4: *List of solvents in which furan-based polyamides (FPAs) have good solubility.*

Solvents in which FPAs are soluble
Dimethyl sulfoxide (DMSO)
N,N-dimethylformamide (DMF)
N-methyl-2-pyrrolidone (NMP)
N-N-dimethylacetamide (DMAc)
Concentrated sulfuric acid (H_2SO_4)

After different trials of solvent volume and temperature, it was possible to dissolve one of the synthesized polyamides (PA6F-2) in DMSO while heating at 100°C. The advantage of using DMSO is the ease of isolating the polymer after dissolution, by precipitating it in water[15]. The necessary quantity of demineralized water was ten times the solvent volume.

Considering that DMFDC has a lower melting point than FDCA (110°C vs. 310°C), two experiments were done using this alternative diacid monomer, to be able to operate at a lower reaction temperature. The latter was set to 230°C based on literature[31]. Fig. *9* shows the polycondensation reaction scheme of DMFDC with HMDA, with methanol as a byproduct. One experiment was done using the nylon salt technique and another using the one-step synthesis. These consisted of experiments 7 and 8.

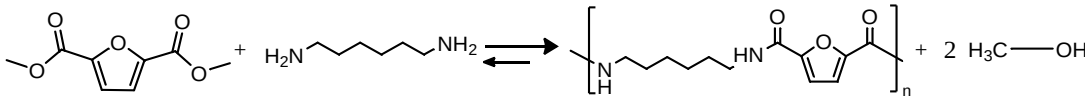


Figure 9: *Reaction scheme of DMFDC with HMDA, producing PA6F.*

4.2 Polymer structure and chemical analysis

Fourier transform infrared (FITR) spectroscopy

The FTIR spectrum of PA6F, synthesized through the nylon salt method using FDCA (fig. *10*), showed characteristic peaks corresponding to the functional groups present in furan-based polyamide. The major peaks are indicated on fig. *10*, *11* and *12* by dotted lines, with the corresponding colour of each spectrum. Most prominently, this includes: peaks at 3340-3210 cm^{-1} (broad peak), 1640 cm^{-1}, 1570 cm^{-1} and 1275 cm^{-1}, all associated with amide functional group; as well as 2930 cm^{-1} and 2854 cm^{-1} peaks representing -CH_2 asymmetric and symmetric stretches[15,43]. Moreover, peaks related to the furan ring[15] were found on the spectra of FDCA and PA6F (fig. *10*), mainly at 3150

cm^{-1} and 3123 cm^{-1} (=CH in furan), 1570 cm^{-1} (specific to C=C in furan) and 1025-760 cm^{-1}. Comparing the FTIR spectra (fig. *11*) of PA6Fs obtained using FDCA and DMFDC diacid monomers and through different synthesis methods (nylon salt and one-step syntheses), it can be seen that the major characteristic peaks previously mentioned are present in all these spectra. Typical peaks of amine (-RNH_2) group were identified on the FTIR spectrum of HMDA (fig. *10*), namely, 1605-1560 cm^{-1} and 900-650 cm^{-1}, in addition to (-CH_2) peaks at 2850 cm^{-1} and 2920 cm^{-1}.

Further, the spectrum of the PA6F obtained using DMFDC (fig. *11*) contains the peaks related to the CO_2 group of esters (1180-1130 cm^{-1}) and more specifically 1165 cm^{-1} peak of the functional group [R-CO_2-Me] (Me = methyl). This alludes to the presence of unreacted DMFDC monomer in the PA6F powder.
As for the copolymers (PA6:10F), FTIR results did not show significant differences between the spectrum of PA6F from nylon salt using FDCA, and the spectra of the copolymers PA6:10F-1 and PA6:10F-2 (fig. *12*) with C6:C10 ratios of 80:20 and 75:25 respectively.

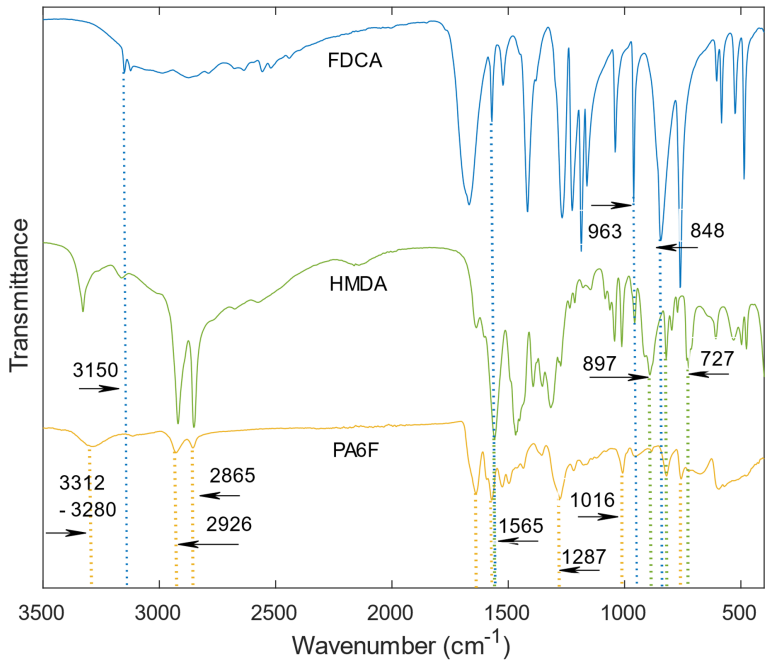


Figure 10: *FTIR spectra of the monomers (FDCA and HMDA) and furan-based polyamide (PA6F from nylon salt synth. using FDCA).*

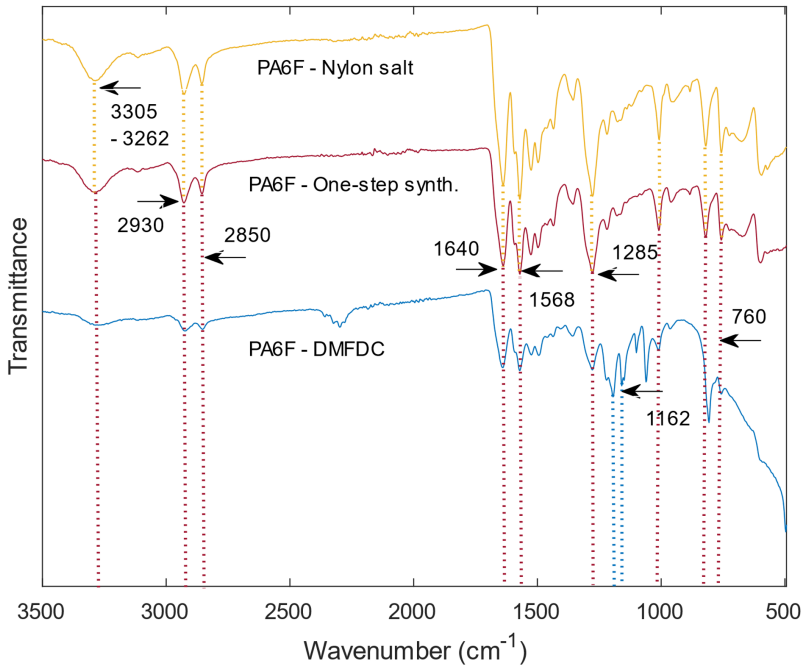


Figure 11: *FTIR spectra of PA6F from different synthesis methods: (1) nylon salt synthesis (FDCA); (2) one-step synthesis (FDCA) and (3) synthesis using DMFDC as the diacid monomer.*

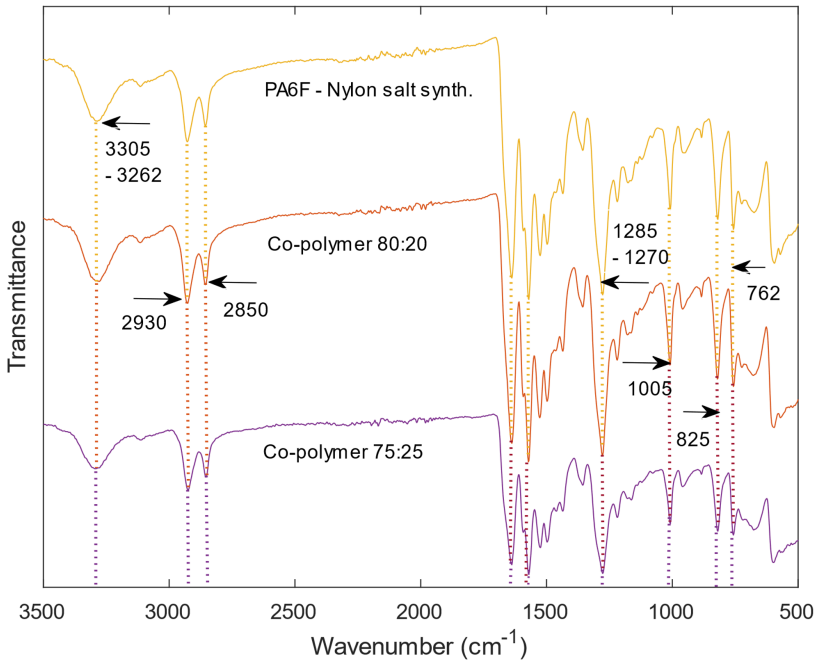


Figure 12: *FTIR spectra of PA6F (nylon salt synth.) and copolymers with C6:C10 ratios (80:20 ; 75:25).*

Nuclear magnetic resonance (NMR)

Results from proton nuclear magnetic resonance (^{1}H NMR) confirmed the structure of the furan-based polyamides. In fig. *14*, the ^{1}H NMR spectra of PA6F obtained from nylon salt synthesis using FDCA (PA6F-3) and PA6F resulting from one-step synthesis using DMFDC (PA6F-8) are shown. Fig. *15* includes the spectra of the copolymers PA6:10F1 and PA6:10F2. The correspondence between the peak signals and protons present in the synthesized polyamides is indicated by the letters (a to e), as depicted on fig. *13*. Moreover, the integral values of the labelled peaks are displayed on the NMR spectra. The signal at 2.5 ppm was identified as being the solvent (DMSO-d_6) peak[51]. The resonance peaks between 1 and 4 ppm (1.3, 1.5 and 3.3 ppm) are associated with the aliphatic part of the diamine compound (fig. *14* and *15*). These correspond to the signal peaks (a), (b) and (c). The major peak at 7.1 ppm (e) and the following one at 8.4-8.5 ppm (d) are characteristic of the furan ring and the amide group (proton of NH) respectively. Hence, the main peaks that are associated with furan-based polyamides are all present in the NMR spectra of distinct PA6Fs (-3 and -8) and of the copolymers PA6:10F-1 and PA6:10F-2 (fig. *14* and *15*). These findings are in accordance as well to experimental data found in literature[14,31].

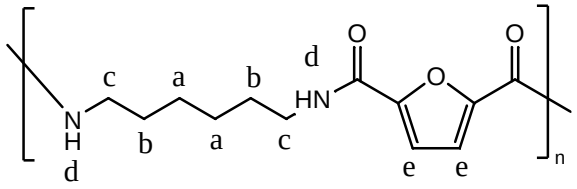


Figure 13: *PA6F with labels (a – e) relating the protons to the NMR peak signals.*

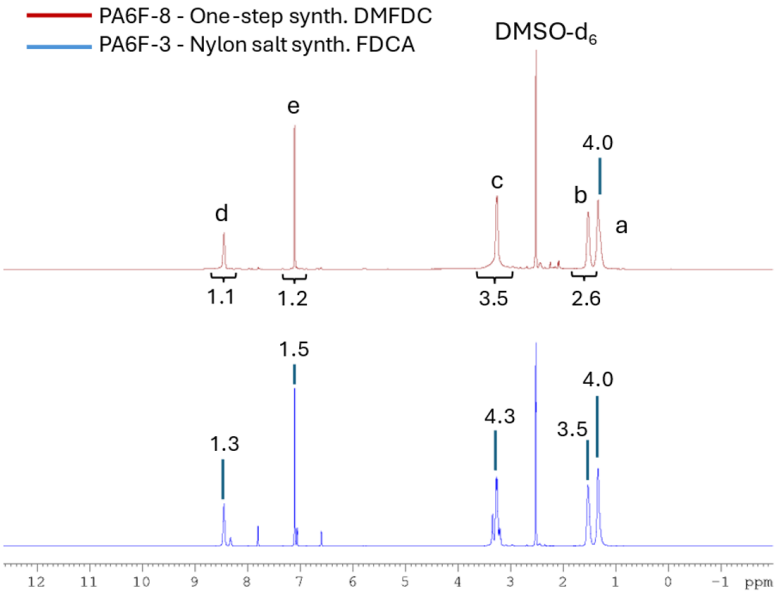


Figure 14: *^{1}H NMR spectra of PA6F-3 and PA6F-8.*

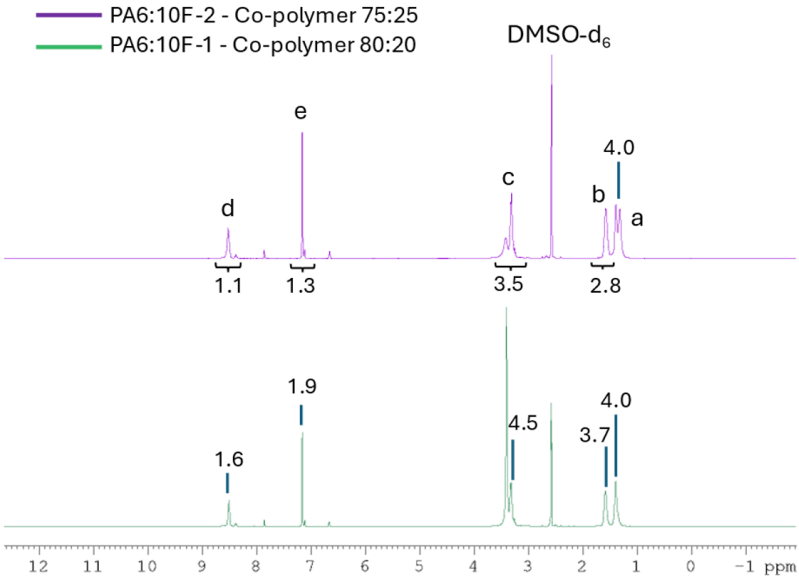


Figure 15: *^{1}H NMR spectra of PA6:10F-1 and PA6:10F-2.*

Comparing the integrals of labelled signal peaks (a - e), the NMR spectra generally showed comparable values to each other. The integral of the first signal peak (a) was calibrated to 4.0, considering that it is associated with four protons in the structure of PA6F (fig. 13). As an approximate estimation of the integrals, this can be considered viable for PA6Fs and PA6:10Fs as well. Nevertheless, since the copolymers contain a small molar percentage of C10 diamine, the peaks from 1 to 4 ppm would be expected to be slightly different than the ones of PA6Fs. It is worth noting that the third integral value displayed on PA6:10F-1 spectrum (fig. 15) relates to the peak at 3.3 ppm, corresponding to the protons labelled (c) on fig. 13. The larger neighbouring peak at 3.4 ppm is not representative of the protons in PA6F.

Size exclusion chromatography (SEC)

Generally, polyamides need to have a weight-average molecular weight (M_w) of at least 20 000 to 25 000 g/mol to exhibit good mechanical properties and to be efficiently used in its intended applications. The results from the size exclusion chromatography (SEC) measurements are presented in table 5. The PA6Fs and copolymers synthesis experiments did not yield high molecular weight polymers, in terms of both number-average (M_n) and weight-average (M_w) values. The obtained values were under the threshold of 20 000 g/mol. Moreover, the average dispersity Đ was found to be 2.1. Since the polyamide PA6F-3 was synthesized using a larger scale reactor (sample shown in fig. 21), enough quantities were available for using it in further polycondensation experiments. This was done as one of the investigated ways to attain higher molecular weights. The resulting products were labelled PA6F-3.1, PA6F-3.2... A slight increase in molecular weight occurred from these further reactions, but not significant enough to conclude on the efficiency of this technique. Based on the SEC results of the polyamides synthesized through the nylon salt technique (PA6F-1,-2,-3 and -5), the two-steps method did not appear to be advantageous over the simpler one (one-step synthesis) for having high molecular weight. In fact, the M_w values of PA6F-4 and the copolymer PA6:10F-2 are comparable to the one of PA6F-1 (table 5). In addition, varying the catalyst (TTIP vs. $NaPO_2H_2$) and increasing its loading from 2 mol% to 4 mol% did not improve the molecular weight of the resulting polyamides.

There are diverse limitations to obtain furan-based polyamides with high molecular weight. Most notably, the extent of reaction of the diacid and diamine monomers through polycondensation can be affected by multiple parameters. The effect of the reaction conditions and relevant variables in the synthesis of FPAs on their molecular weight are discussed in section 4.4.

Table 5: *Results from SEC analysis.*

Sample	M_n (g/mol)	M_w (g/mol)	Dispersity (Đ)
PA6F-1	4400	9900	2.2
PA6F-2	2800	7400	2.7
PA6F-3	1800	5600	3.0
PA6F-3.1	3000	5800	1.9
PA6F-3.2	3100	6000	1.9
PA6F-4	4700	9400	2.0
PA6F-5	3500	6900	2.0
PA6F-6	4600	8100	1.7
PA6F-8	5100	9000	1.7
PA6:10F-1	3300	6100	1.8
PA6:10F-2	4400	9900	2.2

4.3 Thermal analysis

Furan-based PAs have been reported in literature to be fully amorphous, showing no melting point transition during thermal analyses[15,31]. This can be understood on the basis of interchain hydrogen bonding strength and degree of interactions. Crystallization is enhanced when these interactions are stronger[31]. In fact, aliphatic PAs possessing stronger hydrogen bonds than furan-based polyamides (FPAs) are more crystalline[15]. Moreover, the furan ring in FPAs make them more rigid, implying that the polymer chains have lower degrees of freedom. Consequently, the glass transition temperature (T_g) of FPAs is expected to be higher than the one of aliphatic PAs.

Differential scanning calorimetry (DSC) measurements allowed to identify the temperatures at which the samples experienced phase transitions. The degree of crystallinity depends, amongst other factors, on the chemical structure and chain configuration of the synthesized polyamides. Hence, crystallization and melting (first order phase transitions) do not always appear on DSC thermograms. The glass transition temperature (T_g) was determined considering the midpoint of the downward endothermic step on the heating curve. This region was indicated on each thermograph by a square (fig. *16* and *17*). In addition, the curves were demarcated as ‘cooling’ and ‘heating’ on the DSC thermographs. All measured samples showed a clear endothermic shift on the heating curve except for the sample PA6F-2 (fig. *16* and *17*). As both the average and median value, the T_g of the synthesized PA6Fs was found to be 102°C (table *6*). Moreover, the glass transition of copolymers 80:20 and 75:25 occurred at a lower temperature (86°C and 87°C respectively). The findings

for PA6F polyamides are within the range of values mentioned in literature (90-121°C)[12,15,31].

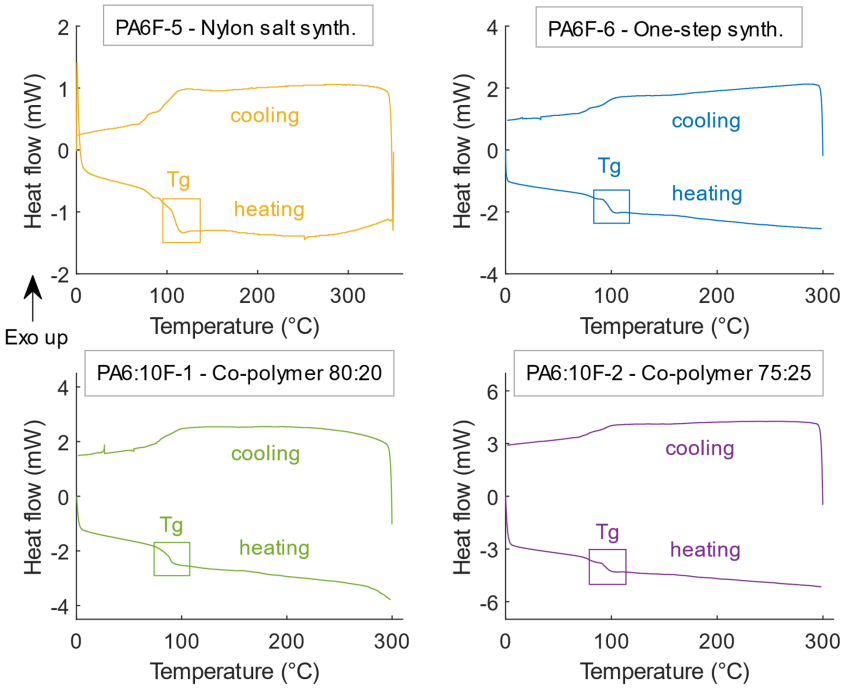


Figure 16: *DSC thermographs of two PA6Fs (PA6F-5 and PA6F-6) and two copolymers.*

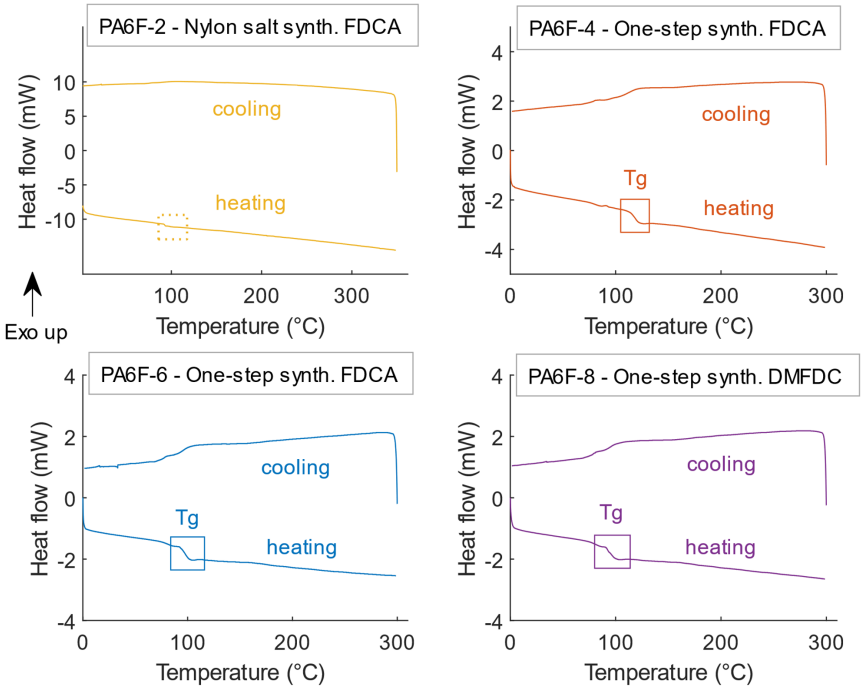


Figure 17: *DSC thermographs of PA6Fs from different synthesis methods.*

Table 6: *Estimated glass transition temperature (T_g) of synthesized polyamides, from DSC measurements.*

Sample	T_g
PA6F-2	93
PA6F-4	122
PA6F-5	102
PA6F-6	97
PA6F-8	98
PA6:10F-1	86
PA6:10F-2	87

Fig. *18* shows the TGA graph of three PA6F samples. One sample was obtained through the nylon salt technique using FDCA (PA6F-5), one via one-step synthesis using DMFDC (PA6F-8) and one copolymer with 80:20 (C6:C10) ratio (PA6:10F-1). The maximum degradation temperature (T_{max}) was identified as the temperature at which the rate of weight loss decreases significantly, after a large increase in weight loss. This can be found graphically on a TGA cure as the lowest point of the steep vertical slope of the curve (fig. *18*). The values of the 5 wt% loss and 10 wt% loss temperatures (T_5 and T_{10}) and the maximum degradation temperature (T_{max}) are presented in table *7*.

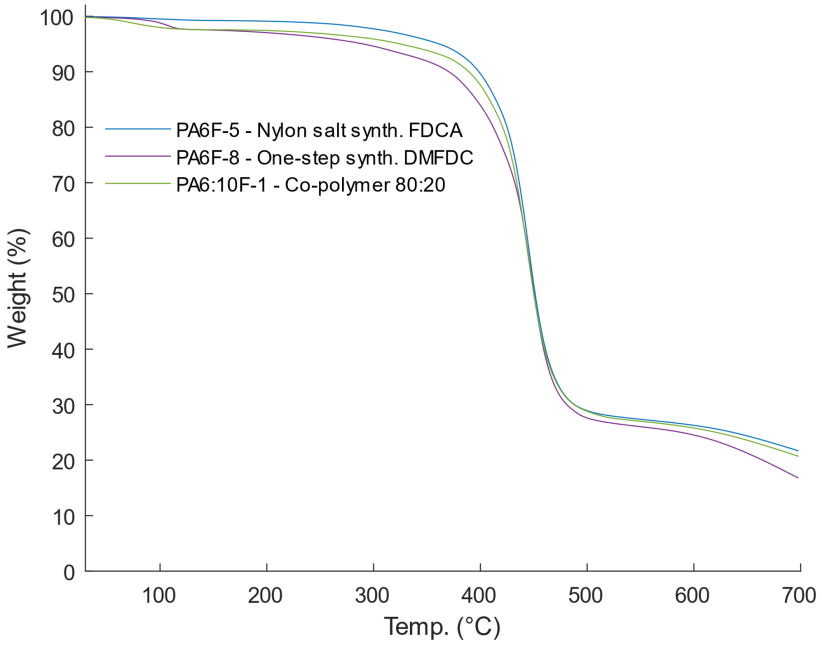


Figure 18: *TGA curves of PA6F-5, PA6F-8 and PA6:10F-1, showing the percentage of initial sample weight (%) vs. temperature (°C).*

Table 7: *T_5, T_{10} and T_{max} values of FDCA and various synthesized polyamides.*

Sample	T_5 (°C)	T_{10} (°C)	T_{max} (°C)
FDCA	264	275	327
PA6F-2	231	390	477
PA6F-3	363	400	477
PA6F-5	362	399	487
PA6F-6	331	390	485
PA6F-8	290	370	482
PA6:10F-1	325	389	485
PA6:10F-2	370	401	482

Results from TGA analysis proved that the polyamides synthesized through various methods, including the copolymers (PA6:10F), have good thermal stability, with an average T_5 and T_{10} of 340°C and 392°C respectively. The maximum degradation temperature (T_{max}) was found to be 482°C on average. The obtained values of the degradation temperatures are comparable to the ones mentioned in literature[12,31,45]. Thermal stability at high temperatures constitutes one of the advantageous properties of furan-based polyamides.

4.4 Towards higher molecular weights

The major goal of this thesis work is to identify and study the reaction conditions that result in the efficient synthesis of furan-based polyamides (FPAs). The most relevant parameters are discussed in this section.

The reaction temperature is an important factor that affects the extent of reaction of the diacid and diamine monomers. The synthesis of FPAs is an endothermic process, meaning that it requires heating for it to proceed or to be efficient. The reaction temperature depends on the type of reaction. For instance, solution/activated and interfacial polymerizations can be operated at lower temperatures than solid-state and melt polycondensation reactions[37]. From the perspective of the green chemistry principles, the latter type of polycondensation is advantageous since it avoids the use of reaction media such as solvents. In the case of this thesis work, all synthesis reactions were melt polycondensations, except for two experiments done on PA6F-3 as an attempt to increase its molecular weight through a solid-state reaction. Based on the multiple experiments performed with an excess diamine of 5 mol%, it was found that the optimal range of the reaction temperature lies between the minimal temperature at which the monomers melt (240-250°C) and the temperature at which FDCA degrades[31]. The degradation of FDCA monomer

through decarboxylation mechanism becomes more probable when the reaction temperature approaches 264°C, based on TGA results (table *7*). For this reason, starting from experiment 5 (nylon salt synth. using FDCA - 4), the initial reaction temperature was set within the range of 248-254°C to ensure the melting of the monomers. Then, it was lowered by 5 to 10°C after a few hours, and further decreased on the second day of the reaction.
One important aspect of FPAs synthesis that is directly affected by temperature is the evaporation of excess diamine and water formed throughout the reaction. In fact, the presence of excess diamine and water shifts the polycondensation reaction to the left (fig. *2*). This reverses the polymerization process, causing a reduction in the molecular weight of the polyamides[52]. Consequently, it is important to optimize the reaction conditions to ensure the adequate removal of water vapor and excess diamine. This was taken into consideration during the synthesis experiments, but the reactor setup made it difficult to optimize the evaporation process.

As another attempt to circumvent the limitations of FDCA, two experiments were performed using DMFDC as the diacid monomer, with which the polycondensation reaction can be run at 230°C (section 4.1). Since the resulting molecular weight (PA6F-8, table *5*) was not higher than those obtained from FDCA, it can be concluded that the reaction temperature was not the limiting factor that primarily caused low molecular weights. Nevertheless, the degradation of FDCA probably played a role and temperature is a non-negligible contributing factor for the efficient synthesis of furan-based polyamides.

One factor that significantly affects the molecular weight of the polyamides is the reaction pressure. In fact, running the polycondensation reaction under vacuum can enhance the polymerization process, resulting in polyamides with high molecular weight[31]. Unfortunately, it was not possible to apply vacuum with the reactor setup that was available during the thesis work.

The stoichiometric ratio of diamine-to-diacid is an important variable to be considered as well. In fact, Kamran et al. reported a significant increase in the melt viscosity and the molecular weight (M_w) of their synthesized PA6F when using 4.5 mol% excess of diamine (HMDA), compared to no excess diamine and 2 mol% HMDA[31]. Within the framework of this work, 5 mol% excess diamine was applied in all experiments except the last one (copolymer 90:10 with 3 times more diamine). This variable was kept constant to be able to study the effect of other factors, such as reaction time, temperature (as discussed above) and the type and amount of catalyst. By comparing the SEC results of the obtained polyamides throughout experiments 1 to 11, it was found that all of lowering the reaction temperature to below 255°C, increasing the catalyst loading from 2 mol% to 4 mol% (% of diacid) and prolonging the

reaction time to more than 24h did not result in a significant improvement in the molecular weight of the polyamides. Hence, it was decided to use 3 times more diamine, added gradually during the reaction, followed by the removal of formed water and excess diamine. In this way, the limitation due to the unfavourable loss of diamine through evaporation (along with nitrogen flow) is minimized since enough diamine would still be available to react with the diacid.

5 Summary

This chapter presents the main conclusions of the thesis project as well as recommendations for future work.

5.1 Conclusions

This thesis work focused on assessing the reaction conditions and experimental parameters that can yield to the efficient synthesis of furan-based polyamides with adequate polymer properties. Various routes exist for the production of bio-based polyamides. Within the framework of this research, partially bio-based polyamides were synthesized through a polycondensation reaction between a diacid monomer and a diamine monomer (C6 diamine -HMDA-). The diacid was bio-based furan dicarboxylic acid (FDCA), except for two experiments in which dimethyl-furandicarboxylate, a derivative of FDCA, was used. Copolymers were made as well using a mix of C6 and C10 diamines. The type of polymerization that was implemented in the experimental work was melt polycondensation, at an initial reaction temperature ranging from 230 to 260°C. Two different techniques were applied, nylon salt synthesis and one-step synthesis. The main factors that were examined during the various experiments were:

- Reaction time
- Reactor temperature
- Type of catalyst and loading (mol% of diacid monomer)
- Diamine-to-diacid stoichiometric (molar) ratio

Different synthesis methods were tried to study the effect of each of these parameters on the molecular weight of the furan-based polyamides. Multiple challenges were faced during the experiments. A prominent one was the loss of diamine as it evaporates at the reaction temperature, aided by nitrogen flow, which is necessary to remove water vapor. Another one was the degradation of FDCA when the reactor temperature approached 260°C. These limitations were tackled to some degree by making adjustments to the synthesis experiments, such as keeping the reaction temperature below 255°C and turning on the nitrogen flow only after four to five hours of reaction time, preceded by an initial short phase of nitrogen purging. In addition, the diamine-to-diacid molar ratio was an important parameter to consider as well. It was set to 5 mol% excess diamine, except for the last experiment in which three times more diamine was used.

The structure and chemical composition (in terms of functional groups) of the synthesized polyamides were analysed using Fourier-transform infrared spectroscopy and proton nuclear magnetic resonance. Results confirmed the

expected structure of the polyamides, and the presence of characteristic functional groups, including the furan ring, amine and amide groups. In this regards, no significant differences were found when comparing PA6Fs from different synthesis methods and C6:C10 copolymers. Size exclusion chromatography revealed that the molecular weights of the PA6Fs and the co-copolymers did not exceed 10 kg/mol. This constitutes the main point of improvement to be addressed in future work (section 5.2).

Concerning the thermal properties of the furan-based polyamides, DSC analysis did not show crystallinity, and the glass transition temperature ranged from 93ºC to 122ºC. Based on the results from TGA analysis, both the PA6Fs and copolymers were found to have high thermal stability, with an average initial degradation temperature (5% weight loss, T_5) of 340ºC. This makes it viable to be used in many applications that demand adequate heat resistivity.

5.2 Recommendations and future work

One important research target for future work is obtaining furan-based polyamides with higher molecular weights, above 20 kg/mol. In order to achieve this, synthesis techniques different than the ones done in this work can be applied. Most importantly, running the polycondensation reactions under vacuum (~15 mbar) would be a crucial adjustment to increase the molecular weight of the FPAs. Adding to this, having proper stirring leads to better diffusion of the monomers, which improves the polycondensation kinetics (higher reaction rates)[52]. To implement this, performing the experiments in a stainless steel reactor equipped with a mechanical stirrer, a heating jacket and a vacuum system would provide a great advantage. Moreover, the effect of the diamine-to-diacid stoichiometric ratio can be further investigated in a more systematic way, by performing a series of experiments with varying mol% excess of diamine (i.e. in addition to 5 mol% and 300 mol% -three times excess-). Furthermore, another research objective that can tackled in future work is the synthesis of fully bio-based polyamides by using a bio-based diamine monomer. Based on market availability and the price of the product, bio-based C5 diamine would be a viable option.

If high molecular weights are attained, the mechanical properties of the synthesized polyamides can be assessed through dynamic mechanical analysis and tensile testing. More specifically, it would be interesting to assess the effects of C5 and C10 diamines on the mechanical properties of the synthesized copolymers. A series of experiments with varying C6:C5 and C6:C10 ratios can be performed to find the optimal range of diamines ratios for a desired flexibility or toughness. Adding to this, differential scanning

calorimetry (DSC) can help identify whether the bio-based polyamides exhibit crystallinity. A crystallisation or melting peak could potentially appear on the DSC thermograph for furan-based polyamides with longer chains. Accordingly, in case of (semi-)crystallinity, the FPAs can be further examined through X-ray diffraction analysis, in order to study the structure of the crystals in them and gain better insight on the physical structure of these polymers[11].

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A. Experimental work – Additional information

Synthesis of PA6F

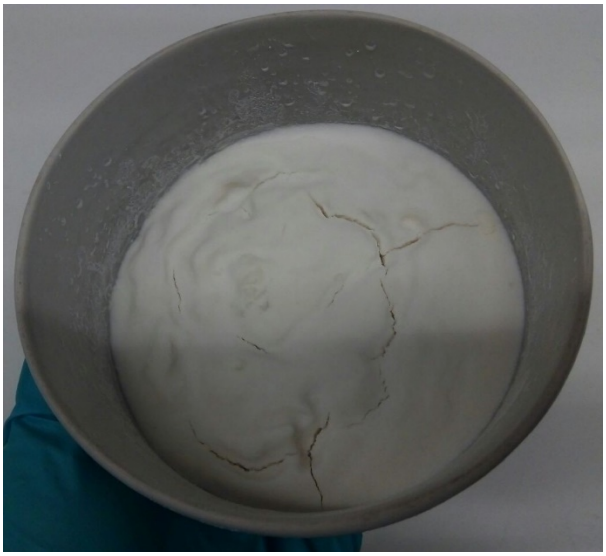

***Figure 19**: Nylon salt formed from FDCA and HMDA.*

***Figure 20:** Three-neck glass reactor setup.*

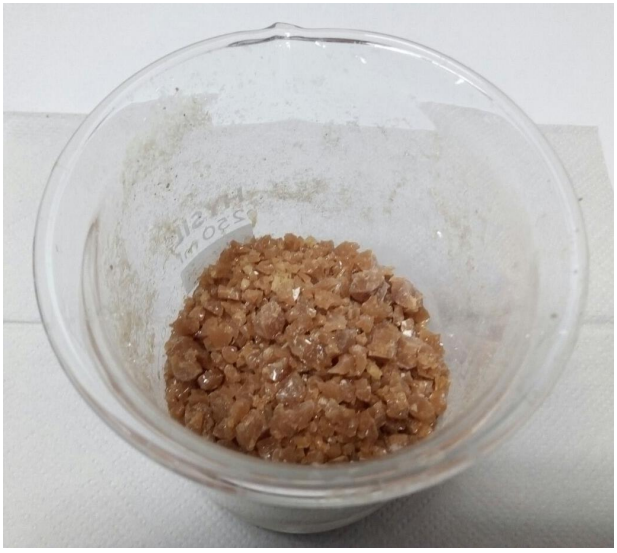

Figure 21: *PA6F-3 crushed powder.*