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Synthesis and characterization of furan based polyamides and polyureas

by

Osama Rashwan

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at

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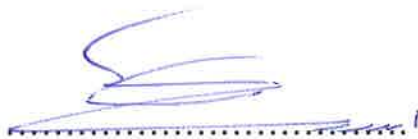
Supervisor: Prof. V. Hugo (CPUT)

Co- Supervisor: Dr. W. G. Weber (US)

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Declaration

I, the undersigned, hereby declare that the work contained in this thesis is my own work and has not previously in its entirety or in part been submitted at any university for a degree.



Osama Rashwan

13/ 12. 2010

Abstract

Aromatic polyamides (PAs) are widely used as high-performance polymers in technical applications due to their unique combination of outstanding thermal, optical, mechanical and chemical properties. Although PAs are mostly utilized where strength or heat resistance is of primary concern, they also find use in other important applications such as in NOMEX membranes for desalination of brackish water or seawater.

PAs do however have some disadvantages such as high melting points, high glass transition temperatures (T_g) and a limited solubility in most organic solvents, which makes their processing difficult. Polyureas (PUs) are generally known for their excellent thermal stability and high chemical resistance due to the presence of thermally stable bonds of aromatic or heterocyclic ring systems along their backbone.

Both polymer systems are poorly researched when it comes to the introduction of furan units into the chains. The same is valid for cases where two or more different diacids or diamines are incorporated. The aim of this study was therefore to investigate the influence of furan units in the polymer chains and the change in properties if the composition of starting materials is varied further.

Nineteen PAs were prepared via the interfacial polymerization method and the homogeneous phase polymerization method. These polymers were prepared either with furan- or isophthalic acids in their chains and then compared with the copolymers, containing both diacids in different ratios. Products were characterized by various analytical techniques.

Furanoyl-2,5-dichloride (FDC) and different amounts of isophthaloyl chloride (IPDC) - 0, 10, 30 and 50% - as the basic starting monomers were reacted individually with four diamines: m-phenylen diamine (MPD), 4,4'-diamino diphenylsulfone (DDS), 4,4'-diamino diphenylether (DDE) and 2,4-bis(4-aminophenyl)-6-phenyl-1,3,5-triazine-2,4,6-triamine (BAT) by interfacial or homogeneous polycondensation reactions.

Two polyureas, starting with furanoyl-2,5-diazide (FDZ) and transformed into the diisocyanate were prepared by reaction with two diamines, namely MPD and DDS in homogeneous solution.

The PAs and PUs were characterized by Fourier-Transform Infrared Spectroscopy (FTIR), Proton NMR (^1H), Carbon NMR (^{13}C), Gel Permeation Chromatography (GPC), Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC).

The water up-take per polymer unit (mol water / repeat unit of the polymer) was measured. The values for 70% Relative Humidity (RH) were between 0.87 and 1.80 moles of water per repeat unit and for 43% RH between 0.40 and 1.35 mols.

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List of abbreviations and symbols

A	Angstroem
BAPPTT	2,4-bis(4-amino phenyl)-6-phenyl-1,3,5-triazine-2,4,6-triamine
°C	Degree Celsius
DDE	4,4'-diamino diphenyl ether
DDS	4,4'-diamino diphenyl sulfone
DMAc	dimethyl acetamide
DMF	dimethylformamide
DMSO	dimethyl sulfoxide
DSC	Differential Scanning Calorimetry
FDC	furanoyl-2,5-dichloride
FDI	furan-2,5-diisocyanate
FDZ	furan-2,5-dicarbonyl diazide
FTIR	Fourier-Transform Infrared Spectroscopy
GPC	Gel Permeation Chromatography
HCl	hydrochloric acid
IPDC	isophthaloyl dichloride
mp	Melting point
MMD	(methacryloxymethyl)methyldiethoxysilane
MPD	m-phenylene diamine
M_n	Number Average Molecular Weight
M_w	Weight Average Molecular Weight
NMP	N-methyl-2-pyrrolidone
NMR	Nuclear Magnetic Resonance Spectroscopy
PA	Polyamide
PDI	Polydispersity Index (M_w / M_n)
PU	Polyurea
PM 1	N,N'-bis[(3-acetylamino)phenyl]isophthalamide
PM 2	N,N'-bis[(3-acetylamino)phenyl]furan-2,5-dicarboxamide
PMMA	polymethyl methacrylate
Py	pyridine
RH	Relative Humidity
RT	Room Temperature

TEBAC

triethyl benzyl ammonium chloride

T_g

Glass Transition Temperature

TGA

Thermogravimetric Analysis

CHAPTER 1: INTRODUCTION AND OBJECTIVES

1.1 Introduction

Aromatic polyamides (PAs) are widely used as high-performance polymers in technical applications due to of their unique combination of outstanding thermal, optical, mechanical and chemical properties¹. They have attracted great scientific interest, which is documented in numerous books and papers²⁻⁵. Although PAs are mostly used where strength or heat resistance is a primary necessity, they also have been used in other applications, such as membranes for desalination of sea water (e.g. the NOMEX membranes)⁶.

However, these polymers have some disadvantages such as high melting temperature, and high glass transition temperatures (T_g)⁷ and limited solubility in most organic solvents. The latter decreases their processability and restricts other applications. In this study an effort was made to overcome some shortcomings such as limited solubility. The overall aim of this study was to prepare selected aromatic PAs that incorporate furan units, study the influence of the furan unit in the polymer chains and comparing them to the more commonly used aromatic or aliphatic diacids in PAs.

The latter are better soluble in organic solvents, but still have high molecular weights and thermal stability. Bearing furan rings constitute a very interesting family of materials because of their properties associated with the features of the heterocyclic furan ring in terms of both chemical and physical behavior¹. The synthesis and characterization of PAs bearing furan moieties have not received much attention to date. Corresponding macromolecular structures with furan units, such as in polyesters and polyurethanes, have been more widely investigated⁸⁻¹².

Polyureas (PUs) are generally known for their excellent thermal stability and high chemical resistance due to the presence of aromatic or heterocyclic rings connected by thermally stable bonds along their backbone^{13,14}. However, very few polyureas with furan units have been prepared¹⁵. Therefore, both polyamides and polyureas with furan moieties within the structures should be studied in more detail.

1.2 Methodology

The aim of this project was to study the influence of furan units in the polymer chain, comparing them to the more commonly used aromatic or aliphatic diacids. Different amounts of the isophthaloyl unit were incorporated into the polymer chain and subsequent changes in the chemical and physical properties of the resulting polymers were investigated and conclusions drawn.

Polymers that contain only furan or only isophthalic acids in their chains were also prepared and then compared with the copolymers units, containing both in different ratios.

Furanoyl-2,5-dichloride (FDC) and different amounts of isophthaloyl dichloride (IPDC) - 0, 10, 30 and 50% - as the basic starting monomers on the "carbonyl-side" were reacted with four different diamines in the aqueous phase using conventional polymerization techniques. Various synthetic methods were also studied.

Because most synthesis techniques are developed for specific monomers, existing methods had to be modified and then used for the synthesis of the above mentioned polymers. Although it is very difficult to establish the most crucial factors that will influence the polymerization process, important factors include: monomer reactivities, monomer stabilities, monomer-solvent interactions, purity of solvents and reagents, stoichiometry of the reaction and the selection of reaction temperatures and reaction times.

1.3 Objectives

The main objective of this study was the preparation of selected aromatic PAs and PUs that incorporated furan units. PAs were to be prepared via both the interfacial polymerization method and the homogeneous phase polymerization method. The PUs were prepared only by the homogenous phase polymerization method. Products were then characterized by various analytical techniques.

1. Synthesize nineteen linear PAs, using the following reagents in various combinations:

The two dichlorides: furanoyl-2,5-dichloride (FDC) and isophthaloyl dichloride (IPDC), in concentrations of 0, 10, 30, 50 or 100% each and the four diamines: m-phenylenediamine (MPD), 4,4'-diaminodiphenylsulfone (DDS), 4,4'-diaminodiphenyl ether (DDE) or the new diamine, 2,4-bis(4-aminophenyl)-6-phenyl-1,3,5-triazine-2,4,6-triazine (BAT), by interfacial or homogeneous polycondensation reactions.

2. Prepare and characterize two model compounds PM 1 and PM 2, prepared from FDC or IPDC respectively and reacted with the diamine 3-acetylamino-aniline
3. Synthesize two PUs, starting with furanoyl-2,5-diazide, which is transformed into the diisocyanate and reacted with two different diamines in homogeneous solution:
4. Compare the NMR data of the model compounds with the related polymers.
5. Characterization of the PAs and PUs by ^1H NMR, ^{13}C NMR, FTIR, TGA, DSC and GPC and interpretation of the data.
6. Compare the polymers in terms of the following properties:
 - a solubility
 - b thermal stability, chemical and physical properties
 - c water uptake at different relative humidities

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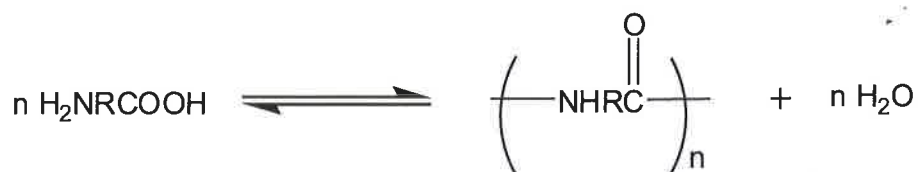
CHAPTER 2: POLYAMIDES

2.1. Introduction

Polyamides (PAs) are polymers that contain recurring amide groups -CO-NH- as integral parts of the main polymer chains. The first linear polyamides such as Nylon-6.6 were synthesized in 1929 by W. H. Carothers of E. I. du Pont de Nemours & Company by the condensation of diamines and dibasic acids. There are a number of methods for the preparation of polyamides. The most widely used is the polycondensation reaction.

Synthetic methods are available for the preparation of medium to high molecular weight polymers at higher temperature, such as melt polymerization and reactions between diacids and diamines or diesters and diamines. The main low temperature methods are interfacial polycondensation and solution polycondensation, which make use of diacid dichlorides and diamines.

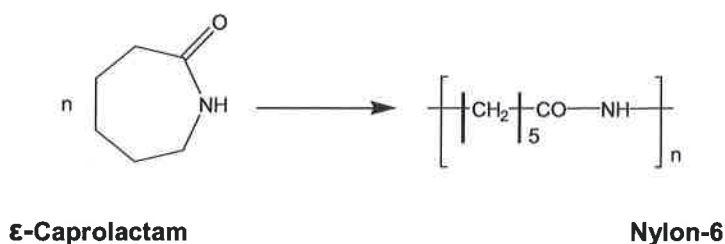
Linear polyamides are produced by utilizing direct amidation where amines react with carboxylic acid functionalities to form the amide group and water, as shown in Scheme 2.1.



Scheme 2.1: Formation of polyamide by direct amidation.

2.2. History and development of polyamides

The commercial success of Nylons led to intensive research aimed at the development of Nylons which were not covered by the original du Pont patents. In 1940 Nylon-6 was developed by I.G. Farbenindustrie via polymerization of ϵ -caprolactam¹, as shown in Scheme 2.2.



Scheme 2.2: Formation of Nylon-6.

After the Second World War the manufacturing for Nylon-6 was undertaken in many countries due to the fact that it was not covered by patent restrictions. Initially the majority of Nylons were used for fiber production, but they have since also become known for their importance in non-fibrous applications in the field of engineering resins, as well as for the production of adhesives and coatings². By the late 1940s there was an increased interest in the so-called super polyamides with high temperature resistance and improved mechanical strength. The first of these polymers introduced the combination of aliphatic and aromatic monomers to produce semi-aromatic polymers (a, b, c), as shown in Figure 2.1.

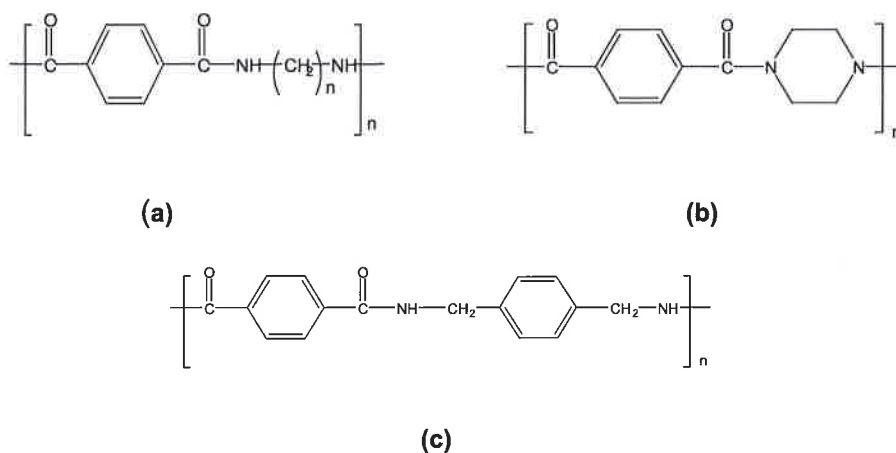
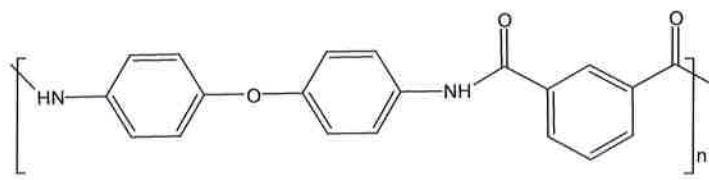
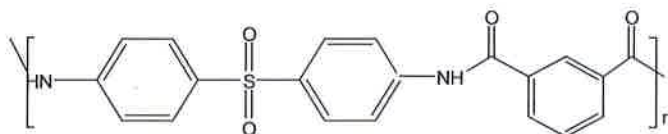


Figure 2.1: Formation of semi-aromatic polyamides.

The first fully aromatic polyamides, however, were produced in the 1940s from meta- or a mixture of meta-and para-orientated phenylene ring units with solubilizing connecting groups such as sulfonyl or oxygen³ (d,e) as shown in Figure 2.2 .



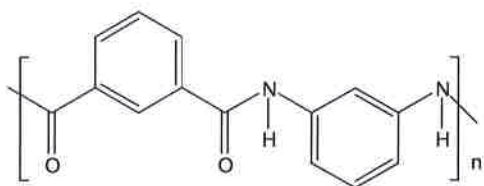
(d)



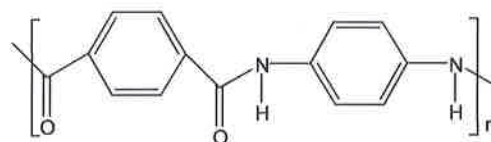
(e)

Figure 2.2: Formation of aromatic polyamides.

This work resulted in the production of Nomex (f) and in 1961 E.I. du Pont de Nemours & Company introduced the first experimental fibers and paper produced from Nomex (f). Production of this polymer continued to grow and reached commercial scale in 1966⁴. Because of the excellent thermal and flame-resistant properties of Nomex (f) the Du Pont Company introduced the para-coupled product Kevlar (g) in 1970, and both of these polymers became of great commercial importance in the later years. Kevlar (g) was not only as flame resistant and thermally stable as Nomex (f), but also displayed exceptional strength and high modulus values, as shown in Figure 2.3.



(f)



(g)

Figure 2.3: Nomex (f) and Kevlar (g)

In 1974 the generic term aramids was adopted by the United States Federal Commission, where aramids were defined as polyamides with at least 85% of the amide linkages attached to two aromatic rings⁵. Typical applications for aramids are listed according to the distinctive properties of these fibers.

2.3 Polyamide applications

Polyamides are widely used in many industries^{6,7} due to their diversity of physical properties, such as a wide range of flexibility combined with toughness, high abrasion resistance, high chemical resistance, excellent weatherability and very low temperature cure, which makes them one of the most widely used polymers in different applications. Polyamides have many applications such as coatings (see Section 2.3.3), adhesives, fiber plastics and their permselective properties are applied in hollow-fiber permeation separation membranes to purify seawater and brackish water (see Section 2.3.1).

2.3.1 Polyamide membranes

Membranes are generally defined as an interface or selective barrier between two phases. Membranes can be classified into different categories. According to used materials, membranes can be divided into natural and synthetic ones^{8, 9}. Four different membrane processes are possible: Reverse Osmosis (RO), Nano Filtration (NF), Ultra Filtration (UF) and Micro Filtration (MF).

The main difference lies in the pore size of the coating layer which influences the type of molecules or ions, which can pass through. Reverse osmosis is the most selective method which rejects all other materials besides water molecules and gases, which can pass through. Around 1980 two and three layered membranes became the industrial standard and replaced the integral membranes previously used. While integral membranes were mostly based on cellulose acetate, polysulfone or polyvinylidene difluoride, the more recent composite membranes show several advantages, such as high flux and salt retention. They consist of a thick support layer of porous polysulfone or polyester, covered with a thin layer of polyamide or polyurea (100-200 μm and 50-100 nm, respectively, as shown in Figure (2.4).

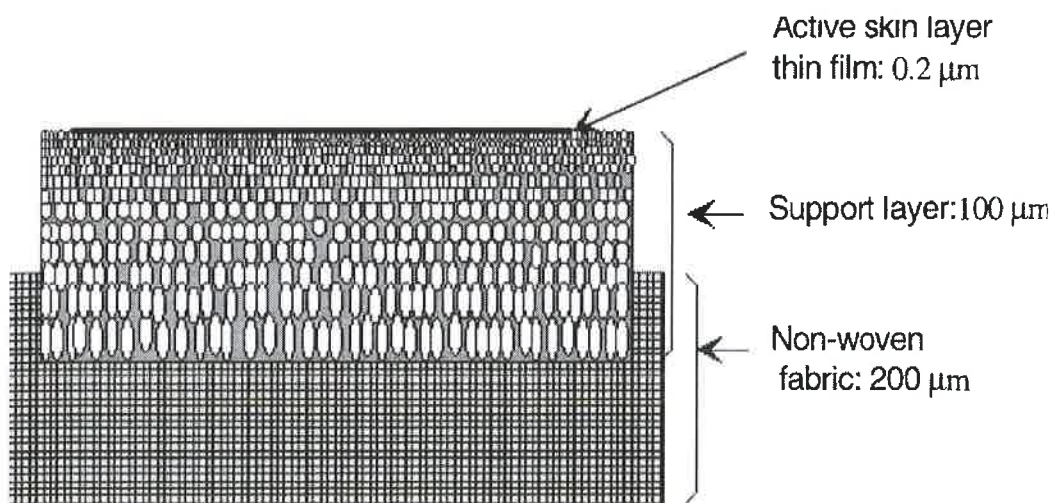


Figure 2.4: Basic structure of a composite RO membrane.

The thin top layer allows water molecules to pass easily and protects the underlying pores of the support layer from bio-fouling and mechanical clogging. These materials normally consists of polyamides, which are deposited directly via interfacial polymerization or introduced as solution, followed by the removal of the solvents¹⁰.

2.3.2 Polyamide thermoplastic elastomers

Polyamide elastomers are important members of the family of thermoplastic elastomers. Thermoplastic polyamide elastomers (TPAE), sometimes referred to as thermoplastic rubbers, are a class of copolymers or a physical mix of polymers (usually a plastic and a rubber)¹¹. They are block copolymers containing soft and hard segments and are used for a variety of unique applications that can not be met by other polymers. Their advantageous properties include high hardness for a given modulus, excellent mechanical and elastic properties, extremely high abrasion resistance, chemical resistance and blood and tissue compatibility. Generally, polyamides block copolymers have low-glass transition "soft" segment (SS) and a rigid "hard" segment (HS), which often has a high T_g and can also show crystalline behaviour¹².

2.3.3 Polyamide coatings

Coating is an old technique and many coating methods have been successfully applied in industry. There are three types of coating methods in use¹³. Brush coating is the simplest method. It is often applied in both industry and private usage.

Dip coating is also a common and simple coating method. The part is dipped into a polymer solution, taken out of the bath and dried. Sometimes the drying is conducted in an oven. After drying the coating is deposited as a hard layer on the surface.

In spray coating very small solution droplets are sprayed to the surface of a substrate by pressurized gas. The solvent evaporates when solution droplets hit the part and the coating is created.

2.3.4 Polyamide fibers

Polyamide fibers are used in many application areas due to their outstanding properties, their simple and economical processing and their high strength¹⁴. Polyamide fibers were synthesized by the reaction of diamines with dicarboxylic acids. The most useful molecules for fibers are long chains with few branches and a very regular built up.

The same applies to the natural polymer cellulose, which for example also forms good fibers. The polymer chains have a few side chains or linkages between sugar units and its chains. Starches contain the same basic sugar units, but do not form useful fibers because their chains are branched and coiled to almost spherical shape.

2.4 Methods of preparation of polyamides

Several techniques are available for the preparation of polyamides:

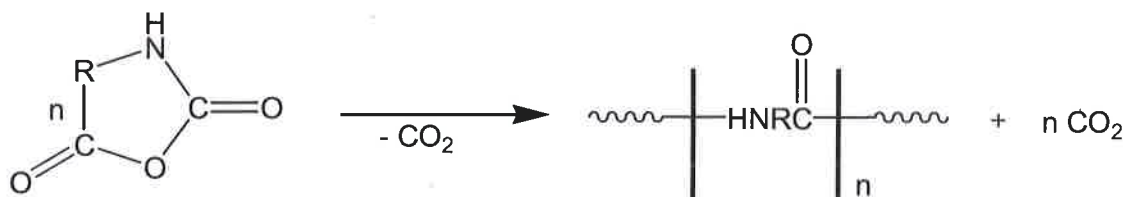
- high-temperature melt polymerization,
- ring-opening polymerization,
- low-temperature solution polymerization (usually for aramids) and
- interfacial polymerization.

2.4.1 High-temperature melt polymerization

High temperature, solventless polymerization has been used with a variety of monomers. Commercially most aliphatic polyamides are prepared by the direct amidation of either diacids or diesters with diamines at elevated temperatures (300 °C)¹⁵,¹⁶. Some aromatic polyamides have been successfully prepared via these high temperature methods.

2.4.2 Ring-opening polymerization

In this process the reactions are effective and are commercially used for preparing high molecular weight polymers from cyclic lactams such as ϵ -caprolactam. No by-products are formed. The example below explains the ring-opening polymerization of N-carboxyanhydrides with elimination of carbon dioxide. It has been used to prepare high molecular weight poly(α -amino acids)¹⁷, as shown in Scheme 2.3.



Scheme 2.3: Formation of poly(α -amino acids).

2.4.3 Low temperature- solution polymerization

The preparation of polyamides at low temperature by the reaction between diamines and diacid chlorides is an important way to high melting polyamides, also including aramids. At low temperatures, acid chlorides react rapidly with free amines and high molecular weights are easily attained for polymers which are unstable at their melting temperatures or for amines with low reactivity in the absence of acid chloride groups¹⁸.

In order to obtain high molecular weight polymers at a low temperature polymerization, the reactivity of the acid chloride must be maintained by excluding water and other interfering substances or solvents. A reaction medium is selected, which keeps the polymer in solution and does not react itself. Pure starting materials in the selected ratio have to be used to achieve PAs with high molecular weights. Otherwise excess of one component blocks the end of the chains, resulting in short chains.

2.4.4 Interfacial polymerization

Interfacial polymerization involves reaction at the interface between water containing a diamine and an inert, water immiscible organic solvent containing a diacid dichloride. An inorganic base such as sodium hydroxide is usually dissolved in the aqueous phase to

bind HCl produced by the reaction. Although high molecular weight polymers can be prepared via this method, the molecular weight distribution is different from that of the homogeneous polymerization. Polymers with much higher and much lower molecular weight are also produced, which make this method not suitable for the production of fibers and films¹⁸.

2.5 Starting materials

Polyamides can be synthesized from various monomers. The most important monomer in this study is furan, which enters into all reactions with diamines and will be discussed in greater detail below:

2.5.1 Furan

2.5.1.1 Introduction

Furan (a) is a well-known compound in a series of five-membered unsaturated (heteroaromatic) heterocyclic ring systems, which include pyrrole (b) and thiophene (c) as shown in Figure in 2.5. This heterocyclic has a very unique chemical behavior, which is often not closely related to that of its homologues pyrrole and thiophene¹⁹.

Structures, bearing furan rings, were used in the synthesis of monomers or other starting materials. As result, a variety of initiating, transfer and terminating agents or conventional polymers, modified by furanic units, are possible ¹⁹.



- a. **X = O (Furan)**
- b. **X = NH (Pyrrole)**
- c. **X = S (Thiophene)**

Figure 2.5: The furan heterocyclis.

2.5.2. First - generation furans

Most of the simple furanic structures are prepared from two starting materials, furfural or furan-2-carboxaldehyde (1) and 5-hydroxymethyl furfural (2) (Figure 2.6). Both can be isolated from saccharidic natural products. Furfural is a well known compound, which was first prepared early last century²⁰. Nowadays, there is a growing interest for chemist on furfural as a renewable source for pharmaceutical products, fragrances or especially polymers.

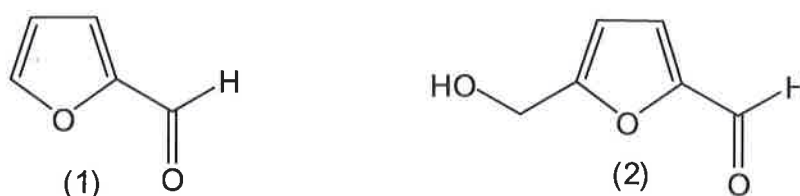


Figure 2.6: First - generation furans.

2.5.3 Derivatives of 5-hydroxy methyl-2-furfural

This section concentrates on furanic monomers bearing two functional groups on one heterocyclic system, structures that are suited for polycondensation reactions. Obviously the structure compound (2) is the ideal precursor to this type of compounds²¹.

2.5.3.1 Furan-2, 5-dicarboxylic acid, chlorides and esters

Total oxidation of both functional groups for compound 2 provides the corresponding diacid 3a which can be converted to its acid chloride 3b and corresponding esters 3c²¹ by standard techniques as shown in Figure 2.7.

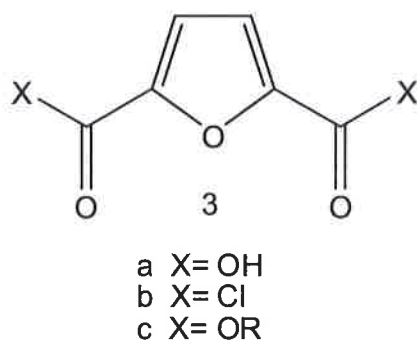


Figure 2.7: Derivatives of 2,5-substituted furans.

2.5.3.2 Furanoyl- 2,5-diisocyanates

Furanoyl diisocyanates, which will be used in the preparation of polymeric ureas, are commonly prepared by the reaction of acid chlorides with sodium azide²². The resulting furanoyl-2,5-diazide is thermolyzed in an inert solvent to furanoyl-2,5-diisocyanate **4** (Curtius reaction)²² and reacted with diamines. On a technical scale, most diisocyanates such as hexamethylenediisocyanate for the production of polyurethanes are manufactured via diamines and phosgene. Another method uses the hydrazide, prepared from the acid chloride, which is reacted with HNO₂ (nitrous acid)²³.

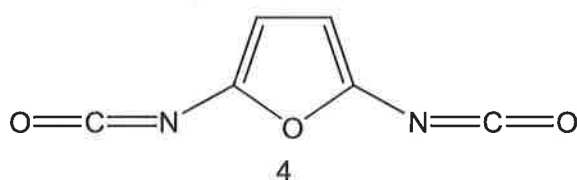


Figure 2.8: Furanoyl-2, 5-diisocyanate.

2.5.4 Furanic polyamides

2.5.4.1 Properties of furanic polyamides

Since the early 1950s^{24 - 26} polymer chemists were interested in the synthesis of furanic PAs. Most of this early work was devoted to the combination of diacid derivatives **3** with aliphatic or aromatic diamines. Furanic PAs built from derivatives of **3** and aromatic amines were reported, but without any structural details. Both the acid **3a** and the 3,4-substituted homologue of furan were used in combination with various aromatic diamines. Polymerization procedures adopted included all the classical methods, as mentioned before (interfacial polymerization, homogenous phase polymerization and direct polycondensation). All of them were successful in terms of yields, molecular weights, thermal and mechanical properties²⁷⁻³⁰.

There are many factors that affect these reactions, such as the degree of purification of the monomers, the nature of the organic medium, the reaction time, the reaction temperature and the structure of the phase-transfer catalyst and its concentration.

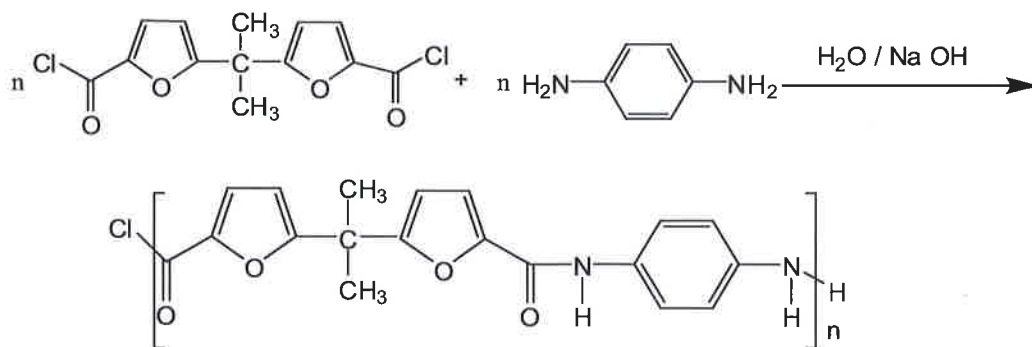
Results vary in terms of yields, molecular weight, molecular weight distribution and the thermal stability of products. Interfacial polymerization, supported by addition of a phase

transfer catalyst such as TEBAC is not applied to aromatic diamines because of their poor solubility in water. Preliminary runs showed disappointing results and the technique was abandoned³⁰.

With furanic diamines (amino alkyl substituted furans)³¹ however, this method was satisfactory. The organic phase was either ethylene chloride or chloroform; the aqueous phase contained KOH to neutralize evolved HCl, but also to regenerate the furanic diamine in situ when its diammonium salt was used. The temperatures ranged from

0-10 °C and reaction times were between 20 and 40 minutes. Still less work has been published on fully furanic PAs, with only a couple of studies describing the interfacial polymerization of diacid chlorides and diamines^{31, 32}.

As mentioned earlier, interfacial polymerization displayed some weaknesses in the PA products, such as low molecular weights of the resulting polymers and lower yields compared to that achieved with homogenous phase reactions. Use of the phase-transfer catalyst triethyl benzyl ammonium chloride (TEPAC) which had already been found to be very efficient in two-phase polyesterification and polyamidation reactions^{33, 34}, is a useful additive. The presence of such a phase transfer agent is indispensable; its absence results in a poor polycondensation reaction (Scheme 2.4).

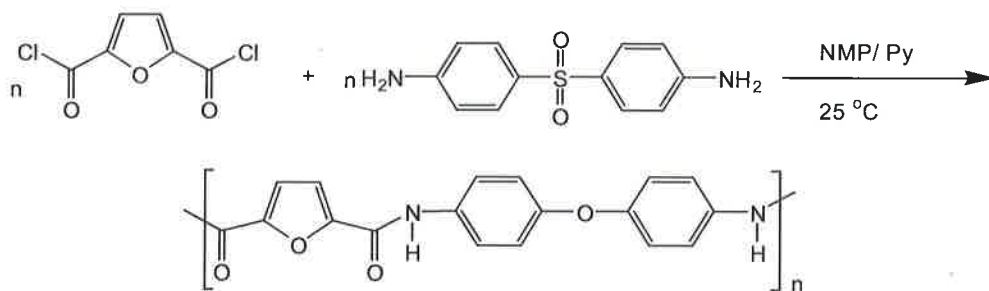


Scheme 2.4: Formation of polyamides by interfacial polymerization.

Homogeneous phase reactions on the other hand, give high molecular weight polymers, in good yields and with good thermal stability. With the homogeneous phase reaction as the best methods to prepare polyamides bearing furan rings, it implies that the aromatic diamines are used in presence of solvents such as NMP. Pyridine or other organic or

inorganic bases act as quencher of the reaction by-product hydrogen chloride as well as a catalyst in the case of pyridine.

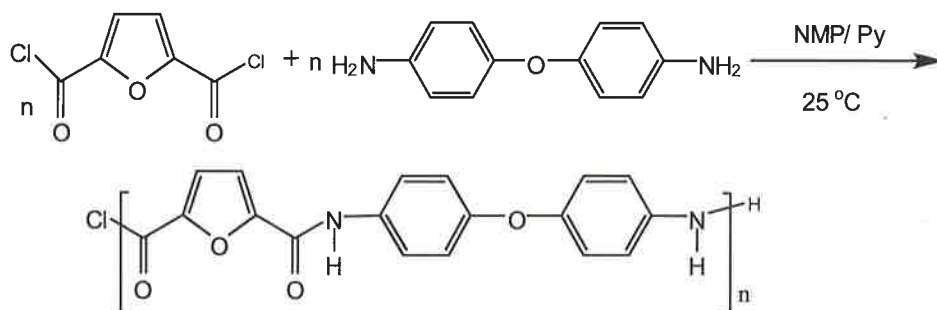
This technique was also utilized for fully aromatic PAs³⁰ and gave the best results with furanic-aromatic combinations, although some optimization of experimental conditions was applied (Scheme 2.5).



Scheme 2.5: Formation of polyamides by homogeneous phase polymerization.

Many interactions, side reactions and reaction conditions need to be taken into consideration. Polymerization reactions did not take place to any appreciable extent in the presence of moisture or other impurities and the reaction was difficult to reproduce in quantitative terms, particularly when the amount of residual water was not controlled³⁵.

In conclusion, from all the published methods by which to prepare furan-based PAs, the following can be said: interfacial polymerization and homogeneous phase polymerization can be considered as the best methods to prepare the PAs to be used in this study. In Chapter 6 the details of the experiments and results are described. Scheme 2.6 shows an example of furanic polyamide.



Scheme 2.6: Example of a furanic polyamide.

2.5.4.2 Thermal properties of Furanic polyamides

The thermal properties of polyamides bearing furan rings can be determined by DSC and TGA analysis. The polyamide displayed only a minor glass transition feature. The thermal properties of every polymer should be different, because function groups which are associated with monomers are affecting the thermal properties. Thus, thermal degradation preceded melting of these polyamides, just as with the corresponding fully aromatic polyamides like Kevlar. The thermal properties for polyamides were different; polymers started decomposing^{30,31,35} in the range of 325 °C to 390 °C.

2.6 Water up-take

The water content of a polymer can be determined by the Karl Fischer method or gravimetric procedures. Water absorption / up-take varies with relative humidity (RH), temperature, functional groups in the polymer and the crystallinity of polymer chains.

Typical Nylon-6.6 or Nylon-6 samples absorb 8-9% water at 100% RH and 7% when annealed. Generally aromatic PAs absorb about 10-15% at 99% RH. In aromatic PAs the water absorption depends largely on position of the nitrogen atom on the heteroring^{36, 37}.

2.7 Permeability

The mechanism and transport behavior of gases and water molecules through polymer films and membranes has increasingly attracted attention in recent years³⁸. Generally speaking, the term permeability is used to describe the penetration of low molecular weight substances through a barrier.

Permeability can be defined as the transmission of a permeant through resisting material. For polymer films, permeability to gases and vapors is often important³⁹. Most often the gases or vapors of interest are water vapor, oxygen, carbon dioxide and nitrogen. Knowledge of the permeability properties of polymer materials for these low molecular weight compounds could lead to their improved utilization. For a specific permeant, the chemical composition and physical properties of the polymeric membrane determine the permeation properties, according to the following relationship⁴⁰,

$$P = D \times S$$

(equ. 2.1)

where P is the permeability and D and S are the diffusion and solubility coefficients respectively. From equation 2.1 one can see that permeability is influenced by the diffusion and solubility coefficients. A low permeability may result from a low diffusion coefficient or a low solubility coefficient or both. These factors in turn can be greatly influenced by the chemical and physical structure of the polymer in use. In this regard, it is very important to investigate the relationship between the chemical and physical properties and the gas transport behavior, to explain the permeability behavior of polymeric materials and coated polymeric films.

Generally, diffusion and solubility of moisture vapor is decreased as the hydrophobicity of the polymer is increased. As a result, permeability is decreased remarkably, as expected from equation 2.1. The T_g influences the quality of the polymer films used as barrier coatings, which in turn can affect the barrier properties of the film.

Permeability can be affected by several physical properties, such as humidity and temperature^{41, 42}. Many polymers, particularly those that have polar groups, can absorb moisture from atmosphere or from a liquid in contact with polymer. Also, if such a polymer is in contact with a humid environment it absorbs water. The ability of different polymers to absorb from a humid environment depends on the type of the polymer.

For instance, water does not affect the permeabilities of some non-polar polymers, including polyolefins, vinylidene chloride copolymers and acrylonitrile copolymer⁴⁰. In other polar polymers, however, including PUs, ethylene and vinyl alcohol copolymers, the permeability increases with increased relative humidity. Permeability often also varies with temperature according to the Arrhenius equation^{41, 42},

$$P = P_0 \exp (- E_p / RT)$$

(equ. 2.2)

whereby P_0 is a constant, E_p is the activation energy for permeation, R is the gas constant and T is the absolute temperature. The temperature dependence of permeability is related to a diffusion coefficient and a solubility coefficient. This can be expressed by the following two equations:

$$D = D_0 \exp (- E_d / RT) \quad (\text{equ. 2.3})$$

$$S = S_0 \exp (- \Delta H_{\text{sol}} / RT) \quad (\text{equ. 2.4})$$

where D_0 and S_0 are constants, E_d is the activation energy for diffusion, and ΔH_{sol} is the heat of solution for the permeation in the polymer. The temperature at which the barrier polymer is used can therefore also be of a great importance. For instance, if the polymer has a T_g higher than the application temperature, the polymer will be in its glassy state, and the segments will have little mobility. Thus, a diffusing molecule will have a much more tortuous path through the polymer, leading to a less permeable material. Therefore, the recommended temperature of use will be below the T_g of the polymer, and the polymer will consequently have improved barrier properties⁴³.

$$D = D_0 \exp (- E_d / RT) \quad (\text{equ. 2.3})$$

$$S = S_0 \exp (- \Delta H_{\text{sol}} / RT) \quad (\text{equ. 2.4})$$

where D_0 and S_0 are constants, E_d is the activation energy for diffusion, and ΔH_{sol} is the heat of solution for the permeation in the polymer. The temperature at which the barrier polymer is used can therefore also be of a great importance. For instance, if the polymer has a T_g higher than the application temperature, the polymer will be in its glassy state, and the segments will have little mobility. Thus, a diffusing molecule will have a much more tortuous path through the polymer, leading to a less permeable material. Therefore, the recommended temperature of use will be below the T_g of the polymer, and the polymer will consequently have improved barrier properties⁴³.

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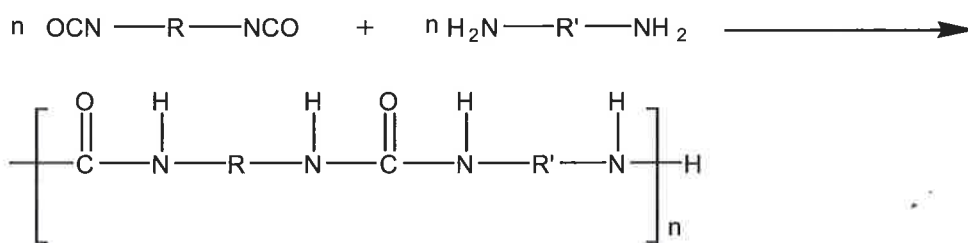
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CHAPTER 3: POLYUREAS

3.1 Introduction

Polyureas (PUs) are synthesized by an addition reaction between diisocyanates and diamines, producing urea linkages. A comprehensive study of the polyureas was made by Otto Bayer in 1947¹. Although the polyamine in these polymers often formed the majority mass component, the name PU refers to the corresponding chemical group linkage and not to the entirety of the polymer backbone. The urea functional group, however, does impart most of the important physical properties such as high hardness, flexibility, tear and tensile strength and chemical and water resistance.

Linear PUs are produced by the reaction between diisocyanates and diamines, as shown in Scheme 3.1. Nowadays, polyureas are used in broad range of applications, as elastomers, sealants, elastoplastics, foams, coatings and adhesives²⁻⁶.



Scheme 3.1: Formation of polyureas from polyisocyanates.

3.2 Historical perspective

The history of PUs begins with Otto Bayer's patent⁷ at Germany's I. G. Farbenindustrie (predecessor of Bayer AG⁸) in 1937, the year of the first disclosure of diisocyanate addition to form PUs. The main impetus for this work was the success of Wallace Carothers at Du Pont in making PAs and polyesters. Bayer and his colleagues were trying to find a route to similar materials without infringing on Du Pont's patents. The synthesis and basic reactions of isocyanates had been explored at the beginning of the nineteenth century by Wurtz and others⁹. Bayer utilized the known addition reaction of the isocyanate group with alcohols and amines to form macromolecules from diisocyanates and either diols or diamines. This first led to the preparation of PUs from

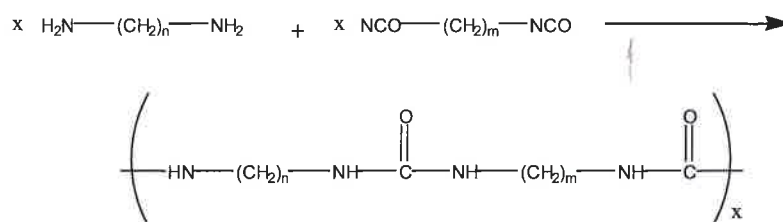
hexamethylene diamine and hexamethylene diisocyanate but these polymers proved to be unsuitable for the preparation of fibers or thermoplastics.

3.3 Methods of preparation of polyureas

Much of the early work on the synthesis of PUs was carried out by Otto Bayer¹ in order to produce alternative fiber-forming polymers analogous to those originally patented by Carothers¹⁰. Technically, the most important methods used for PU formation are based on the reaction between diamines and diisocyanates³.

3.3.1 Synthesis of polyureas from diamines and diisocyanates

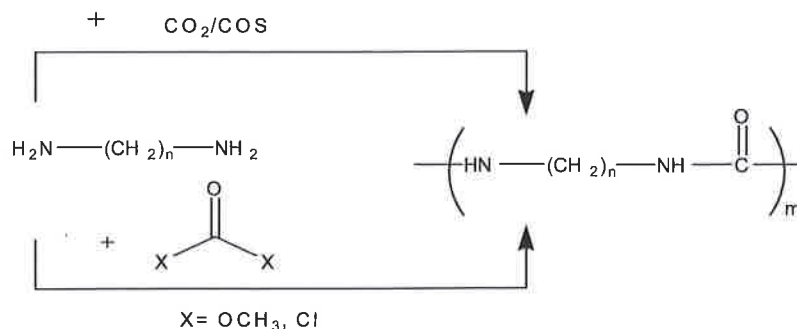
One immediate advantage of these step-growth polymerization reactions is that PUs are formed without the evolution of condensation by-products, as shown in Scheme 3.2.



Scheme 3.2: Formation of polyureas from diamines and diisocyanate.

3.3.2 Synthesis of polyureas from diamines and carbonic acid derivatives

There are also other methods to prepare polyureas, based on reactions involving diamines and carbonic acid derivatives such as carbon dioxide, carbonoxy sulfide, metal carbonates, phosgene, urethanes and urea³ (see Scheme 3.3.).



Scheme 3.3: Formation of polyureas from diamines and carbonic acid derivatives.

3.4 Thermal properties for polyureas

Thermoplastics, including PUs, containing aromatic groups in the main chain, have been widely studied¹. A number of attempts have been made to enhance the thermal and mechanical properties of these thermoplastics¹². Aromatic PUs are generally high-performance thermoplastics because of their reasonably high glass-transition temperatures (T_g), high decomposition temperature and good mechanical properties¹³. These properties are the result of hydrogen bonding between the polymer chains. However, these wholly aromatic PUs are often infusible and insoluble and hence difficult to process.

3.5 References

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CHAPTER 4: EXPERIMENTAL

4.1 Introduction

The experimental procedures used to synthesize the polyamides (PAs) and polyureas (PUs) are described in this chapter. The first task was to synthesize furanoyl-2,5-dichloride (FDC). This monomer was then to be used in combination with isophthaloyl dichloride (IPDC) (different ratios, 100%, 90:10, 70:30 and 50:50) with selected diamines. The resulting polymers were characterized by ^1H NMR and ^{13}C NMR, FTIR, TGA, DSC and GPC. Furanoyl-2,5-dichloride FDC was chosen as one of the main monomers for several reasons. A publication by Mitiakoudis and Gandini (see Lit.3 in chapter 6) use FDC in their experiments and some of the polymers prepared are repeated in this work to compare the methods and analytical data.

Three of the aromatic diamines (MPD, DDS, DDE) are commercially available. To extend the range of diamines, an unpublished heterocyclic diamine (BAT) was prepared, characterized and used as monomer.

PM 1 and PM 2 are unpublished model compounds, prepared by reacting the IPCD or FDC, respectively, with a diamino compound 3-acetylamino aniline, whereby one amino group is protected from reaction with the acid chloride by acetylation. They were synthesized to help with the assignment of the NMR signals of the similar structured polyamides.

4.2 Synthesis of monomers

4.2.1 Synthesis of furanoyl-2,5-dichloride (FDC) from furan-2,5-dicarboxylic acid (FDCA)

There are several published methods for the synthesis of FDC¹⁻⁶. The following method was used in this study:

Furan-2,5-dicarboxylic acid (FDCA; 150 g, 0.96 mol) and N,N'-dimethylformamide (DMF, 2 drops) were added to thionyl chloride (343 g, 2.88 mol, ratio thionyl chloride to diacid 3:1). The mixture was stirred and heated to 75 °C under the exclusion of moisture. The solid slowly dissolved and HCl and SO₂ were liberated. After 3 days the now clear solution was cooled and dry hexane (40 ml) was added. The crystals were filtered off

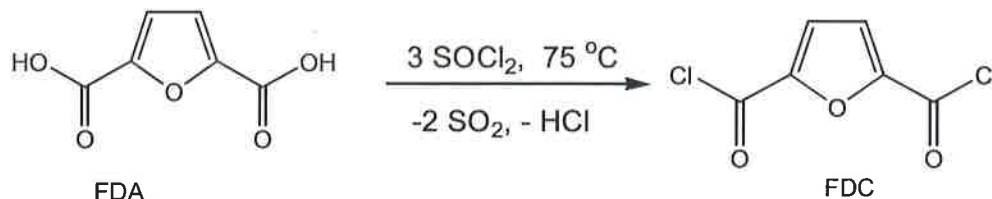
and washed with few millilitres of hexane. The acid chloride was dried under vacuum and recrystallised from hexane.

$C_6H_2O_3Cl_2$, $M = 192.98$

$m = 170$ g (yield 92%)

colorless crystals, mp: 78–80 °C (hexane); mp (lit.⁴) 78–79 °C

1H NMR ($CDCl_3$): 7.22 (s, 2H, CH); 1H NMR ($CDCl_3$) (lit.⁷): 7.12 (s, 2H, CH)



Scheme 4.1: Formation of furanoyl-2,5-dichloride (FDC).

4.2.2 Synthesis of 2,4-bis (4-aminophenyl)-6-phenyl-1,3,5-triazine- 2,4,6- triamine (BAT)

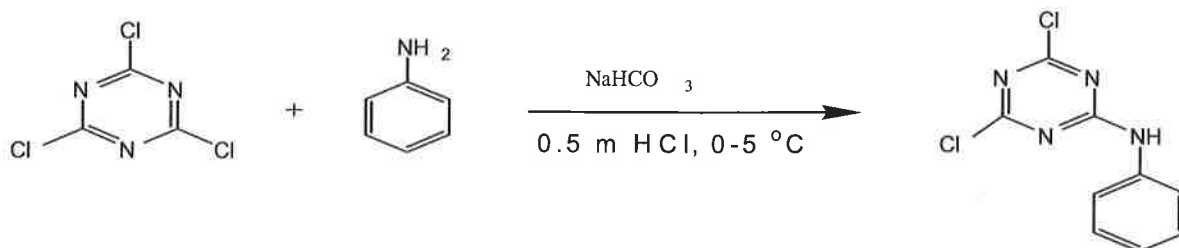
4.2.2.1 Synthesis of 2-anilino-4,6-dichloro-1,3,5-triazine ⁸

A solution of cyanurichloride or 2,4,6-trichloro-1,3,5-triazine (40.0 g, 217 mmol) in 375 ml acetone was stirred at 0 °C and freshly distilled aniline (20.2 g, 217 mmol) in 300 ml acetone added within 30 minutes, followed by an aqueous solution of 18.2 g sodium hydrogen carbonate (217 mmol) in 225 ml water over one hour. The temperature was kept at 0-5 °C. Stirring was continued for another hour in the ice bath and one hour at room temperature. 0.5 molar HCl was added until an oil was formed. The oil was separated and stirred with water for a few minutes. The resulting crystals are separated and washed several times with water (washing with acetone as described in the literature is not recommended because of good solubility).

$C_9H_6N_4Cl_2$, $M = 241$

$m = 44$ g (yield 84%)

mp = 138–139 °C, mp (lit.⁹) 135–136 °C.



Scheme 4.2: Formation of 2-anilino-4,6-dichloro-1,3,5- triazine.

4.2.2.2 Synthesis of 2,4-bis(4-acetylaminophenyl)-6-phenyl-1,3,5-triazin-2,4,6-triamine

2-Anilino-4,6-dichloro-1,3,5-triazine (43.4 g, 180 mmol), 4-amino acetanilide (57.0 g, 380 mmol) and sodium carbonate (20.1 g, 190 mmol) in ethanol (95%, 300 ml) were stirred at room temperature for 15 minutes. Carbon dioxide evolved, the temperature increased to 45 °C and the colour changed to brown. The mixture was then boiled under reflux for 12 hours and cooled. The grey solid was filtered off and washed repeatedly with water. The product was then hydrolyzed without further purification or characterization to yield the final product:

m = 88.5 g (yield > 100%).

4.2.2.3 Synthesis of 2,4-bis(4-aminophenyl)-6-phenyl-1,3,5-triazine-2,4,6-triamine

(BAT)

The above mentioned solid was added to concentrated HCl (60 ml) and water (120 ml) and refluxed for 9 hours. The solid was filtered off and suspended in water (200 ml), to which solid sodium carbonate was added until the solution was alkaline. The solid was again filtered off, washed with water and dried to yield the product.

m = 86.0 g (yield > 100%).

NMR data showed, besides the desired product, the presence of much unchanged acetyl amino starting material.

The hydrolysis was therefore repeated under different conditions as follows:

Concentrated sulfuric acid (250 g, 2.45 mol) was poured onto crushed ice (600 g) and the recovered solid from the first hydrolysis experiment added. The suspension was heated to 100 °C. After 5 hours of refluxing a clear solution was formed.

The heating was continued for another hour and then the solution was cooled. The next day the formed solid was filtered off. The solid was stirred in water (500 ml) and the

solution made alkaline by step-wise addition of 20% sodium hydroxide solution. The solid was separated, washed several times with water and dried under vacuum at 80 °C for 8 h.

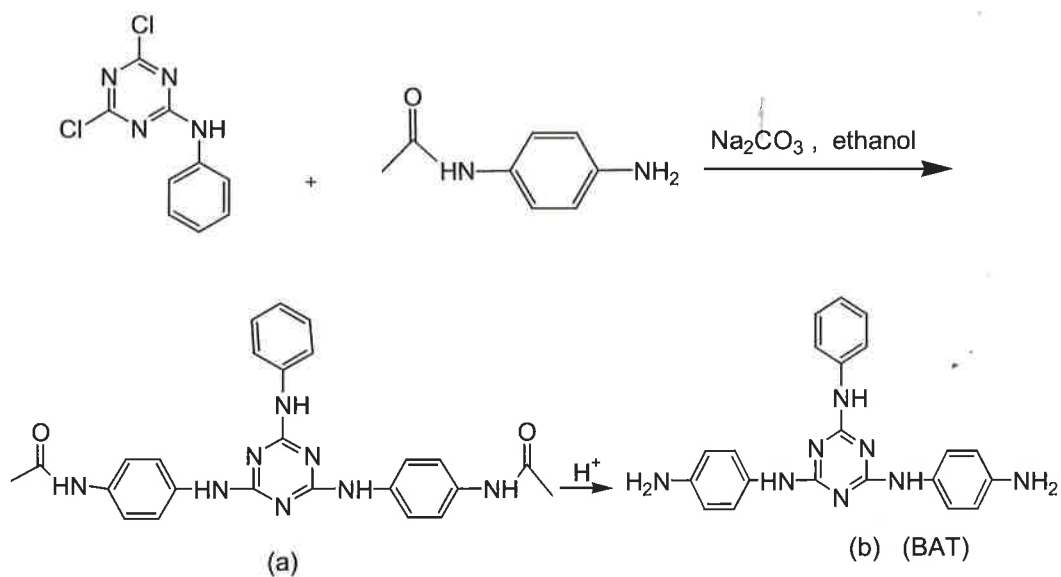
$C_{21}H_{20}N_8$, $M = 384$

$m = 60.6$ g (88%),

mp 218–220 °C

1H NMR (DMSO- d_6): 4.78 (s, 4H, NH_2), 6.53 (d, 4H, CH), 6.93 (t, 1H, CH), 7.23 (t, 2H, CH), 7.33 (d, 4H, CH), 7.79 (d, 2H, CH), 8.63 (s, 2H, NH), 8.93 (s, 1H, NH)

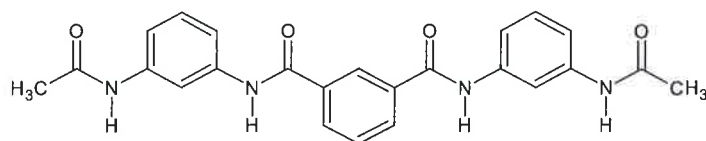
^{13}C NMR (DMSO- d_6): 113.76, 119.83, 121.36, 122.58, 128.17, 128.94, 140.35, 144.05, 163.97, 164.0



Scheme 4.3: Formation of 2,4-bis(4-acetylaminophenyl)-6-phenyl-1,3,5-triazine (a) and formation of 2,4-bis(4-aminophenyl)-6-phenyl-1,3,5-triazine-2,4,6-triamine (b) (BAT).

4.3 Synthesis of model amides PM 1 and PM 2

4.3.1 Synthesis of N,N'-bis[(3-acetylamino)phenyl]isophthalamide (PM 1)



A suspension of 3-acetylamino aniline (7.5 g, 50 mmol) and dry pyridine (3.95 g, 50 mmol) in dry NMP (40 ml) was stirred at 0 °C in an ice bath. IPCD (5.1 g, 25 mmol), dissolved in dry NMP (20 ml) was added dropwise over 50 minutes. The resulting clear solution resulted was stirred for another 90 minutes at room temperature. The mixture was then poured into water (250 ml). The white solid was filtered off, washed twice with water (30 ml) and then dried at 70 °C overnight. The solid was recrystallised from DMSO.

$C_{24}H_{22}N_4O_4$, $M = 430.45$

$m = 10.35$ g (96%)

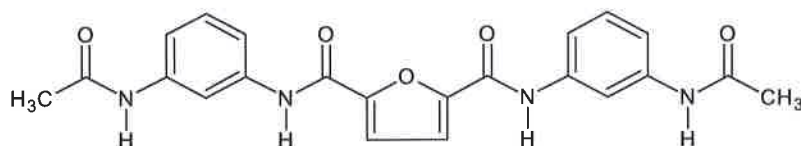
white powder, mp: 309–311 °C (DMSO).

The product was soluble in DMSO and NMP, but is insoluble in water, acetone, acetic acid and chloroform.

1H NMR (DMSO- d_6): 2.06 (s, 6H, CH₃), 7.27 (t, 2H, CH), 7.35 (d, 2H, CH), 7.46 (d, 2H, CH), 7.68 (t, 1H, CH), 8.13 (m, 4H, CH), 8.52 (s, 1H, CH), 9.99 (s, 2H, NH), 10.43 (s, 2H, NH)

^{13}C NMR (DMSO- d_6): 23.98, 111.31, 114.69, 115.28, 127.01, 128.47, 128.68, 130.62, 135.08, 139.22, 139.50, 165.05, 168.29.

4.3.2 Synthesis of N,N'-bis[(3-acetylamino)phenyl]furan-2.5-dicarboxamide(PM 2)



A similar procedure to that described above for the preparation of PM 1 was used for the preparation of PM 2. Here furanoyl-2,5-dichloride (FDC, 4.85 g, 25 mmol) was used instead of the IPCD. The addition time was 90 minutes and stirring at room temperature was continued for 150 minutes. The resulting solid was recrystallised from hot DMSO.

$C_{22}H_{20}N_4O_5$, $M = 420.42$

$m = 9.6$ g (yield 91%),

grayish powder; mp: 196–198 °C (DMSO).

¹H-NMR (DMSO-d₆): 2.06 (s, 6H, CH₃), 7.30 (t, 2H, CH), 7.36 (d, 2H, CH), 7.42 (s, 2H, CH), 7.47 (d, 2H, CH), 8.09 (s, 2H, CH), 10.04 (s, 2H, NH), 10.34 (s, 2H, NH)

¹³C-NMR (DMSO-d₆): 23.98, 111.41, 115.12, 115.49, 115.99, 128.89, 138.12, 139.65, 148.15, 155.47, 168.39.

4.4 Preparation of polyamides

4.4.1 Introduction

The synthesis of PAs requires all monomer reagents, solvents and intermediates to be free from moisture and of highest possible purity. Any trace amount of water during PA synthesis will react with acid chlorides and form free acids, which will not react further under the given reaction conditions. Any deviation of the 1:1-ratio between acid chlorides and amines results in short-chained polymers, which is undesirable. Other side reactions include crosslinking, the reaction of HCl with amino groups to form salts and oxidation of diamines. These can be minimised by using low temperatures, an inert gas atmosphere and the additions of pyridine or other bases to capture the hydrogen chloride that is released ¹⁰.

PAs can be synthesized by two methods: the interfacial polymerization method and the homogeneous phase polymerization method. The interfacial polymerization method only takes place at the interface between two immiscible solvents. The interfacial polymerization method entails using two different monomers dissolved in two immiscible solvents such as water and a chlorinated solvent, respectively. Phase transfer catalysts, such as TEBAC to facilitate the reaction and basic reagents such as pyridine to bind the formed hydrochloric acid via salt formation are added.

The homogeneous phase method takes place without the requirement for the use of a phase transfer catalyst as required in the previous method. This method is especially suitable for the preparation of aromatic PAs ¹¹. The main advantages associated with this procedure are the direct use of the furanoyl 2,5-dichloride and diamines without phase transfer catalysts, better yields (see Table 4.2.), fewer side reactions and a simple work-up procedure¹². The HCl is again neutralized by pyridine. Contrary to a method with an added acid acceptor, Butuc and Gherasim ¹³ describe a procedure, in

which the HCl is neutralized only after the reaction is complete, by washing the solid polymer with diluted alkali.

4.4.2 Starting materials

The materials used for synthesis of the PAs are tabulated in Table 4.1.

At the outset of this study a large number of polymers were prepared with the following di- or triamines: piperazine, 2,6-diamino pyridine, p-phenyldiamine and 2,4,6-triamino-triazine (melamine). These are however not included in Table 4.1 and not mentioned further in the thesis, for the following reasons: p-phenyldiamine was soon replaced by m-phenyldiamine. There is a higher reactivity of PA membranes with elementary chlorine or hypochlorites, when p-phenyldiamine instead of m-phenyldiamine is used¹⁴. That property is detrimental to shelf life and performance of PAs as membrane material in water purification plants. The reactivity of the trifunctional melamine (added to the diamines in 5-10 mol-%) is very low¹⁵, its amine function behaves more like an amide amino group and no crosslinking reaction takes place. As a result, the reacting monomers are not anymore present at a 1:1-ratio and very short chains are formed.

Piperazine and 2,6-diamino pyridine afford PAs, that are quite soluble in most organic solvents, which is not ideal for its intended uses.

The following reagents were purified and dried as follows prior to use. DDS and DDE were recrystallised from ethanol. MPD was dissolved in dichloromethane (DCM), precipitated in hexane and dried over 3Å molecular sieve. FDC was recrystallised from hexane and dried over phosphorus pentoxide (P₂O₅). NMP was distilled over calcium hydride (CaH₂) and stored over 3Å molecular sieve. Pyridine was distilled over potassium hydroxide (KOH) and dried over 3 Å molecular sieve. Chloroform as solvent was washed with water before use to remove any stabiliser (ethanol).

4.4.3 Experimental setup

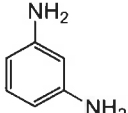
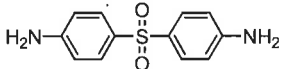
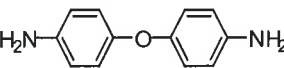
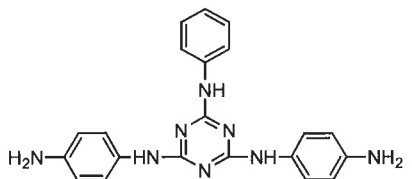
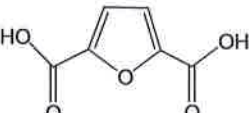
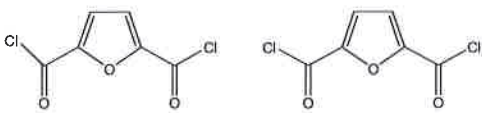
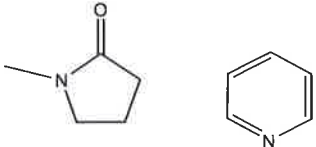
The following equipment was used for PA synthesis: a 250-ml three-neck flask, nitrogen gas inlet, oil bath, reflux condenser, temperature controller, magnetic stirrer, bubbler and dropping funnel,

4.4.4 Formulations

The quantities of MPD, DDS, DDE, BAT, FDC and IPDC used to synthesize the PAs were calculated as mole % according to their respective molecular masses. Table 4.2 lists all PA formulations with the ratios of reagents used, methods and yields.

The base pyridine was generally used as an acceptor for the hydrochloric acid that is released during reaction and it also acts as co-solvent. Several experiments were also carried out with other bases, such as sodium hydroxide, sodium carbonate and triethylamine. They offered no advantage in terms of product yield or purity. DCM or chloroform was used as solvent. TEBAC was the only phase transfer catalyst tested in some interfacial polymerization reactions.

Table 4.1: Reagents used for the preparation of PAs

Reagents	Chemical structure	Source
MPD		Sigma-Aldrich
DDS		Sigma-Aldrich
DDE		Pfaltz & Bauer
BAT		Prepared from 3-amino acetanilide (Aldrich, 97%), aniline and cyanuric chloride (Akros Organics, 99 %)
FDA		APIN Chemicals (97%)
FDC and IPDC		FDC: prepared IPDC: Fluka (98%)
NMP and pyridine		Fluka (98 %)

4.4.5 Experimental procedure

The PAs were prepared by either interfacial polymerization or homogeneous phase polymerization. The given yields are calculated using the mole concept, assuming pure polymers. Respective typical examples of the procedures are now described.

4.4.5.1 Interfacial polymerization (preparation of PA 7)

MPD (1.62 g, 15 mmol), TEBAC (0.19 g, 0.85 mmol) and pyridine (2.4 g, 30 mmol) were dissolved in a DCM (45 ml) / water (20 ml) mixture. The mixture was stirred at room temperature and then a solution of FDC (1.45 g, 7.5 mmol; 50%) and IPDC (1.52 g, 7.5 mmol; 50%) in DCM (45 ml) was added over 15 minutes at room temperature (RT). The stirring was continued for 3 hours at RT. The mixture then was poured, under stirring, into water (150 ml). The solid was filtered off, washed several times with water until neutral (pH checked), then followed by washings with acetone (50 ml) and DCM (50 ml) and dried.

white powder, $m = 2.40$ g (yield 69%)

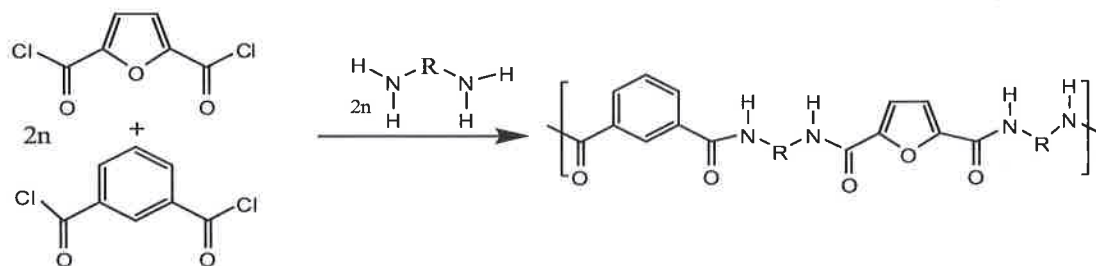
4.4.5.2 Homogeneous phase polymerization (preparation of PA 16)

DDE (3.0 g, 15 mmol) and pyridine (2.4 g, 30 mmol) were dissolved in dry NMP (45 ml) at 0 °C (ice bath). FDC (1.45 g, 7.5 mmol; 50 %) and IPDC (1.52 g, 7.5 mmol; 50%), were dissolved in dry NMP (45 ml) and added to the amine solution. The temperature was allowed to rise slowly to RT and stirring was continued for 3 hours. The mixture was poured into water (200 ml) and the solid filtered off. After washings with water (pH control), acetone (50 ml) and DCM (50 ml), the solid was filtered off and dried, first at RT and later at 90 °C under vacuum.

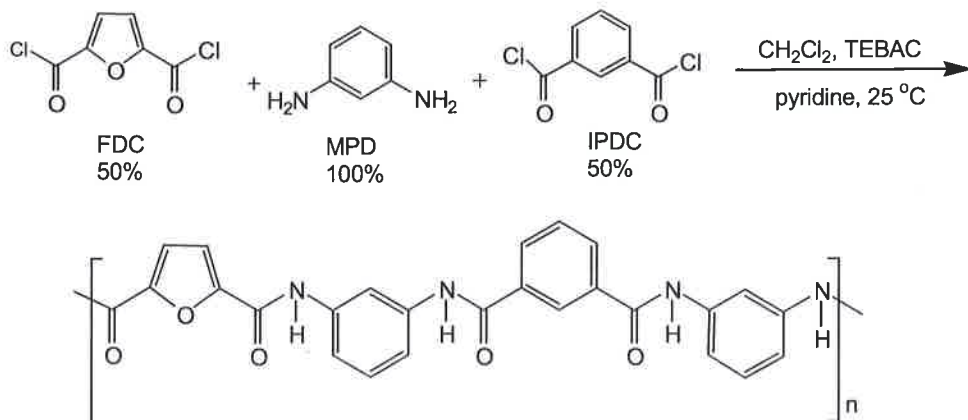
white powder, $m = 4.05$ g (83%).

4.4.6 Reaction scheme of the synthesis of polyamides

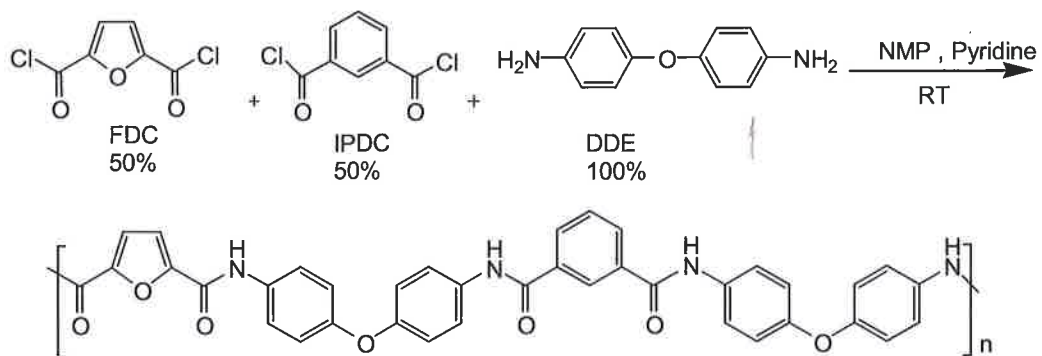
An outline of the synthesis of the polyamides is shown in Scheme 4.4



Scheme 4.4: General preparation of polyamides.



Scheme 4.5: Preparation of polyamide PA 7 by interfacial polymerization.



Scheme 4.6: Preparation of polyamide PA 16 by homogenous phase polymerization.

Table 4.2: Formulations of the prepared PAs: PA 1 - PA 19

Polymers	FDC (%)	IPDC (%)	MPD (%)	DDE (%)	DDS (%)	BAT (%)	Method	Yields (%)
PA 1	100	0			100		H	90
PA 2	50	50			100		H	92
PA 3	70	30			100		H	91
PA 4	90	10			100		H	91
PA 5	0	100	100				I	61
PA 6	100	0	100				I	22
PA 7	50	50	100				I	69
PA 8	70	30	100				I	60
PA 9	90	10	100				I	64
PA 10	0	100				100	H	91
PA 11	100	0				100	H	83
PA 12	50	50				100	H	78
PA 13	70	30				100	H	91
PA 14	90	10				100	H	81
PA 15	100	0		100			H	81
PA 16	50	50		100			H	83
PA 17	70	30		100			H	86
PA 18	90	10		100			H	88
PA 19	0	100		100			H	97

H: Homogeneous phase polymerization (NMP, Py)

I: Interfacial polymerization (DCM, water, Py)

4.5 Preparation of polyureas

4.5.1 Introduction

Most PUs are formed via solution polymerization in a solution of monomers with isocyanate groups as the active site and with a second type of monomer such as a diamine. Replacing the diamines with diols affords polyurethanes, a very important type

of polymer. In this study PUs were compared with similar PAs in terms of thermal stability physical and mechanical properties, although the monomer units are not the same and the conclusions are not representative for the class of polymers. The polyureas PU 1 and PU 2 were synthesized by reaction of furan-2,5-diisocyanate with *m*-phenylenediamine (MPD) or 4,4'-diamino diphenyl sulfone (DDS) in toluene / NMP.

The isocyanate itself is prepared by refluxing furan-2,5-dicarbonyl diazide in toluene for 4 hours¹⁶. The furan-2,5-dicarbonyl diazide was synthesized from FDC and sodium azide in ether / water (with 69% yield) or acetone/ water (62% yield)^{7,17}.

Attempts to prepare the diazide directly from furan-2,5-dicarboxylic acid and methyl chloroformate yielded mainly furan-2,5-dimethyl ester¹⁸. The prepared PUs were characterised by ¹H NMR, ¹³C NMR, GPC, FTIR, DSC, TGA and water up-take.

4.5.2 Synthesis of monomers

4.5.2.1 Synthesis of furan-2,5-dicarbonyl diazide (FDZ)

FDC (9.65 g, 50 mmol) was dissolved in acetone (100 ml), cooled in an ice bath and sodium azide (7.8 g, 120 mmol) in water (30 ml) was added dropwise over 20 minutes. The mixture was stirred at 0 °C for 30 minutes, followed by 1 hour at RT. The acetone was evaporated off and the resulting solid washed with water. The product was recrystallised from hexane and dried over phosphorus pentoxide under vacuum.

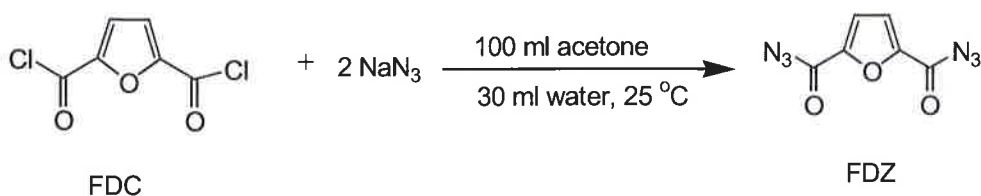
C₆H₂N₆O₃, M = 206

m = 6.4 g (yield 62%)

white needles, mp: 109 -110 °C (hexane); mp (lit.⁴) 108 - 109 °C

¹H NMR (CDCl₃): δ (ppm): 7.30 (d, 2H, CH)

¹³C NMR (CDCl₃): δ (ppm): 162.20, 148.32, 119.99.



Scheme 4.7: Preparation of furan-2,5-dicarbonyl diazide (FDZ)

4.5.2.2 Synthesis of furan-2,5-diisocyanate (FDI)

The preparation of FDI requires absolutely dry diazide FDZ. Therefore FDZ was first dried for several days over P_2O_5 in a dessicator under vacuum immediately prior to use. In spite of working under dry conditions and using dry FDI we always obtained by-product, which separated from the hot toluene as a very fine brown powder. The solid had to be filtered off before the isocyanate solution could be used further. The structure of that possible polymer could not be determined because of its complicated NMR spectra.

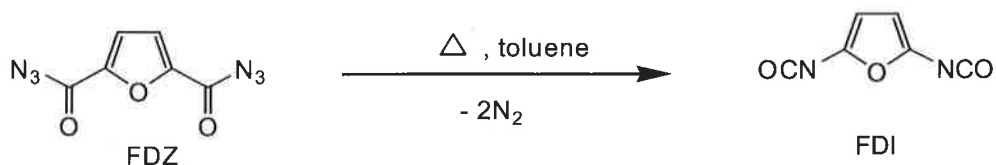
Traces of water reacting with already formed diisocyanate could decompose it to the diamino furan, which could react with the diisocyanate to an polyurea, made up only from furan units. The yield of that solid varies from 9 to 25% by mass of the starting diazide. Also the colour is variable from light brown to very dark. To find out more about the way the brown substance is formed and its structure, we prepared the substance independently in different ways, such as decomposing FDZ in toluene under addition of equimolar or excess water. Another run was done with previously prepared and filtered FDI-solution which was stirred overnight in an open container, exposing the solution to air moisture only. Up to 64% of the introduced mass of FDA could be isolated as brown polymeric powders. The NMR spectra of those are similar, but not identical, with spectra previously recorded for the by-product.

FDZ (2.78 g, 13.5 mmol) in dry toluene (40 ml) was refluxed for 4 hours under dry nitrogen. This reaction can be followed by the evolution of nitrogen via a bubbler (after temporarily stopping the nitrogen flow from the cylinder). The FDI was not isolated, but used as a toluene solution. It was filtered directly into a dry dropping funnel for use in the next step, i.e. the preparation of the PUs.

Nielek and Lesiak⁷ isolated the isocyanate by distillation from a toluene solution under argon. The following results were obtained by them:

yield 84.5%, bp_{14} 57.5 °C,

1H NMR ($CDCl_3$): δ (ppm): 5.66 (s, 2H, CH1).

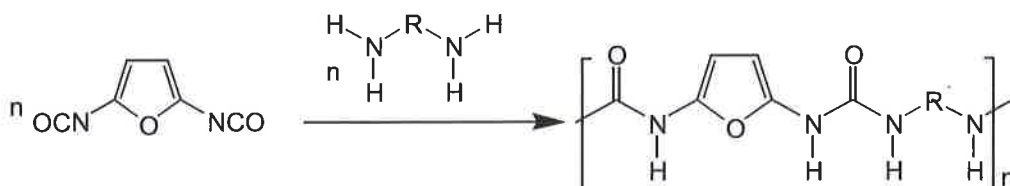


Scheme 4.8: Preparation of furan-2,5-diisocyanate (FDI).

4.5.3 Preparation of PU 1 and PU 2

An outline of the preparation of PUs is shown in Scheme 4.9.

The two synthesized polyureas show NMR spectra which are much more complicated than one would expect for the envisaged structures. Crosslinking or other processes seemingly contribute to the structures. The polymers are insoluble in all common and tested solvents. Only NMP and DMSO dissolve the polymers very slowly and under elevated temperatures. To modify the urea structure and increase its solubility in common organic solvents, a reaction of the polyureas with oxalyl chloride to the poly(parabanic acids)^{19,20} should be looked at at a later stage. Only preliminary experiments with a model compound were done so far and are not reported here.

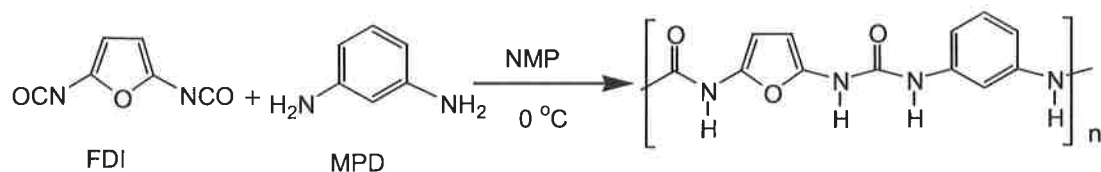


Scheme 4.9: Preparation of polyureas.

4.5.3.1 Synthesis of PU 1

MPD (1.19 g, 11 mmol) was dissolved in dry NMP (30 ml) and cooled to 0 °C in an ice bath. The filtered isocyanate solution (max. 13.5 mmol if fully reacted) in toluene (40 ml) was added dropwise over 30 minutes. The reaction mixture was stirred for 24 hours at RT. Toluene was removed and the residue poured into water (200 ml). The resulting solid was filtered off, washed three times with water and dried.

Yellow powder, $m = 2.0$ g (yield 70%).

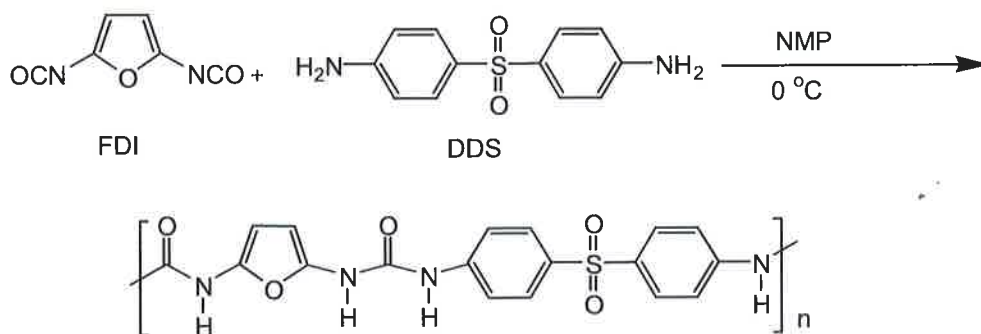


Scheme 4.10: Preparation of PU 1.

4.5.3.2 Synthesis of PU 2

DDS (2.75 g, 11 mmol) was dissolved in NMP (30 ml) and cooled to 0 °C in ice bath. The filtered isocyanate solution (max. 13.5 mmol) in toluene (40 ml) was added dropwise over 30 minutes. The reaction mixture was stirred 24 hours at RT. Toluene was removed and the residue poured into water (200 ml). The resulting solid was filtered off, washed three times with water, and dried.

Yellow powder, m = 2.98 g (68%).



Scheme 4.11: Preparation of PU2.

4.6 Water up-take by polyamides and polyureas ²¹⁻²⁶

Polymers with hydrophilic functional groups can absorb water, resulting in a weight increase, which can be measured under controlled conditions. The water uptake of the prepared PAs and PUs was determined. The following procedure was used:

Powdered polymer samples (0.9–1 g) were dried at 100 °C for 24 hours in a vacuum oven, until constant weight. Then all samples in their individual open glass containers were placed in a dessicator, in which the RH was 70%. The latter was achieved by using an saturated solution of sodium chloride (NaCl) in water. A RH of 43% could be obtained from a saturated solution of potassium carbonate (K₂CO₃) in water. The samples were

regularly weighed over a period of three days, until a constant weight was recorded. The ratios of weight gains to the weights of the original PUs were calculated using equation 3.1²⁶.

$$\text{mass gain (\%)} = 100 (m_{\text{wet}} - m_{\text{dry}}) / m_{\text{dry}} \quad (\text{eq 3.1})$$

whereby m_{wet} and m_{dry} are the masses of moist and dried samples, respectively.

4.7 References

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CHAPTER 5: CHARACTERIZATION

5.1 Introduction

The following analytical techniques were used to characterize the starting materials and the prepared PAs and PUs:

- Fourier-Transform Infrared Spectroscopy (FTIR)
- Nuclear Magnetic Resonance Spectroscopy (NMR)
 - ^1H NMR
 - ^{13}C NMR
- Gel Permeation Chromatography (GPC)
- Thermogravimetry (TGA)
- Differential Scanning Calorimetry (DSC)

5.2 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR was used to follow the emergence and disappearance of peaks of functional groups during the preparation of the PAs and PUs that were synthesised¹⁻³. Infrared spectra were obtained with a Perkin Elmer 1650 FTIR spectrophotometer and recorded by averaging 32 scans.

5.3 Nuclear Magnetic Resonance Spectroscopy (NMR)

The structures of PAs and PUs were determined by NMR analysis.

5.3.1 Proton NMR (^1H NMR)

^1H NMR spectra were measured on a Varian 400 MHz instrument using DMSO- d_6 or CDCl_3 as solvent, depending on the solubility of the materials being analyzed. DMSO was used as solvent for all PAs and PUs. All spectra were referenced to tetramethylsilane (TMS) at 0 ppm or the tabulated residual solvent peak.

5.3.2 Carbon NMR (^{13}C NMR)

^{13}C NMR spectra were obtained in the same manner as the proton spectra, but at a frequency 100 MHz. Long runs, overnight, were used due to the low solubility of most polymers.

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5.4 Gel Permeation Chromatography (GPC)

GPC is widely used to obtain molecular weight and molecular weight distribution data. In the conventional mode, a GPC column is first calibrated with polystyrene standards, whose molecular weight is known, in order to determine the relationship between elution volume and the molecular weight of the polystyrene standard.

The molecular weight of an unknown polymer is determined by comparing the elution volume of this polymer to that of the polystyrene standard, assuming the same elution volume results in the same molecular weight. Therefore, this molecular weight is actually referred to as the molecular weight compared to polystyrene. Obviously, the conventional method cannot yield the absolute molecular weight of the polymer since the elution volume is only directly proportional to the size of the polymer, which in turn is related to the hydrodynamic volume of the polymer. For homopolymers, condensation polymers and strictly alternating copolymers there is a correlation between elution time and molar mass.

Thus, chemically similar polymer standards of known molar mass can be used for calibration. One must exercise care when analysing heterogeneous system such as copolymers and polymer blends by GPC. The dimensional distribution of macromolecules can generally only unambiguously correlate with the (methacryloxymethyl)methyldiethoxysilane (MMD) within one heterogeneity type. For samples consisting of molecules of different chemical compositions, the distributions obtained represent average of dimensional distributions of molecules having different compositions and therefore can not be attributed to certain types of molecules.

GPC was used to determine the molecular weights of the PAs and PUs prepared in this study. Samples of PAs and PUs were dried at 90 °C for 3 days under vacuum and then dissolved in DMAc. GPC analysis was carried out using a Waters model 610 pump, Waters model WISP 717 auto injector, model 410 refractive index detector and model 486UV detector at 254 nm. DMAc was used as solvent at a flow rate of 1.0 ml / min. Calibration was done using poly(methyl methacrylate) (PMMA) standards.

5.5 Thermogravimetric analysis (TGA)

TGA is especially useful for studying polymers and composite materials^{4,6}. It measures the amount and the rate of change in the weight of material as a function of temperature or time in a controlled atmosphere. TGA measurements are primarily used to determine the thermal stabilities of polymers and other compounds at temperatures up to 1000 °C.

TGA can be used to characterize a material that exhibits weight loss or gain due to decomposition, oxidation or dehydration. Results of TGA analysis provide information on the composition of multicomponent systems, the thermal and oxidative stability of materials, their estimated lifetime and decomposition kinetics.

TGA analyses of the PAs and PUs were carried out using a TGA-50 SHIMADZU thermogravimetric instrument with a TA-50 WSI thermal analyzer, connected to a computer. Samples (10–15 mg) were degraded in a nitrogen or air atmosphere (flow rate 50 ml / min) at a heating rate of 2.5–10 °C / min.

5.6 Differential Scanning Calorimetry (DSC)

DSC analyses of the various polymers were carried out with a TA Instruments Q100 DSC system. The DSC was calibrated by measuring the melting temperature of indium metal according to a standard procedure. All measurements were conducted under a nitrogen atmosphere flow and at a purge gas flow rate of 50 ml / min. The samples (1.0–3.0 mg) were heated in aluminum pans from 25 to 220 °C at 10 °C / min, held isothermally at 220 °C for 5 min, and then cooled to -30 °C at a rate of 10 °C / min. The crystallization curve was recorded. At -30 °C, the temperature was kept constant for 5 min, after which the melting curve was recorded between -30 and 190 °C at a heating rate of 10 °C / min.

5.7 References

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CHAPTER 6: RESULTS AND DISCUSSION

The results of experiments carried out to prepare and characterize the PAs and PUs are presented here.

6.1 ^1H NMR analysis

^1H NMR analysis of the monomers MPD and DDE was carried out to determine their purity¹.

^1H NMR of the PAs and PUs was carried to characterize them.

6.1.1 ^1H NMR of the MPD and DDE monomers

^1H NMR spectra of MPD and DDE monomers in DMSO-d_6 were recorded to check for purity and water content (see Figures 6.1 and 6.2). The spectral data are summarized in Table 6.1^{1,2} and were used as reference to identify the signals of the resulting polymers and polymer mixtures.

The spectra of DDS, FDC and IPDC are included in Appendix A.

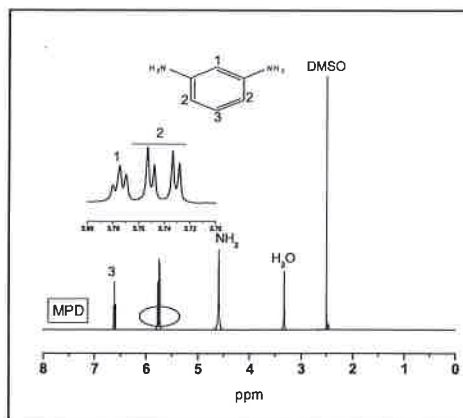


Figure 6.1: ^1H NMR spectrum of MPD

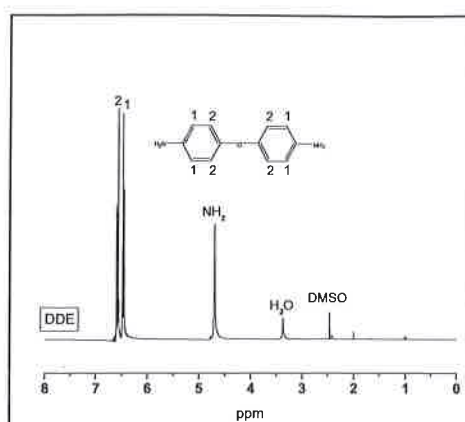


Figure 6.2: ^1H NMR spectrum of DDE

Table 6.1: ^1H NMR data for MPD and DDE monomers (solvent DMSO-d_6)

MPD: protons	MPD: shift (ppm)	DDE: protons	DDE: shift (ppm)
H (1)	5.77	H (1)	6.49–6.52
H (2)	5.72–5.75	H (2)	6.60–6.63
H (3)	6.63		

6.1.2 ^1H NMR spectra of PM 1 and PM 2 (Model compounds)

Data pertaining to the ^1H NMR and ^{13}C NMR spectra of PM 1 and PM 2 were reported in Section 4.3.2. The ^1H NMR and ^{13}C NMR spectra of PM 1 and PM 2 are close in terms of signals despite the differences in acid chlorides as illustrated in Appendix C.

6.1.3 ^1H NMR of the PAs

6.1.3.1 PA 1

The ^1H NMR spectrum of PA 1 and peak assignments are shown in Figure 6.3. The resonance signals for the two different aromatic ring protons appear at 8 ppm²⁹, whereas the resonance signals for the furan protons appear at around 7.5 ppm³¹,

depending on the position of the furan protons of the neighboring polyamide groups. Characteristic signals of the N-H protons appear in the region 10.71 ppm³.

The signal at 3.41 ppm is attributed to the residual water introduced by washing of the polymer. Despite thorough drying of the PAs before all analytical work commenced, these peaks remained present. The appearance of such water peaks in similar polymeric structures has also been reported by Mitiakoudis^{3,4}, indicating how tightly the water is bound by internal structures within such polymers or how hygroscopic these polymers are.

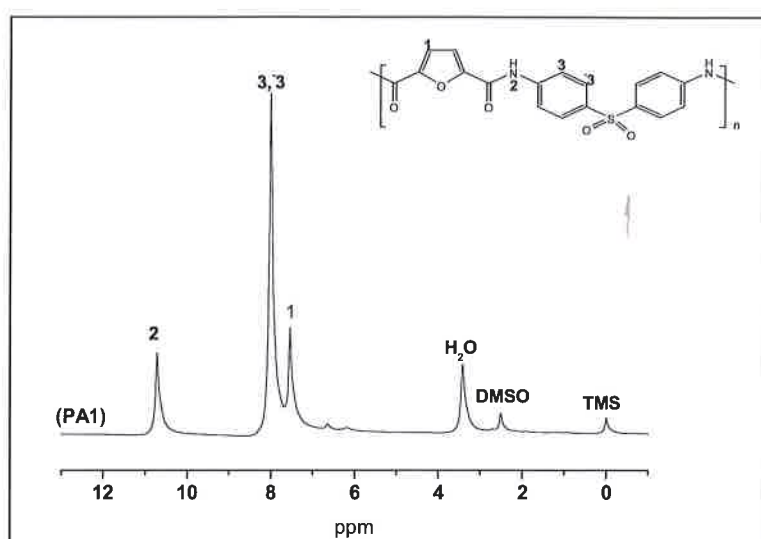


Figure 6.3: ¹H NMR spectrum of PA 1 in DMSO-d₆.

6.1.3.2 PA 3 - PA 4

The ¹H NMR spectra of PA 3 and PA 4 and related spectral data are shown in Figure 6.4 and Table 6.2, respectively. These PAs differ in the ratio between the FDC and IPDC used to prepare them. Similar peaks appear, but with different integration ratios. It is the NH signals at around 10.8 ppm that allows the calculation of the ratio between the different acid chlorides in the final polymer. For PA 4, the 90:10 FDC : IPDC-ratio in the starting mixture gives a 89 : 11 ratio in the polymer (determined by ¹H NMR). For PA 3, the 70:30 FDC : IPDC-ratio gives a 71 : 29 ratio in the polymer (determined by ¹H NMR).

Indications are therefore that the reactivity ratios of FDC and IPDC are similar, because the intended ratios between the two reagents were achieved with reasonable accuracy. The signals at 8.51–8.53 ppm originate from the aromatic protons of IPDC⁵. In PA 4 there is some overlap of the signals of the aromatic protons of DDS. The signals between 2 and 3 ppm are those of the methylene and methyl protons of the residual solvent NMP, which could not be removed fully. The presence of water is indicated at around 3.41 ppm.

Similar spectra of PA 2–PA 4, PA 12–PA14 and PA 16–PA 18 are shown in Appendix B.

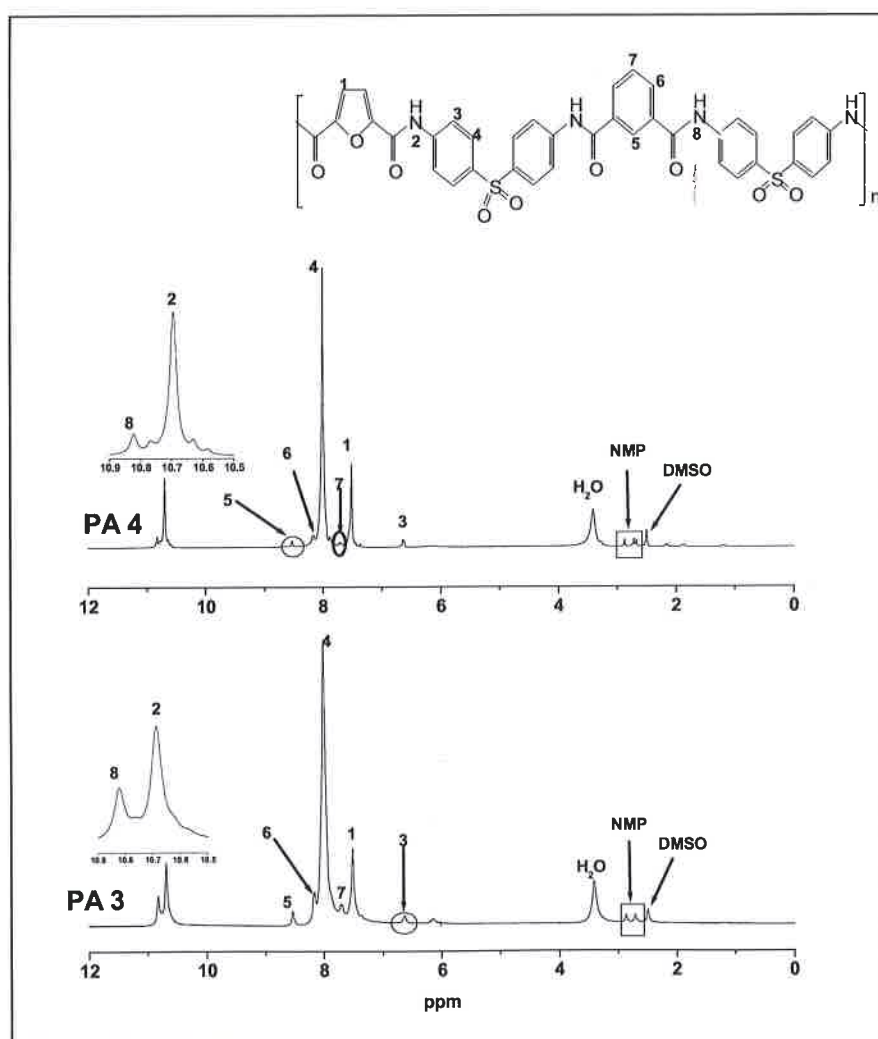


Figure 6.4: ¹H NMR spectra of PA 3 and PA 4 in DMSO- d₆.

Table 6.2: ^1H NMR data for PA 3 and PA 4 (solvent DMSO- d_6)

^1H NMR of PA 3	NMR shift (ppm)	^1H NMR of PA 4	NMR shift (ppm)
1(H)	7.50 ppm	1(H)	7.47ppm
2(H)	10.68 ppm	2(H)	10.65ppm
3(H)	6.64 ppm	3(H)	6.60 ppm
4(H)	8.00 ppm	4(H)	7.96 ppm
5(H)	8.53 ppm	5(H)	8.51 ppm
6(H)	8.17ppm	6(H)	8.16 ppm
7(H)	7.70 ppm	7(H)	7.69 ppm
8(H) / NH	10.81 ppm	8(H) / NH	10.82 ppm

6.1.3.3 PA 15, PA 17 and PA 19

The ^1H NMR spectra of PA 15, PA 17 and PA 19 are shown in Figure 6.5. (PA 15, with only FDC; PA 17 with 70:30 mixture between FDC and IPDC; PA 19 with only IPDC). Polymers with different acid chlorides and similar reactivity display statistical appearance of the units in the polymer chain and furnish complicated NMR spectra as a result.

The impact of each of the two acid chlorides FDC and IPDC on the NMR spectrum of PA 17 is clearly visible; the signals of both of the "parent" spectra can be detected⁶. Signals at about 2.64–2.66 ppm originate from amide hydrogens which absorb in the same range as acyl hydrogens (adjacent to C=O). They are slightly deshielded by the carbonyl group.

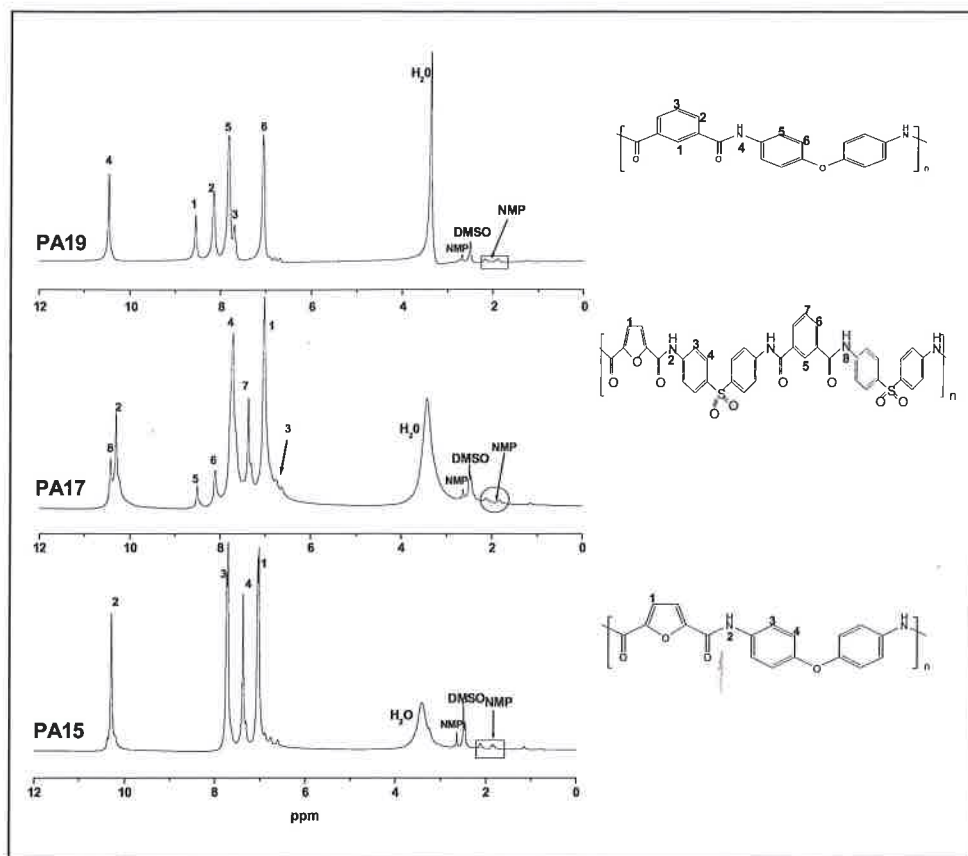


Figure 6.5: ^1H NMR spectrum of PA 15, PA 17 and PA 19 in $\text{DMSO}-d_6$.

6.1.3.4 PA 3, PA 11 and PA 16

The ^1H NMR spectra of PA 3, PA 11 and PA 16 are shown and compared in Figure 6.6. They were prepared with different ratios of acid chlorides and with different diamino compounds. There is also a difference in the peak positions of the furan protons. This is due to the different types of monomers and their functional groups used in the preparations. The signals in the region 7.49–7.80 ppm are attributed to the furan protons.⁸ Terminal amine groups in the region 2.6–2.65 ppm are visible for PA 11 and PA 16, but not for PA 3.

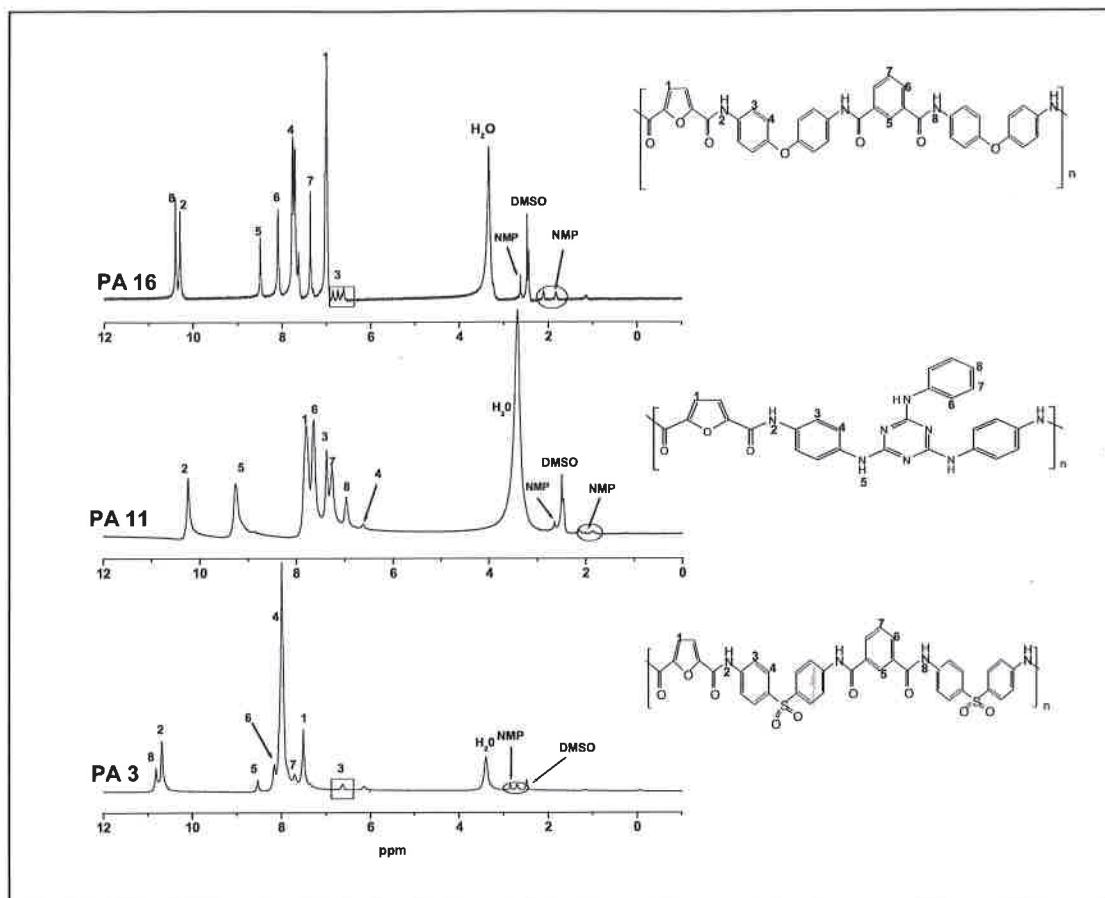


Figure 6.6: ^1H NMR spectrum of PA 3, PA 11 and PA 16 in $\text{DMSO}-d_6$.

6.1.4 ^1H NMR comparison between PA 1 and PU 2

The ^1H NMR data of PA 1 and PU 2, respectively a polyamide and a polyurea, with the same furanoyl and diamino diphenyl sulfone units, are tabulated in Table 6.3. As expected, the signals of the protons of the furan systems for PA 1 and PU 2 differ and the aromatic protons of PA 1 and PU 2 differ too.

There is a difference in the positions of the signals of both functional groups of the PA 1 and PU 2. The two broad signals in the region 5.2–6.0 ppm of the PU 2 are attributed to the urea N-H functions⁷. The signal at about 7.14 ppm is assigned to the furan protons of the PU 2; it is close to that of the PA 1⁷. The signals at about 8.67 ppm are attributed to N-H protons of the PU 2, whereas the protons of the amide groups of the PA 1 appear in the region of about 10.71 ppm.

Table 6.3: ^1H NMR of PA 1 and PU 2 (solvent DMSO-d_6)

PA 1 protons	NMR shift (ppm)	PU2 protons	NMR shift (ppm)
H Fu 1(H)	7.53	N H urea 1(H)	6.01
N-H 2(H)	10.71	H Fu	7.14
H aromatic 3(H)	8.19	NH urea	5.20
		N-H	8.67
		H aromatic 5(H)	7.65

6.2 ^{13}C NMR analysis

6.2.1 PA 1

The ^{13}C NMR spectrum of PA 1 and its peak assignments are shown in Figure 6.7. The ^{13}C NMR spectra of all the PAs show aromatic carbons at 148.51–120.76 ppm. The signals at 116.92 ppm and 142.90 ppm are attributed to furan carbons, whereas the resonance signals for the carbonyl carbon appear at 156.37 ppm, depending on the position of the carbonyl carbon with respect to neighboring amide groups^{3,9}.

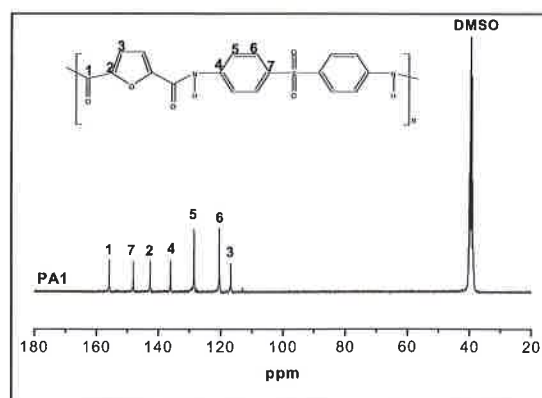


Figure 6.7: ^{13}C NMR spectrum of PA 1 in DMSO-d_6 .

6.2.2 PA 2 - PA 3

Figure 6.8 shows the ^{13}C NMR spectra of PA 2 and PA 3. These differ in the ratios of FDC to IPDC used in their preparation. PA 2 and PA 3 show aromatic carbons in the range 142.88–113.35 ppm, with the exception of the signals at 148.16 ppm and 116.97 ppm, which are attributed to the furan carbons of PA 2 and PA 3, respectively⁸. There are also signals originating from residual solvent NMP, which appear at around 17.14–48.57 ppm. Data are tabulated in Table 6.4.

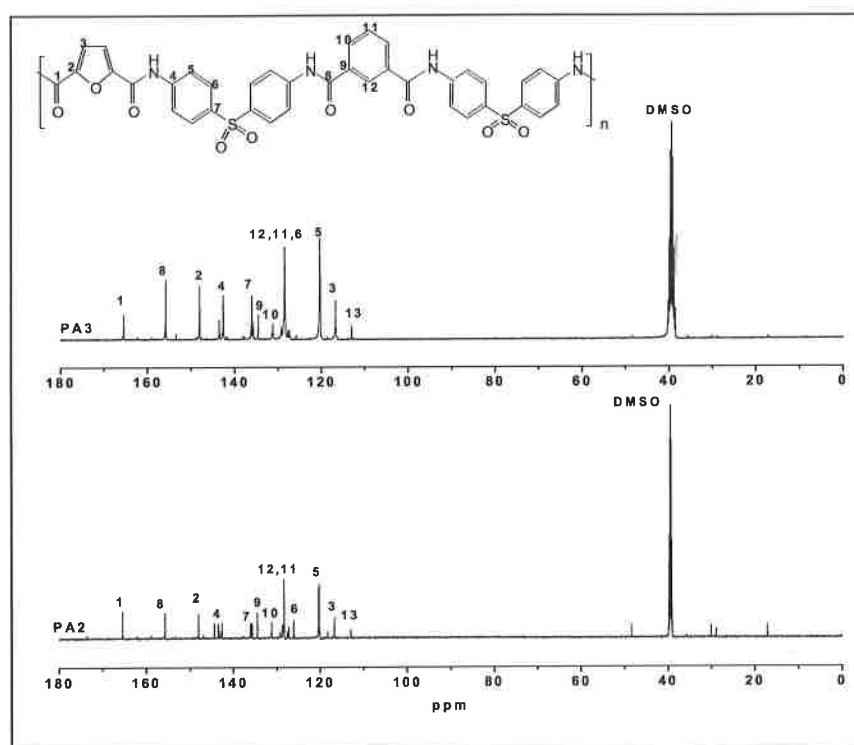


Figure 6.8: ^{13}C NMR spectra of PA 2 and PA 3 in DMSO-d_6 .

Table 6.4: ^{13}C NMR data for PA 1 and PA 3 (solvent DMSO- d_6)

PA 1 carbons	NMR shift(ppm)	PA 3 carbons	NMR shift(ppm)
C(1)	156.37	C(1)	166.05
C(2)	142.90	C(2)	148.48
C(3)	116.92	C(3)	116.74
C(4)	136.27	C(4)	142.88
C(5)	128.49	C(5)	127.01
C(6)	120.76	C(6)	120.42
C(7)	148.51	C(7)	136.51
-	-	C(8)	156.35
-	-	C(9)	134.55
-	-	C(10)	131.41
-	-	C(11)	127.58
-	-	C(12)	128.46
-	-	C(13)	113.35

6.2.3 PA15, PA 17 and PA 19

Figure 6.9 shows a comparison between the spectra of PA 15 (prepared using the dichloride FDC), PA 17 (prepared using the dichlorides FDC and IPDC) and PA 19 (prepared using the dichloride IPDC). There are only minor differences between the positions of the signals due to the presence of different functional groups. The signals that appear at 116.16 ppm and 148.46 ppm are attributed to the furan carbons of PA 15 and PA 17, respectively¹⁰. The signals of the carbon atoms of the carbonyl group appear at 155.59 ppm (PA 15), 165.19 and 155.35 ppm (PA 17) and 164.95 ppm (PA 19), respectively.

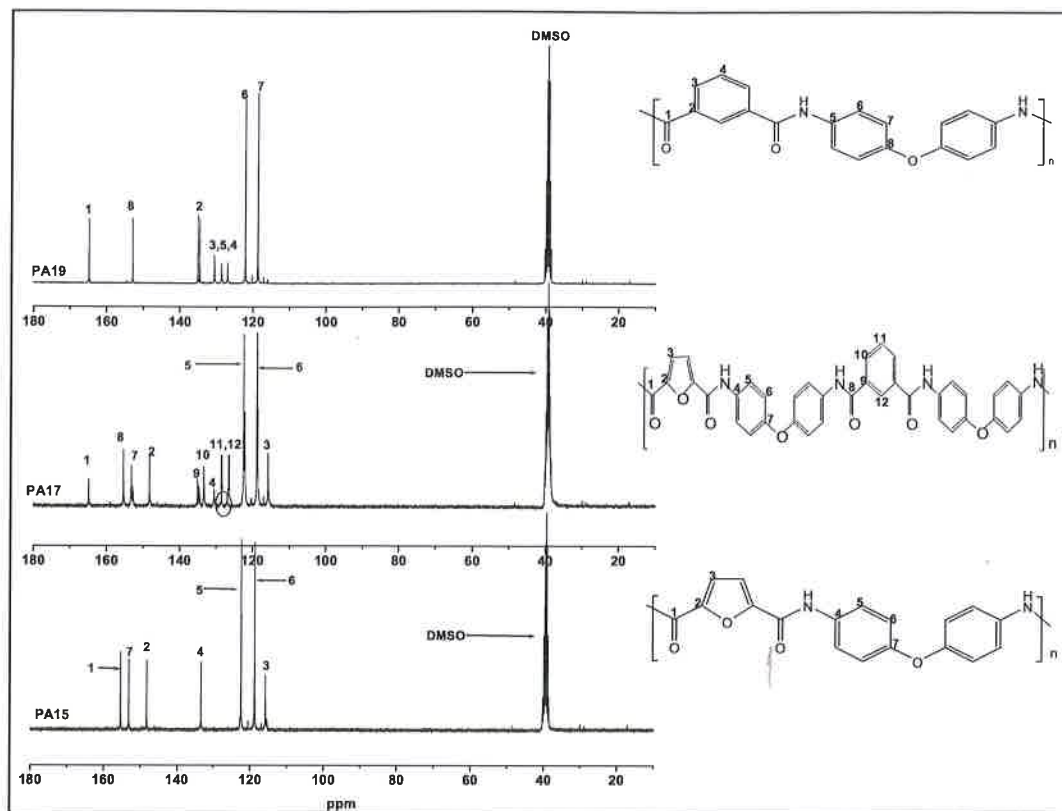


Figure 6.9: ^{13}C NMR spectra of PA 15, PA 17 and PA 19 in $\text{DMSO}-d_6$.

6.2.4 PA 3, PA 11 and PA 18

Figure 6.10 shows a comparison between the spectra of PA 3, PA 11 and PA18. There are very clear differences between the signals of the aromatic carbon atoms and the carbonyl groups atoms. The signals that appear at 116.74 ppm / 148.4 ppm, 115.89 ppm / 148.29 ppm and 116.12 ppm / 148.42 ppm are attributed to the furan carbons, respectively¹¹. The signals of the carbon atoms in the carbonyl group appear at 165.05 ppm / 156.35 ppm, 164.24 ppm and 155.55 ppm for PA 3, PA 11 and PA18, respectively¹². The signal at around 116 ppm, which belongs to the furan system, is naturally missing in the spectra of PA19 (only isophthalic acid monomer).

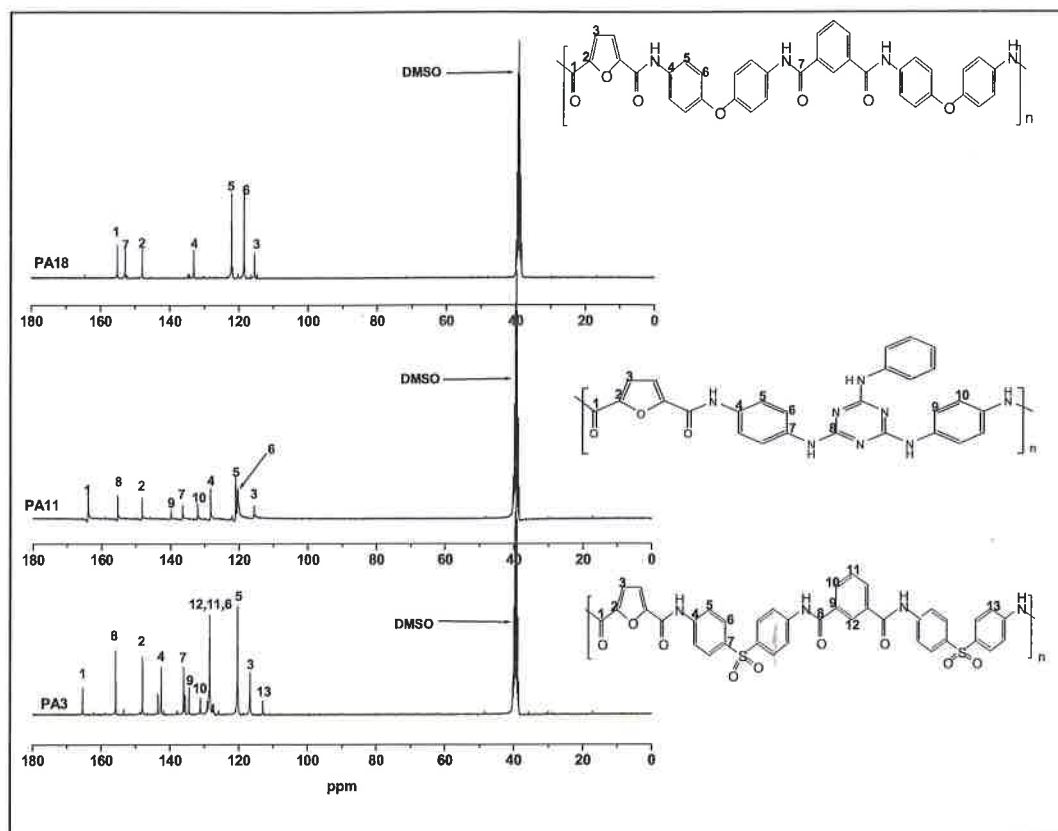


Figure 6.10: ^{13}C NMR spectrum of PA 3, PA 11 and PA 18 in $\text{DMSO}-d_6$.

6.3 Fourier- Transform Infrared Spectroscopy (FTIR)

FTIR analysis was used to characterize the synthesized PAs and the PUs. This technique can also be used to monitor the transformations in reactions which take place during in the preparation of PUs, namely the change of amine groups into amide groups, and the disappearance of isocyanate groups

6.3.1 Characterization of the PAs

The structure of the PAs was verified by FTIR spectroscopy (see Figure 6.11 for PA 1). The N-H groups show absorption peaks between 3475 and 3150 cm^{-1} , due to the asymmetrical and symmetrical N-H stretching of the amide group (R-CO-NH_2)³.

Amides show a very strong absorption peaks for the C=O group in the range 1680–1630 cm^{-1} .³ The peaks at about 1640–1550 cm^{-1} are due to the N-H bend for primary and secondary amides^{1,2}. The peaks about 3300 cm^{-1} are due to the N-H stretching of PA groups¹. The peaks at about 1550 cm^{-1} and 1500 cm^{-1} are due to the C=C of the furans. The peaks at about 1640 cm^{-1} and 1600 cm^{-1} are due to the C=C double bonds of the aromatic systems.¹ These C=C aryl peaks are not seen in Figure 6.11; the spectrum is dominated by the N-H bend peaks of the PA groups at about 1640 cm^{-1} and 1550 cm^{-1} .

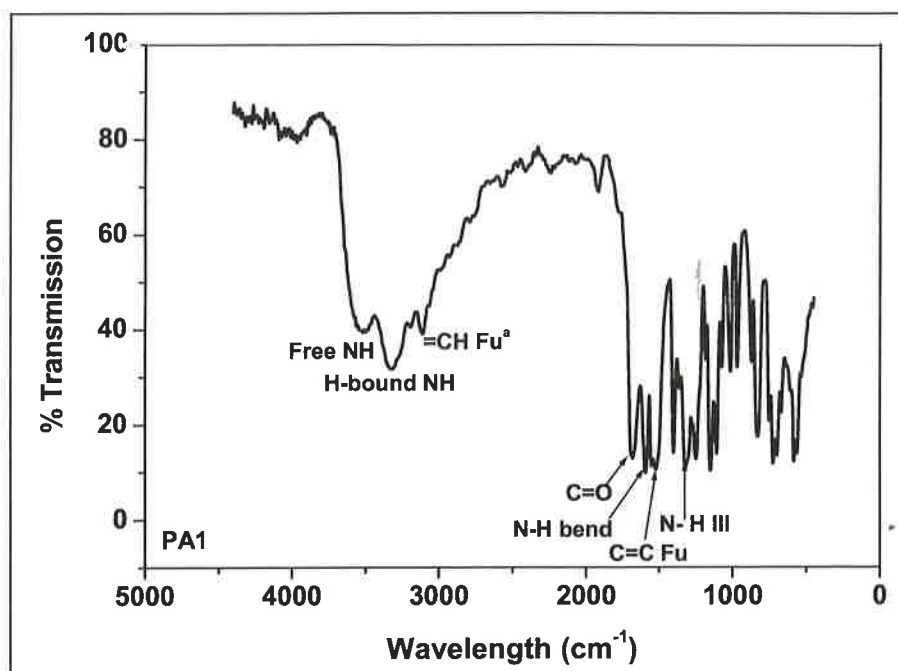


Figure 6.11: FTIR spectrum of PA 1.

Table 6.5: FTIR data for PA 1 – PA 4

Assignment	PA1	PA2	PA3	PA4	Reference
Stretching vibration of the polyamide free- NH	3473	3472	3472	3470	1
Stretching vibration of the H-bond NH	3322	3328	3315	3315	3
Stretching vibration of the =CH Fua	3113	3115	3119	3109	3
Amide I, stretching vibration of the C=O bond	1673	1667	1677	1675	3
Amide II, stretching vibration of the N-H bend Amide III, stretching vibration of N-H	1594 1307	1590 1314	1583 1320	1594 1316	13
Stretching vibration of the C=C Fu	1529	1516	1523	1520	3
Stretching vibration of the C=C Ar	1605	1609	1612	1608	2
Stretching vibration of the Fu breathing	1015	1009	1015	1015	3,1
Stretching vibration of the 2,5- disubstituted FU	961 829 722	967 835 710	961 830 716	961 829 716	3,2

6.3.2 PA 15, PA 16 and PA 19

The FTIR spectra of PA 15, PA 16 and PA 19 are shown in Figure 6.12. The peak at 3319 cm^{-1} is assigned to the free NH^1 . The peak at 3119 cm^{-1} is assigned to the NH stretching peak of the PA^3 . The very strong peak at 1670 cm^{-1} is due to the carbonyl group of the PAs ². The peak at 1590 cm^{-1} is assigned to N-H bend of primary and secondary amides ^{2,3}.

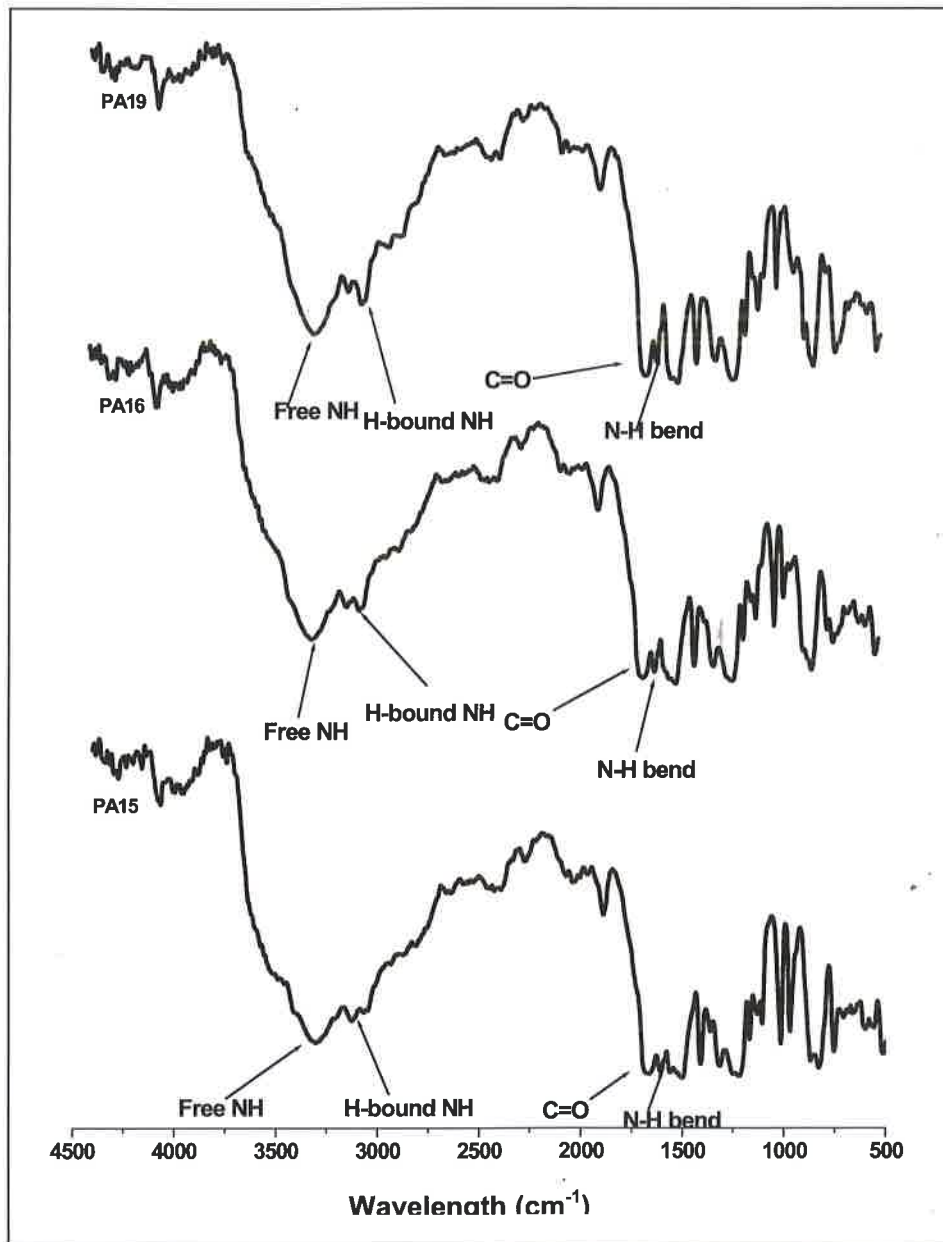


Figure 6.12: FTIR spectra of PA 15, PA 16 and PA 19.

Table 6.6: FTIR data of selected PAs and PUs

Assignment	PA9	PA10	PA 12	PA 17	PU 1	PU 2	Reference
Stretching vibration of the free NH	3406	3411	3406	3416	3456	3460	1,7
Stretching vibration of the H-bound NH	3291	3301	3306	3311	3286	3306	2,7
Stretching vibration of the =CH Fu	3105	3082	3115	3119	2961	2962	1, 2,7
Stretching vibration of the NCO	-	-	-	-	2243	2245	7
Amide I, stretching vibration of the C=O bond	1666	1652	1655	1661	1651	1651	2,7
Amide II, stretching vibration of the N-H bend	1589	1569	1536	-	1577	1551	1,3,7
Stretching vibration of the C=C Fu	1531	-	-	1527	1526	1527	13,14
Stretching vibration of the C=C Ar	1608	-	-	1608	-	1608	3,7,14
Stretching vibration of the Fu breathing	1011	1011	1019	1012	1014	1016	1,2,14
Stretching vibration of the 2,5- disubstituted FU	958 824 742	963 817 752	963 805 754	963 829 752	960 834 757	968 842 767	1,3,7

6.3.3 PA 4, PA 8 and PA 16

The FTIR spectra of PA 4, PA 8 and PA 16 are shown in Figure 6.13 and compared. In PA 4 the peak at 3470 cm^{-1} is assigned to free NH, and in PA 8 and PA 16 the peaks that appear at about 3287 cm^{-1} are assigned to free NH³. In PA 4 the peak at 3315 cm^{-1} is attributed to H-bound NH, and in PA 8 and PA 16 the peaks at about 3130 cm^{-1} are assigned to H-bound NH².

In PA 4 the C=O peak appears at 1675 cm^{-1} . These peaks sometimes overlap with the N-H bending peaks, in the range of $1640\text{--}1620\text{ cm}^{-1}$, as seen in PA 8 and PA 16 respectively^{1,2}. The peaks at about 1550 cm^{-1} and 1500 cm^{-1} are attributed to the C=C of furan ring, as seen in PA 4¹³. The peaks at around 1640 cm^{-1} and 1600 cm^{-1} are due to

the C=C of the aryls². These C=C aryl peaks² disappear in PA 8 and PA 16; where they are dominated by N-H bending peaks and C=C double bonds of the furan rings³.

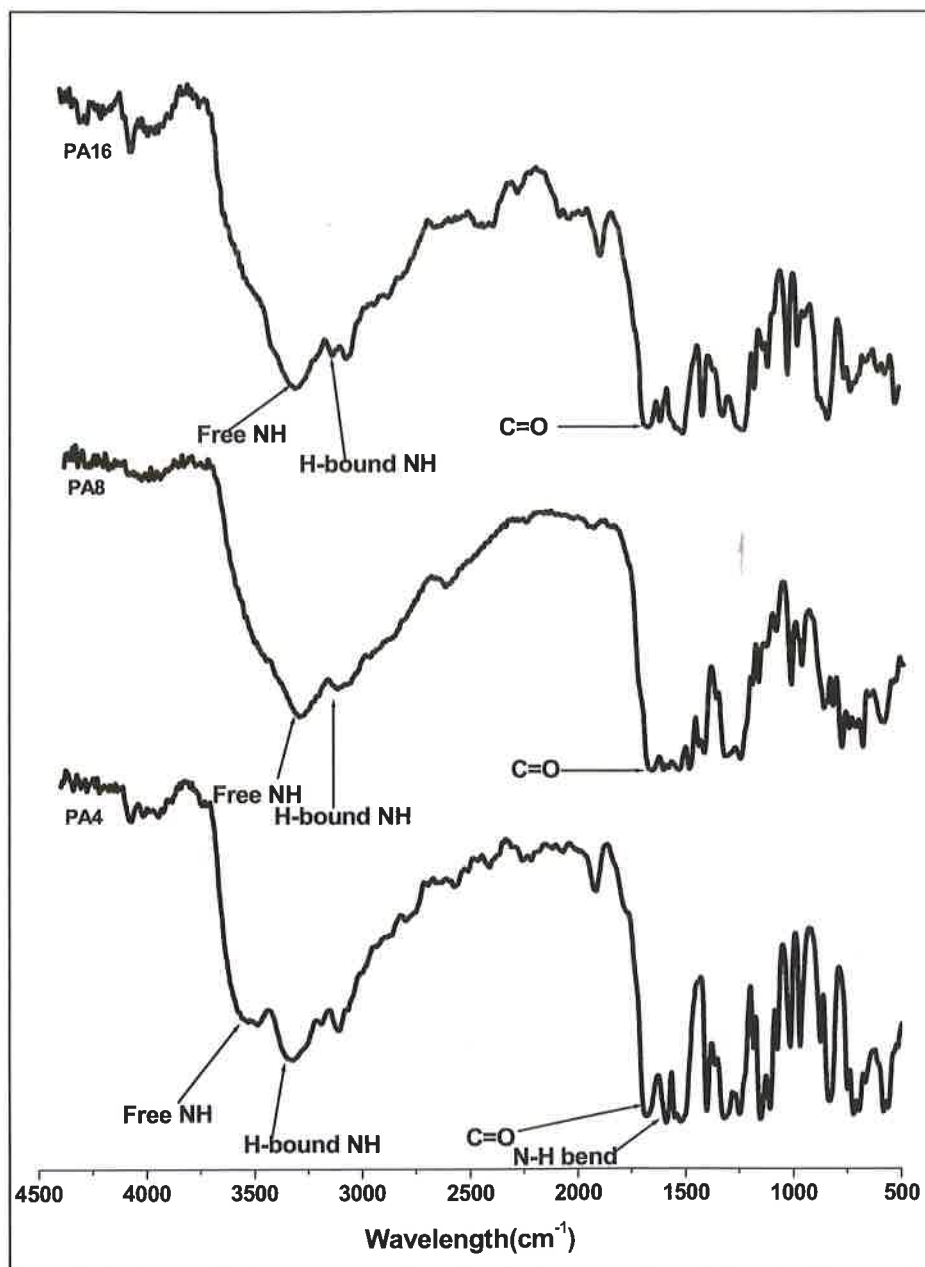


Figure 6.13: FTIR spectra PA 4, PA 8 and PA 16.

6.3.4 Comparison between PA 4 and PU 2

The FTIR spectra of PA 4 and PU 2 are shown in Figure 6.14. Several peaks overlap at about 1600 cm^{-1} and 1500 cm^{-1} , especially in PU 2. In PA 4 the free NH peak appears at 3470 cm^{-1} and in PU 2 it appears at 3456 cm^{-1} . In PA 4 the peak at 3315 cm^{-1} is attributed to H-bound NH and in PU 2 it appears at about 3286 cm^{-1} . The band at about 3109 cm^{-1} is attributed to =CH of the furans for PA 4 and that at about 2961 cm^{-1} is attributed to =CH of the furans for PU 2.

The band at about 2243 cm^{-1} is attributed for NCO for PU 2^{7, 14}. The C=O band at about 1675 cm^{-1} is assigned to PA 4 and that at about 1651 cm^{-1} for PU 2. The band at about 1594 cm^{-1} is attributed to NH bend for PA 4 and that at about 1594 cm^{-1} is assigned to NH bend for PU 2. The band at 1520 cm^{-1} is assigned to C=C of furane for PA 4 and that at 1526 cm^{-1} is assigned to PU 2. The peak at 1610 cm^{-1} and 1600 cm^{-1} is attributed for C=C aryl. These C=C aryl peaks^{3,14} disappear in PA 4 and PU 2 as shown in figure 6.14 and are dominated by the N-H bending band of the polyamide and polyureas groups at about 1640 cm^{-1} and 1550 cm^{-1} .

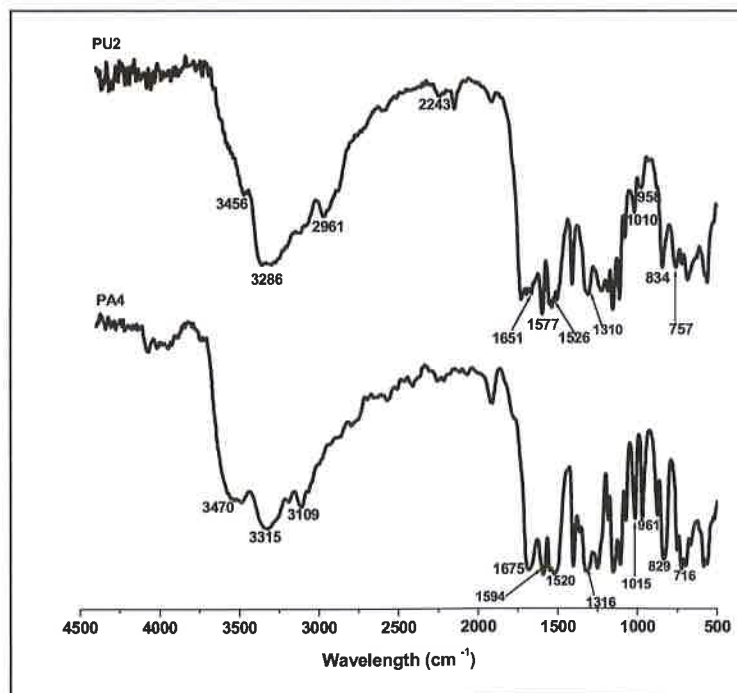


Figure 6.14: FTIR spectra of PA 4 and PU 2.

6.4 Gel permeation chromatography (GPC)

GPC analysis was done to characterize the PAs and PUs in terms of molecular weight and molecular weight distribution. Experimental details were described in Section 5.4.

6.4.1 GPC of PA 1

Figure 6.15 shows the bimodal GPC trace of PA 1. The shoulder is due to a low molecular weight fraction. Homogenous phase polymerization was used to synthesize the PA 1, which could lead to a broad molecular weight distribution. The weight-average molecular weight (M_w), number-average molecular weight (M_n) and the polydispersity index (PDI) obtained for PA 1 by GPC were 79174 g mol^{-1} , 62766 g mol^{-1} and 1.26, respectively (for the main peak).

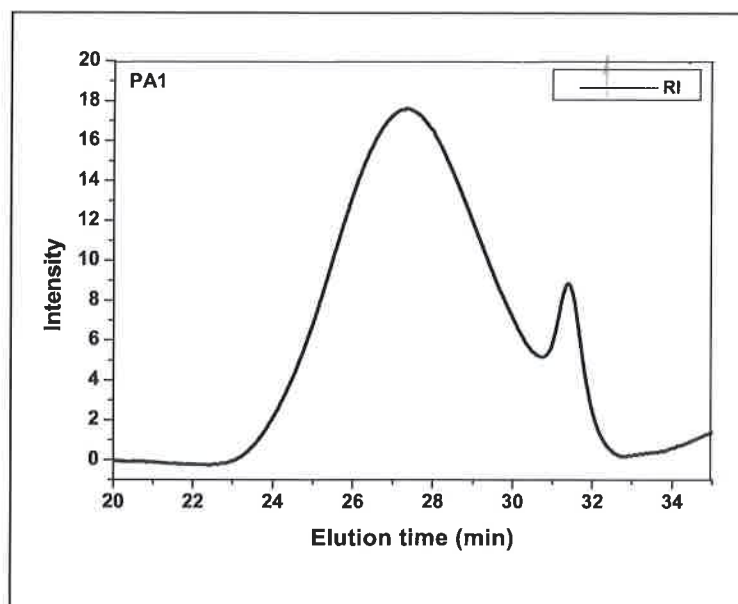


Figure 6.15: GPC chromatogram of PA 1.

6.4.2 GPC of PA 2 - PA 4

Figure 6.16 shows the GPC traces of PA 2–PA 4, all of which have shoulders, due to low molecular weight fractions. Homogenous phase polymerization and interfacial polymerization were used to synthesize these PAs, which could lead to broad molecular weight distribution. The M_w , M_n and PDI values are tabulated in Table 6.7. The PA 2 –

PA 4 have relatively narrow molecular weight distributions. These data were obtained during GPC analysis with poly(methylmethacrylate) (PMMA) standards and absolute N,N-dimethylacetamide (DMAc) was used as solvent. There are small peaks for PA 2 – PA 4 in the 31–32 minutes elution time range, which suggest contributions by lower molecular weight components and excess DDS monomer¹⁵.

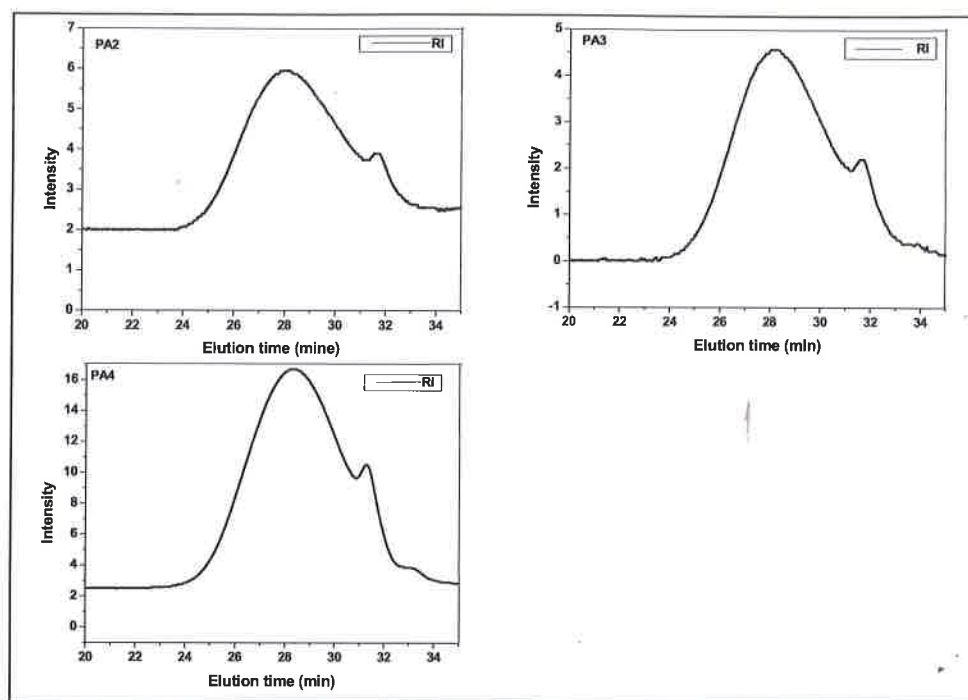


Figure 6.16: GPC chromatograms of PA 2 – PA 4.

Table 6.7: M_n , M_w and PDI values of PA 2 – PA 4

Polymer	M_n (g mol ⁻¹)	M_w (g mol ⁻¹)	PDI
PA 2	16807	33015	1.96
PA 3	14625	30808	2.10
PA 4	54298	62411	1.14

6.4.3 GPC of PA 15 - PA 17 and PA 19

Figure 6.17 and Table 6.8 show the GPC traces and data of PA 15 – PA 17 and PA 19 which were synthesized by homogenous phase polymerization. The M_w , M_n and PDI values of PA 15 – PA 17 were very similar. These values differed from those of PA 19, but the values for PA 19 were similar to those of PA 1 (refer to Figure 6.15). There is a small peak in the GPC traces, caused by the presence of lower molecular weight components and excess DDE monomer¹⁵.

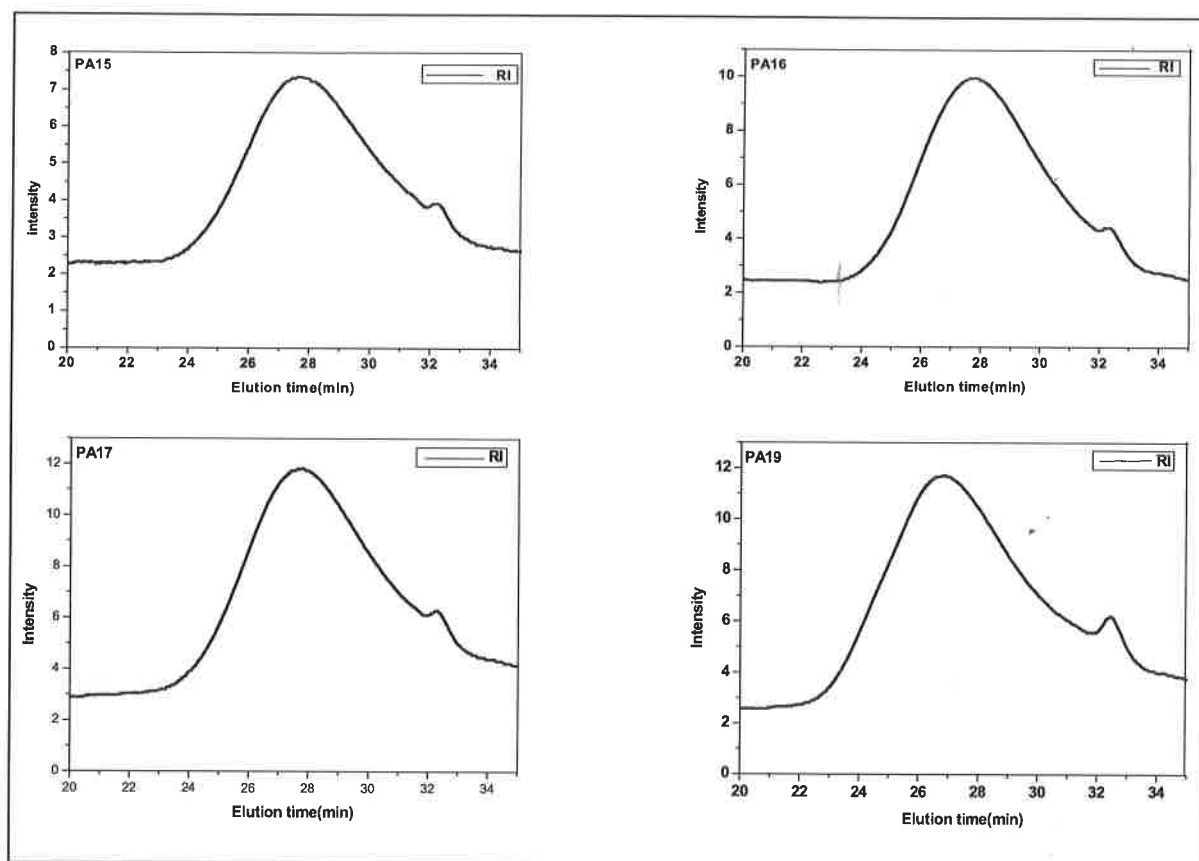


Figure 6.17: GPC traces of PA 15 – PA 17 and PA 19.

Table 6.8: M_n , M_w and PDI values of PA 15 – PA 17 and PA 19

Polymer	M_n (g mol ⁻¹)	M_w (g mol ⁻¹)	PDI
PA 15	15667	39774	2.53
PA 16	15685	38268	2.43
PA 17	14205	39379	2.77
PA 19	15584	59175	3.79

6.4.4 GPC of PA1, PA 13 and PA 18

Figure 6.18 and Table 6.9 show the GPC traces of PA 1, PA 13 and PA 18, which were synthesized by homogenous phase polymerization. The GPC data of these are compared in order to determine the impact of functional groups on the values of M_n , M_w and polydispersity and also on the molecular weight distributions (broad or narrow). Again it is seen that the functional groups had an effect on the emergence of small peaks, as was found for PA 1 - PA 4.

Table 6.9: M_n , M_w and PDI for PA 1, PA 13 and PA 18

Polymer	M_n (g mol ⁻¹)	M_w (g mol ⁻¹)	PDI
PA 1	62766	79174	1.26
PA 13	13802	32674	2.36
PA 18	15269	37947	2.48

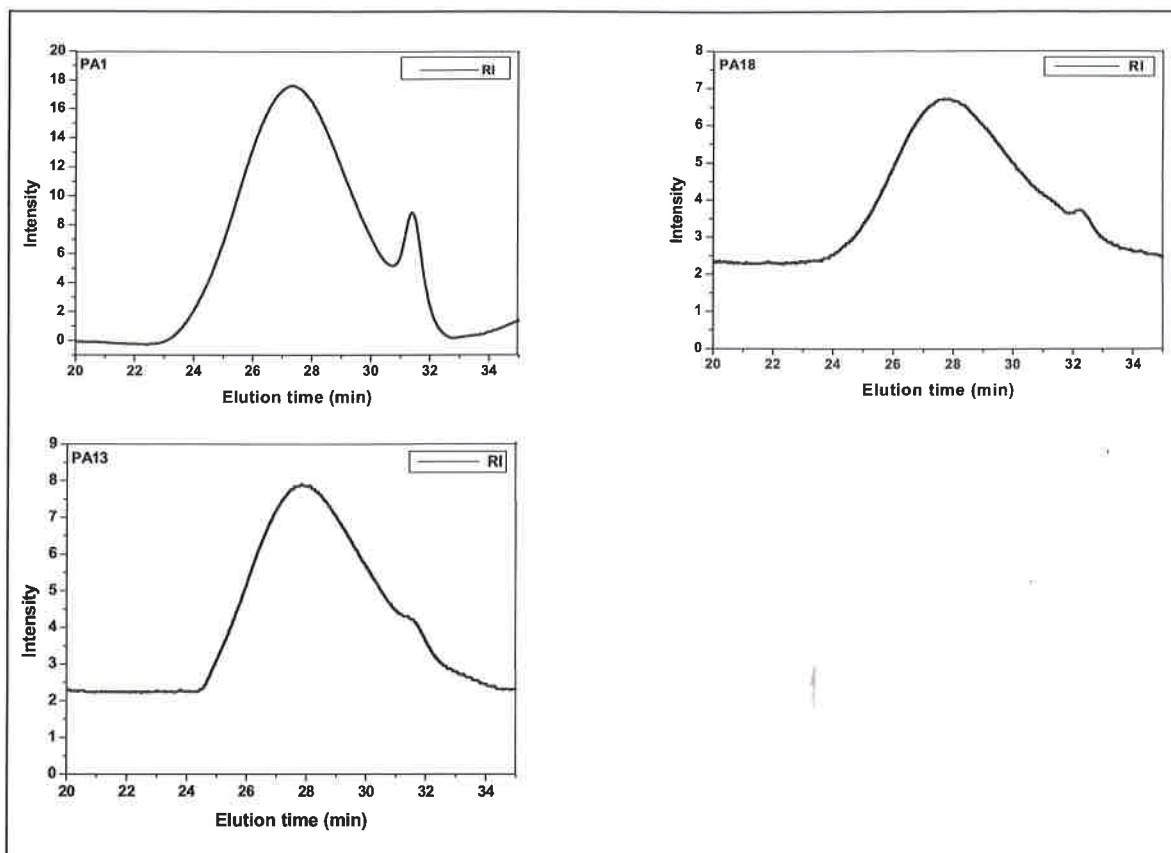


Figure 6.18: GPC traces of PA 1, PA 13 and PA 18.

6.4.5 Comparison between PA 11 and PU 1

Figure 6.19 and Table 6.10 show the GPC traces of PA 11 and PU 1. Both polymers were synthesized by homogenous phase polymerization. The M_w , M_n and PDI values are tabulated in Table 6.10. Compared to values for the standard range for polycondensation reactions these the polymers have quite a narrow molecular weight distribution and have few oligomers¹⁶.

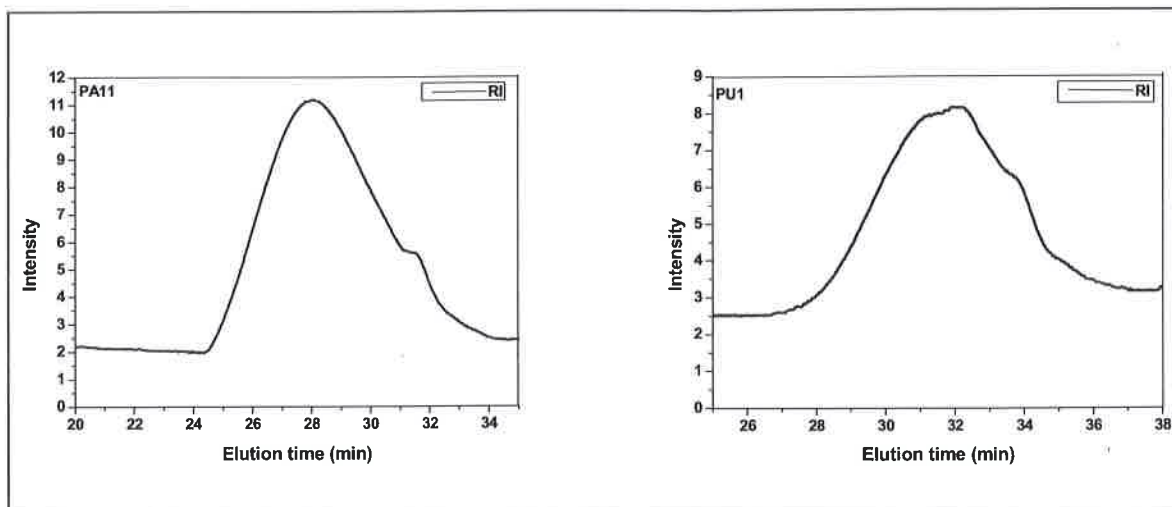


Figure 6.19: GPC traces of PA 11 and PU 1.

Table 6.10: M_n , M_w and PDI values of PA 11 and PU 1

Polymer	M_n (g mol ⁻¹)	M_w (g mol ⁻¹)	PDI
PA 11	14851	31827	2.14
PU 1	3580	7892	2.20

6.5 Thermogravimetric analysis (TGA)

Various techniques have been used to study the thermal degradation of polymers, including pyrolysis mass spectroscopy, thermal volatilization analysis and etc¹⁷. However, TGA analysis is the most widely used for polymers^{18, 19}. Dried samples of PAs and PUs were analysed to investigate their thermal stability.

6.5.1 Thermal stability of PA 1

Figure 6.20 displays the patterns of decomposition of PA 1, which took place in three stages. In the first stage there was a small weight loss of 5% in the temperature range 72–79 °C, due to moisture being released (PAs are hygroscopic – amide groups are involved in hydrogen bonding with adsorbed water molecules)¹⁶⁻¹⁸ and to the residual

NMP solvent evaporation. The second step of the degradation took place at a temperature of about 470 °C. The third step of the degradation took place at about 560 °C and may be attributed to the oxidation of the residual material. This stage ended with the loss of the volatile fractions and a mass loss that did not change much after 650 °C.

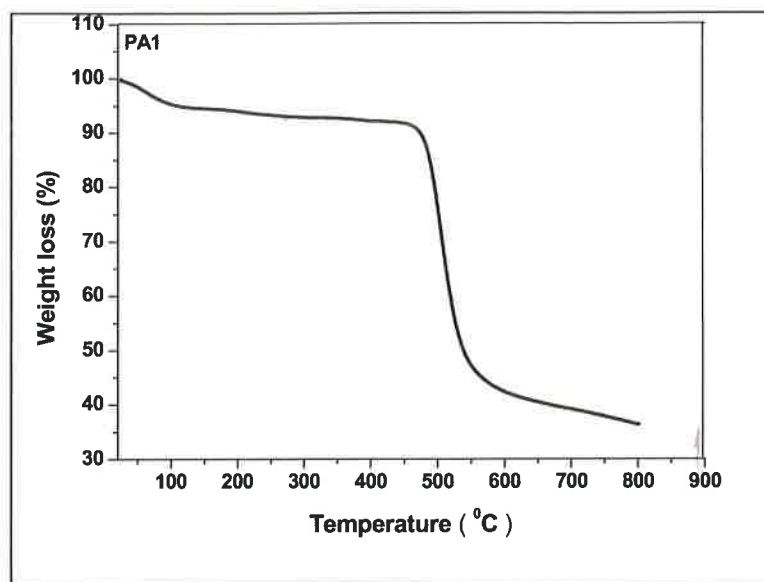


Figure 6.20: TGA curve of PA 1.

6.5.2 Thermal stability of PA 1- PA 4

Figure 6.21 shows the TGA curves of PA 1 – PA 4, prepared using different ratios of FDC and IPDC and the decomposition that takes place in three stages. In the first stage there is a small weight loss of about 2–5% at the beginning of the TG curves of the PA 1 – PA 4 in the temperature range 70–79 °C. As mentioned in Section 6.5.1, this is due to the evaporation of the residual water remaining in the polymer even after drying^{1,20}.

In the second stage of the degradation there are differences between the curves in Figure 6.21(a) and (b): PA 2 – PA 4 had degradation temperatures of about 447 °C, compared to PA1 that had a degradation temperature of 470 °C indicating that PA 2 –PA 4 contained larger amounts of water than PA 1. The third step of the degradation takes place at a temperature of about 560 °C for PA 1 and about 590 °C for PA 2 – PA 4. That

step may be attributed to the oxidation of the residual material. This stage ends with the loss of the volatile fractions and a mass loss that does not change much after 650 °C²¹.

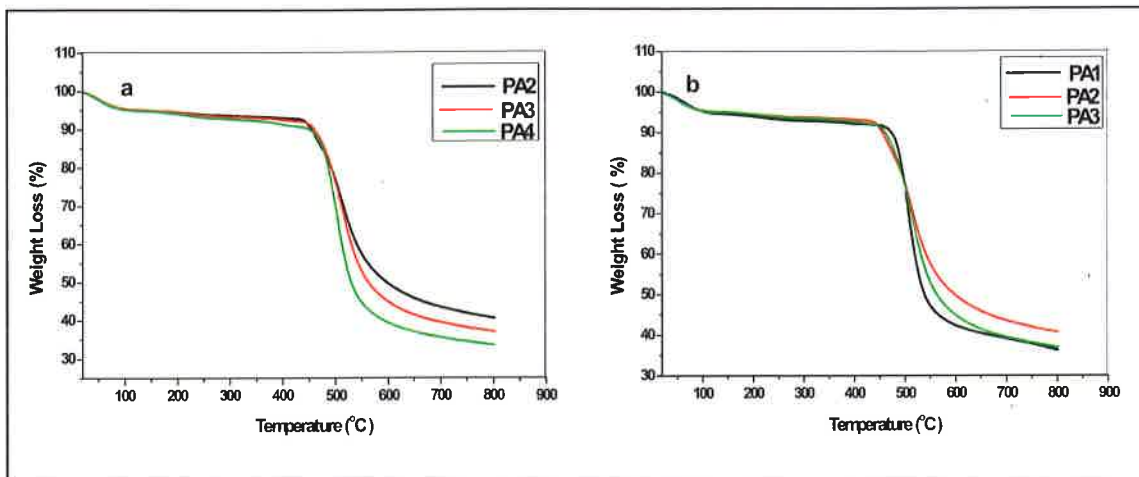


Figure 6.21: TGA curves of PA 1 – PA 4.

6.5.3 Thermal stability of PA 15 - PA 19

Figure 6.22 displays the decomposition of PA 15 – PA 19, which takes place in three stages. In the first stage there is a small weight loss of about 2–5% in the temperature range 70–85 °C, attributed to water remaining in the polymer (even after extensive drying)^{20,22}. In the second stage of the degradation there are differences noted in the curves in Figure 6.22 (a) and (b). PA 16 – PA 18 degraded at temperatures of about 420– 430 °C, while PA 19 only degraded at about 460 °C.

This proposed reason for this is that PA 16 – PA 18 contained more water than PA 19. The third stage of the degradation takes place at temperatures of about 640 °C²³ due to the oxidation of the residual material. This stage ends with the loss of the volatile fractions and a mass loss that does not change much after 750 °C.

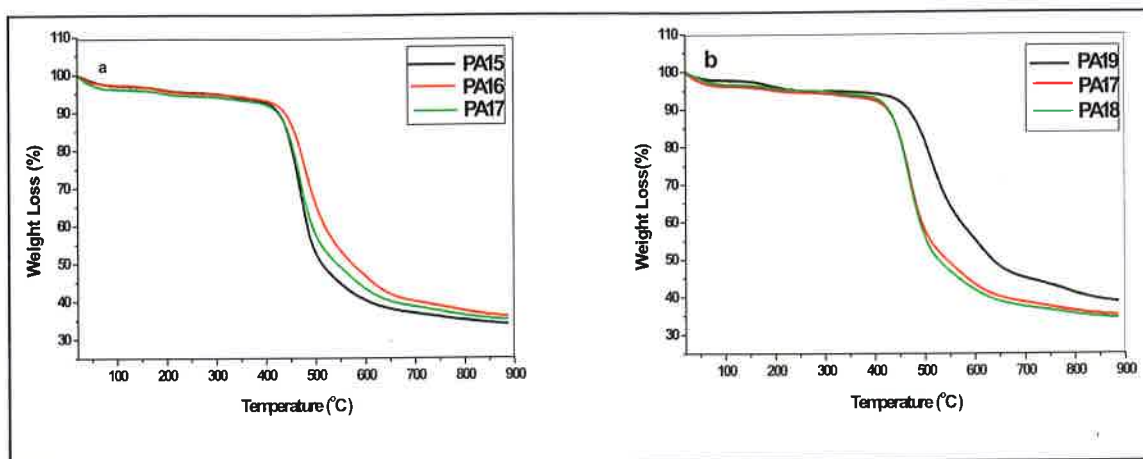


Figure 6.22: TGA curves of PA 15 – PA 19.

6.5.4 Thermal stability of PA 1 - PA 4, PA 10 - PA 13 and PA 15 - PA 19

Figure 6.23 displays the patterns of decomposition of the three types of polymers and with different ratios between the two acid chlorides. The first stage of the degradation of all types show a small weight loss of about 2–5% in the temperature range 70–100 °C, attributed to the evaporation of the residual water remaining in the polymer even after drying. In the second stage of degradation there are only small differences between polymers in Figure 6.23 (a). In PA 1 there is decomposition at 470 °C and in PA 4 there is decomposition at about 447 °C, while in PA 15 and PA 18 there is decomposition at about 412 °C.

In the Figure 6.23 (b) the degradation curves are different, in a temperature range of 430–447 °C. PA 10 and PA 11 differ in the type of diacid monomer used in their preparation, but in both polymers BAT is used as the amine component. The curves are quite similar. Likewise for PA 2 and PA 3, where different acid chlorides and in different ratios were used. For those, more weight loss is encountered. PA 12 and PA 13 and PA 16 and PA 17 use two acid chlorides (FDC and IPDC) in different ratios and show similar behaviour. Here the amine component used is the deciding factor for the weight loss. When DDE was used in the preparation of PAs, there was more weight loss than when BAT was used.

As previously noted, degradation will be equal in the case of different component ratios regardless of the type of polymer. Amine monomers play the greater role in the PA degradation and their influence should be investigated further. The third stage of the degradation takes place in the temperature range of 570–650 °C and may be attributed to the oxidation of the residual material^{24, 28}. This stage ends with the loss of the volatile fractions and a mass loss that does not change much after 800 °C.

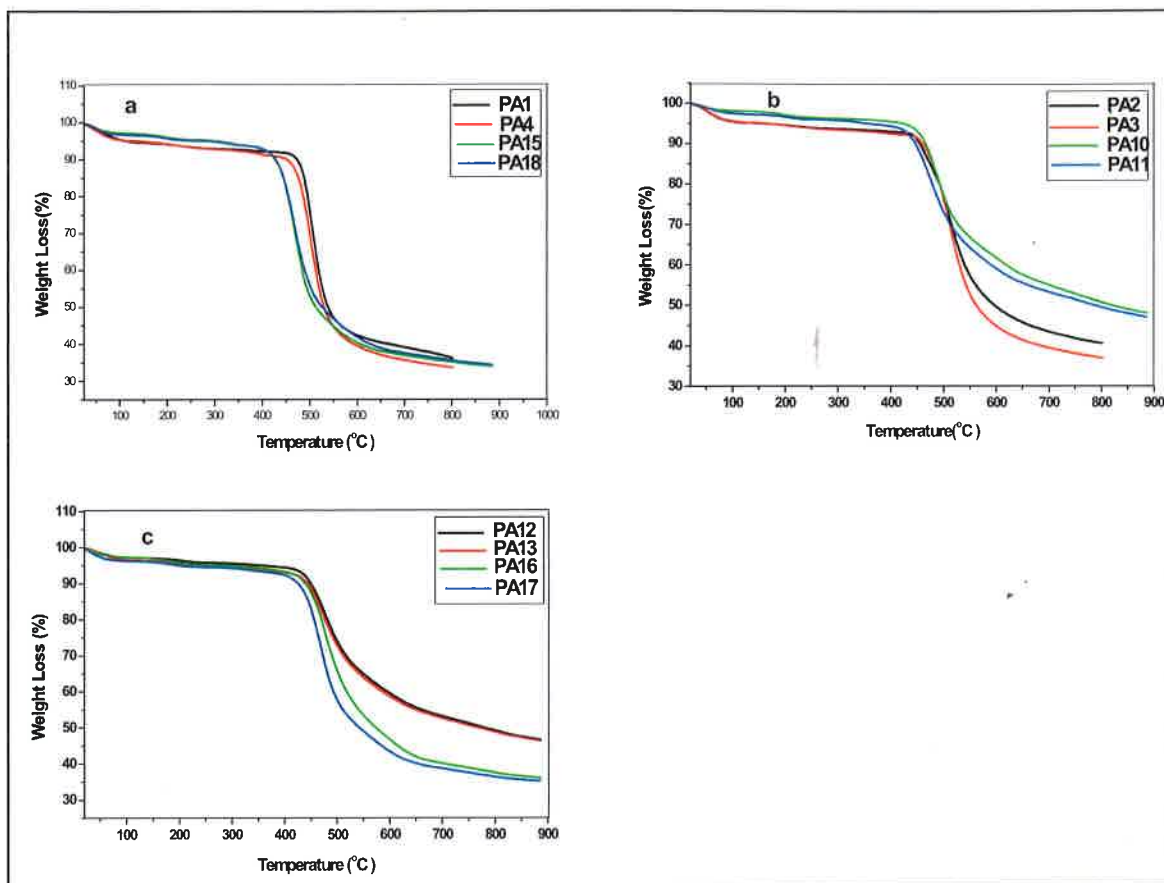


Figure 6.23: TGA curves of PA 1 – PA 4, PA 10 – PA 13 and PA 15 – PA 19.

6.5.5 Comparison between PA 15 and PU 2

Figure 6.24 displays the TGA curves of the decomposition of PA 15 and PU 2 and a comparison between them. In the first stage of the degradation are for both of them weight losses of about 3–5% at the temperature range 70–90 °C, which are attributed to

the evaporation of the residual water and solvent (NMP) remaining in the polymers even after drying.

The second stage of degradation shows clear differences between the polyamide PA 15 (polyamide with 100% FDC and 100% DDE) and the polyurea PU 2 (furan building block and DDS) in terms of thermal stability. PU 2 decomposes with a weight loss of about 10% already at low temperatures of 160–200 °C, and continues to lose weight steadily^{29,30}, while PA 15 decomposes and loses only about 10% weight up to temperatures of 412 °C, followed by further and steeper weight losses.

The third stage of the degradation of PA 15 takes place at about 640 °C, while degradation of PU 2 takes place at about 500 °C, due to oxidation of the residual material. This stage ends with the loss of the volatile fractions and a mass loss that does not change much after 750 °C for PA 15 and 500 °C for PU 2. Hence indications are that the thermal properties of PA 15 are better than those of PU 2.

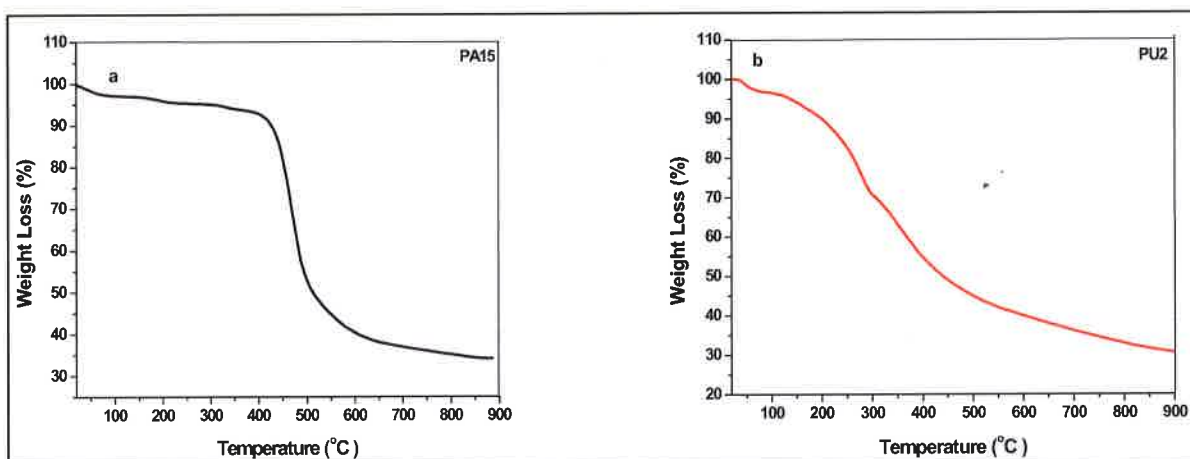


Figure 6.24: TGA curves of PA 15 and PU 2.

6.6 Differential scanning calorimetry (DSC)

The DSC thermograms of polyamides (PA 1 - PA 19) and polyureas (PU 1 and PU 2) were recorded under nitrogen at a heating rate of 10 °C / min. It is advisable that the sample is cycled twice to remove traces of absorbed moisture or solvent.

6.6.1 DSC data of PAs and PUs

Figure 6.25 and Table 6.11 show the heating curves and the T_g values of several PAs and PUs. There are differences between the different types of PAs themselves in terms of thermal properties as well as between the PAs and PUs. The glass transition temperatures of PA 1 – PA 4 show a similarity at the first heating, at around 91 °C (Table 6.11)^{1, 3}. For PA 10 and PA 17 in the second heating there are traces that do not display any transitions or endotherms up to 350 °C, which could be assigned to melting transitions^{16, 29}. These results indicate that the polymers PA 10 and PA 17 have an amorphous nature²⁰. The DSC traces for PU 2 for the first heating shown a T_g of 130.55 °C³¹⁻³².

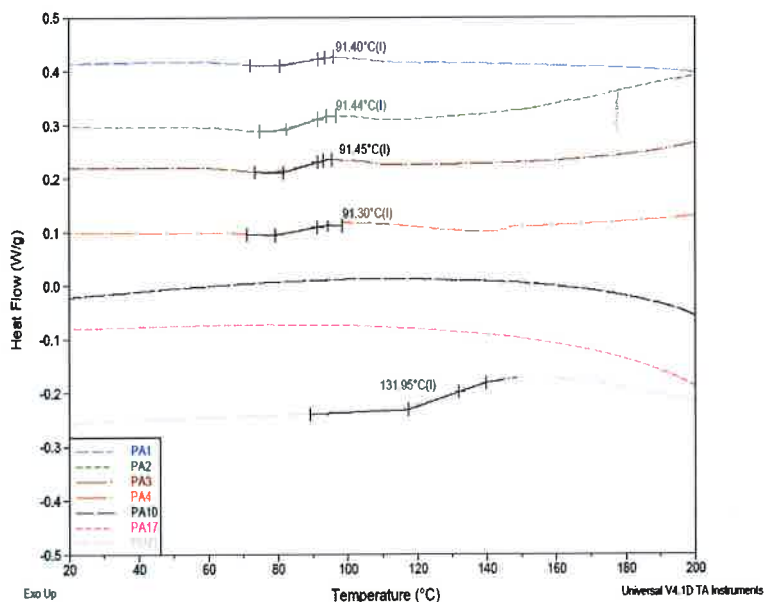


Figure 6.25: DSC curves for Polyamide and polyureas (first heating traces).

Table 6.11: Glass transition temperatures (T_g values) of PAs and PUs

Code	PA 1	PA 2	PA 3	PA 4	PA 5	PA 7	PA 8	PA 9	PA 10	PA 11
T_g(°C)	91.40	91.44	91.45	91.30	345.20	350.60	355.40	340.33	370.44	353.32
Code	PA 12	PA 13	PA 14	PA 15	PA 16	PA 17	PA 18	PA 19	PU 1	PU 2
T_g(°C)	365.13	344.56	351.45	349.18	362.44	365.30	361.41	363.33	131.95	130.55

6.7 Water up-take of the PAs and PUs

Water in polymers is absorbed preferably via hydrophilic groups such as OH, NH or ring hetero atoms. Water up-take data (mol water per polymer unit) for the PAs and PUs were recorded at 70% RH and 43% RH and shown in tables and figures below. The weight increase for all samples at saturation was between 4.10 and 7.95% at 70% RH and between 1.50 and 4.60% at 43% RH, respectively.

As expected, the higher the relative humidity the greater the value of water up-take¹². The differences in the values for water up-take are due to different compositions of the PAs and PUs (including type of diamino compound, ratio between the two diacid chlorides, mode of preparation, polymer PDI and molecular weight). See Tables 6.12 and 6.13³³⁻³⁵. Figure 6.26 shows the relationship between time and mass increase for PAs and PUs at two different relative moisture content of the air (RH). The PUs reached saturation later than the PAs. Figure 6.27 shows the relationship between water up-take (in the number of moles water per polymer unit) and the composition of the PAs and PUs. Water up-take varies between 0.87 and 1.80 moles of water at 70% RH and between 0.4 and 1.35 moles water at 43% RH. The value of the number of moles of water per mol of repeat unit was highest for the polyamide PA 4 at 43% and for PA 13 at 70% RH.

Table 6.12: Water up-take by PAs and PUs at 70% RH

	PA1	PA2	PA3	PA4	PA5	PA7	PA8	PA9	PA10	PA11
polymer dry (g)	0.957	0.960	0.938	0.970	0.964	0.959	0.980	0.960	0.977	0.971
polymer wet (g)	1.026	1.021	1.002	1.035	1.013	1.024	1.054	1.043	1.019	1.029
mass gain (%)	7.21	6.35	6.82	6.70	5.10	6.77	7.55	8.64	4.30	5.97
	PA12	PA13	PA14	PA15	PA16	PA17	PA18	PA19	PU20	PU21
polymer dry (g)	0.984	0.981	0.967	0.987	0.965	0.964	0.970	0.978	0.900	0.913
polymer wet (g)	1.036	1.038	1.029	1.048	1.013	1.013	1.027	1.019	0.950	0.963
mass gain (%)	5.28	5.81	6.41	6.18	4.97	5.10	5.87	4.19	5.55	5.47

Table 6.13: Water up-take by PAs and PUs at 43% RH

	PA1	PA2	PA3	PA4	PA5	PA7	PA8	PA9	PA10	PA11
polymer dry (g)	0.964	0.966	0.945	0.978	0.964	0.966	0.986	0.964	0.978	0.978
polymer wet (g)	0.998	0.994	0.974	1.008	0.983	0.996	1.03	1.004	0.998	1.004
mass gain (%)	3.52	2.90	3.10	3.10	1.97	3.10	4.46	4.14	2.10	2.65
	PA12	PA13	PA14	PA15	PA16	PA17	PA18	PA19	PU20	PU21
polymer dry (g)	0.990	0.988	0.975	0.995	0.970	0.967	0.974	0.983	0.886	0.908
polymer wet (g)	1.013	1.003	1.022	1.022	0.990	0.990	1.002	1.001	0.906	0.928
mass gain (%)	2.32	1.51	4.82	2.71	2.10	2.37	2.87	1.83	2.25	2.20

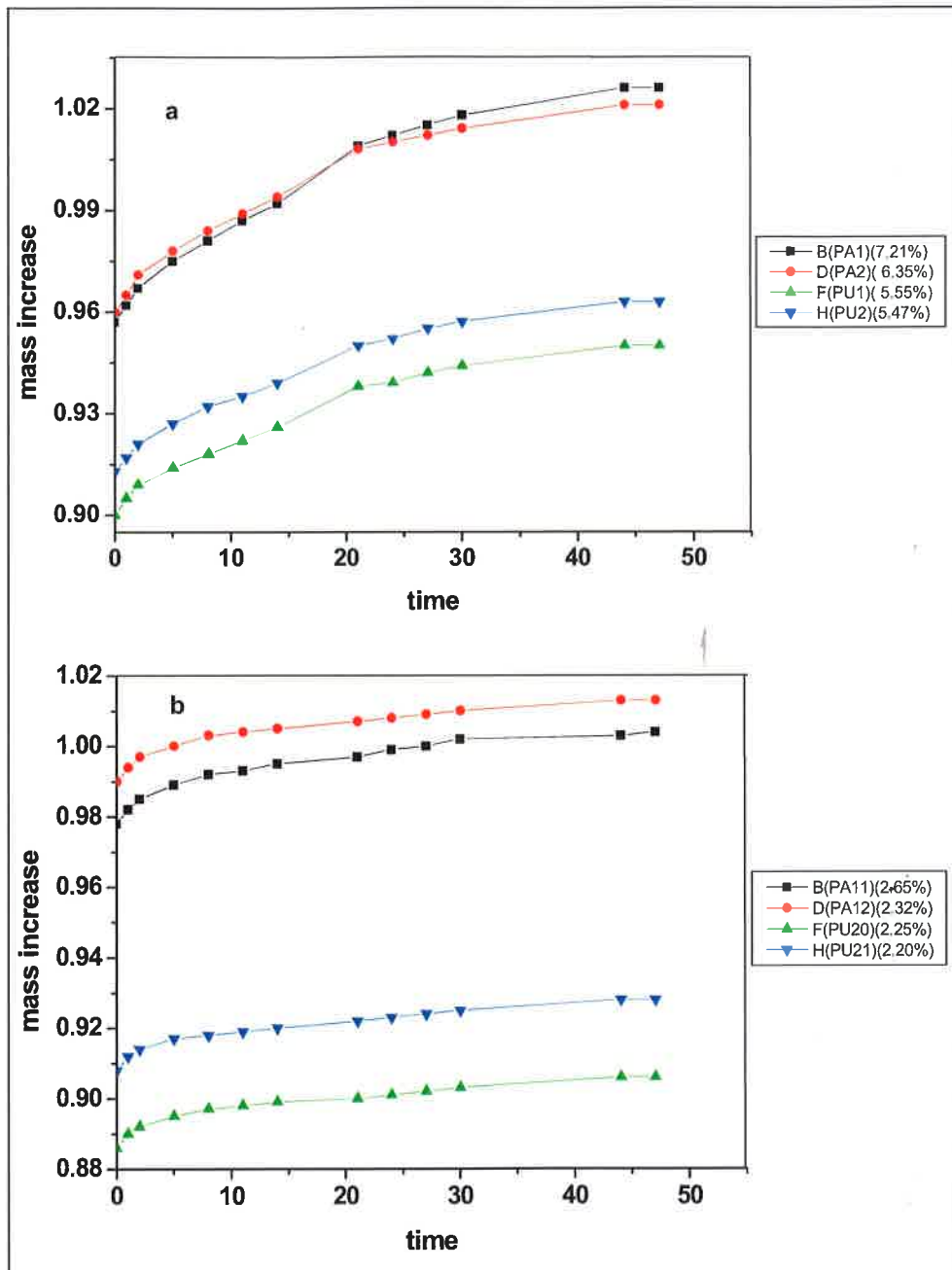


Figure 6.26: Water up-take by selected PAs and PUs at (a) 70% RH and (b) 43% RH.

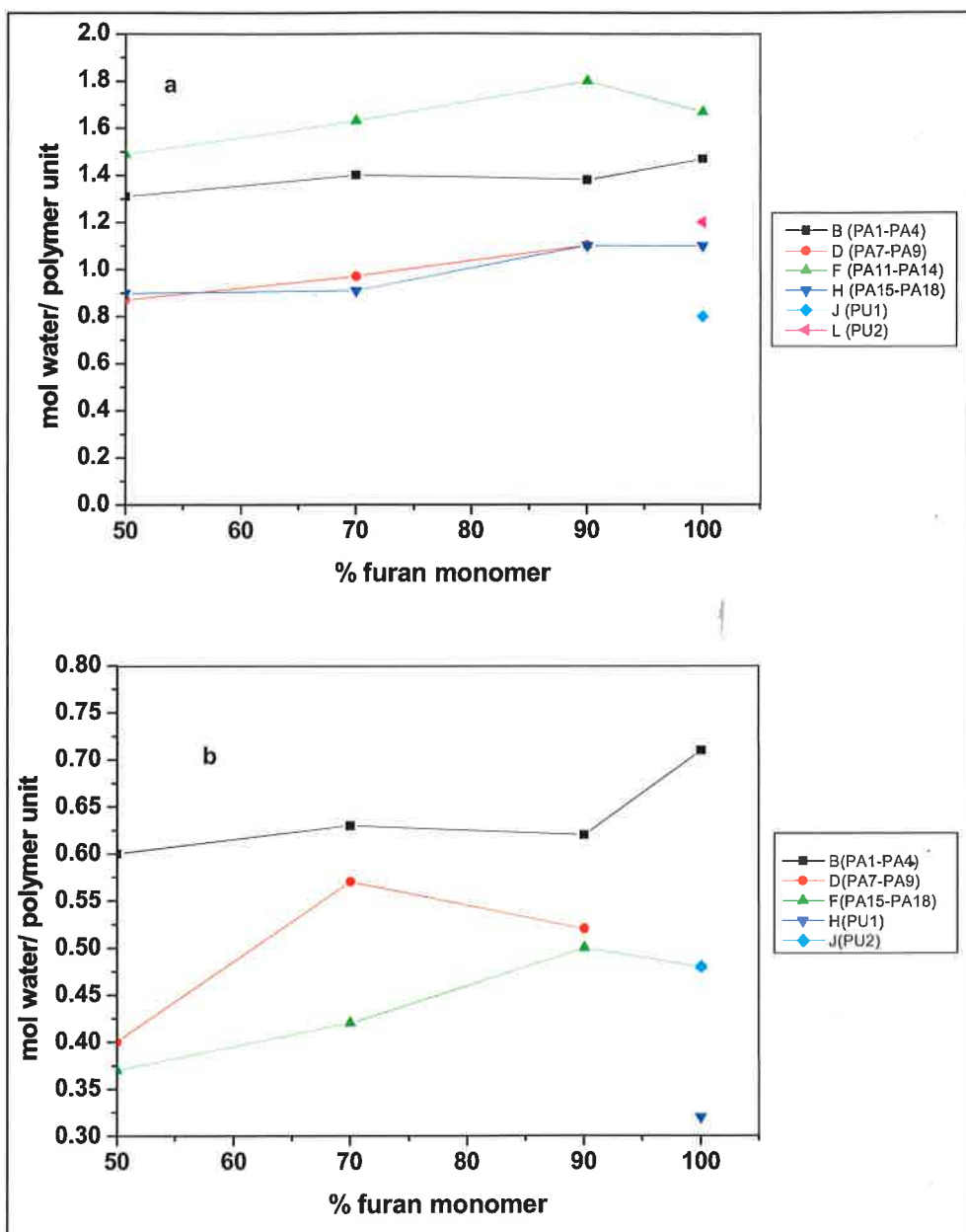


Figure 6.27: Water up-take (mol water per polymer unit) at (a) 70 % RH and (b) 43 % RH

6.8 References

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CHAPTER 7: CONCLUSIONS AND FUTURE WORK

7.1 Conclusions

1. Nineteen polyamides (PAs) were successfully synthesized by either homogenous or interfacial polycondensation of furanoyl-2,5-dichloride (FDC) and isophthaloyl dichloride (IPDC). The ratio between FDC and IPDC was altered from 100% FDC to 90%, 70%, 50% and 0%.
2. In homogenous phase polymerization the diamines and pyridine were dissolved in N-methylpyrrolidone (NMP), followed by dropwise addition of the dissolved acid chlorides (FDC+IPDC) in NMP.
3. In interfacial polymerization the diamines and pyridine were dissolved in dichloromethane (DCM), followed by the addition of FDC and / or IPDC in DCM.
4. The homogeneous phase polymerization was found to be the better method because it gave the highest yield of PAs and with a better purity.
5. Two polyureas (PUs) were prepared by reaction of furan-2,5-diisocyanate with two different diamines [m-phenylene diamine (MPD) and 4,4'-diamino diphenyl sulfone (DDS)].
6. The molecular structures of the PAs and PUs were confirmed by FTIR, TGA, ^1H NMR, ^{13}C NMR, DSC and GPC and their water up-take was determined.
7. All PAs and PUs showed good thermal stability with comparatively high glass transition temperatures (up to 280 °C). The PAs, that were prepared with the newly synthesized diamine BAT, such as PA 10 – PA 14, were the most thermal stable.
8. PAs and PUs were investigated for their ability to absorb water into the polymer chain structure. This feature is a helpful characteristic in determining whether materials are suitable for use in separation membranes for water purification. The water up-take per polymer unit (mol water / repeat unit) was between 0.87 and 1.80 moles of water at 70 % RH and 0.4 and 1.35 moles water at 43% RH. It was highest for the PA 4 at 43% and for PA 13 at 70%.
9. Water up-take comparison between polymers with only one diacid unit in the chains (for furan PA 1, PA 6, PA 11 and PA 15 or isophthalic acid for PA 5, PA 10 and PA 19) show no real differences between each other or to the mixed polymers such as PA 2 or PA 12. The highest values for water up-take in mixed

polymers are measured, when the ratio between FDC and IPDC is around 70 : 30 by mol-ratio.

7.2 Future work

1. It is envisaged to extend the range of PAs for comparisons by introducing block copolymer of the AB or ABA type.
2. Selected PAs should be produced in larger quantities, transformed into membranes by spraying polymer solutions on support layers and tested for desalination properties.
3. Characterize the PAs by other analytical techniques such as MALDI-TOF, solid state NMR or gradient elution liquid chromatography to draw conclusions about end groups or chemical composition in general.

APPENDIXES

Appendix A: ^1H NMR of the DDS, FDC and IPDC

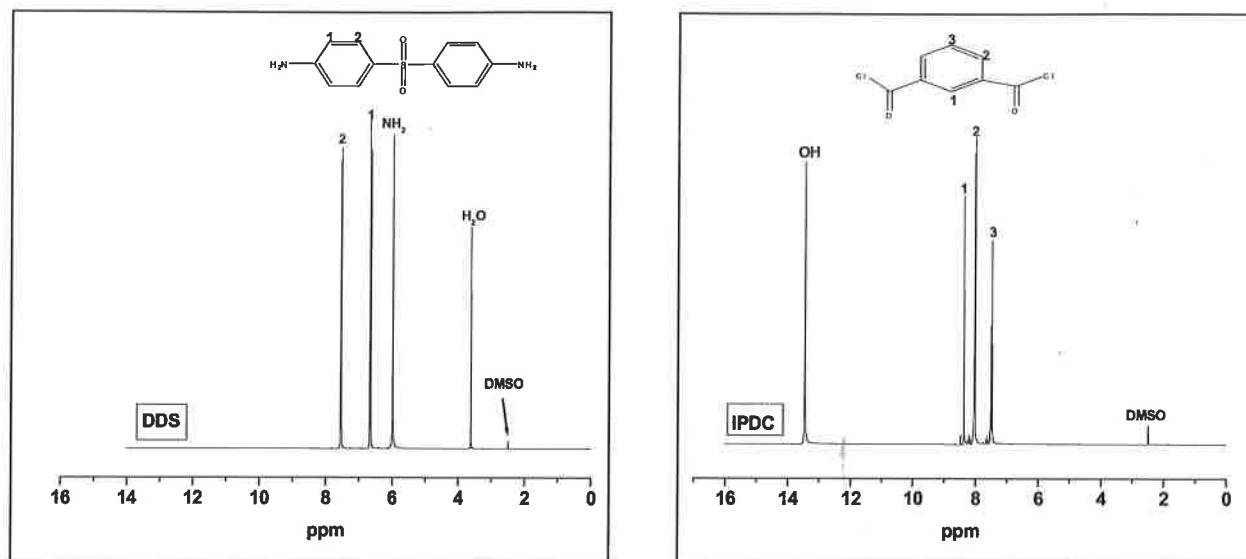


Figure A1: ^1H NMR spectra of the DDS and IPDC in DMSO-d_6 .

Appendix B:

Composition of the PA 2 - PA 4, PA 12 - PA 14 and PA 16 - PA18

Table B 1: Integration NH of the FDC, IPDC at different ratios

Polymers	Integration (FDC)	Integration (IPDC)	Ratios (FDC, IPDC) FDC % , IPDC %
PA 2	1.04	1.00	51%, 49%
PA 3	2.44	1.00	71%, 29%
PA 4	7.92	1.00	89%, 11%
PA 12	0.96	1.00	49%, 51%
PA 13	2.41	1.00	70%, 30%
PA 14	10.58	1.00	91%, 9%
PA 16	0.98	1.00	49%, 51%
PA 17	2.41	1.00	71%, 29%
PA 18	10.79	1.00	91%, 9%

Appendix C: NMR spectra of the model compounds PM 1 and PM 2

C 1: ^1H NMR of PM 1

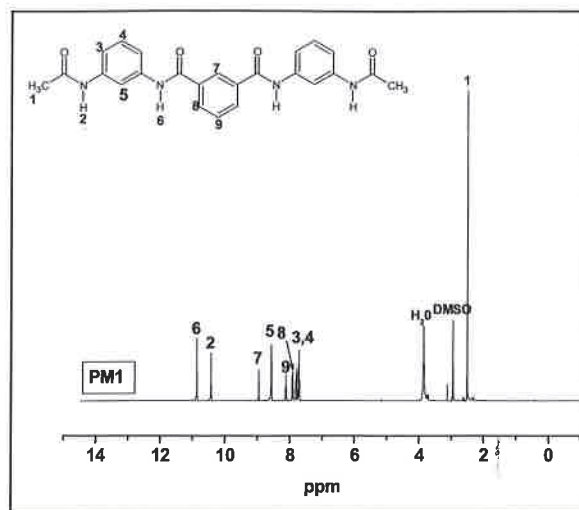


Figure C1: ^1H NMR spectrum of PM 1 in DMSO- d_6

C 2: ^{13}C NMR of PM 1

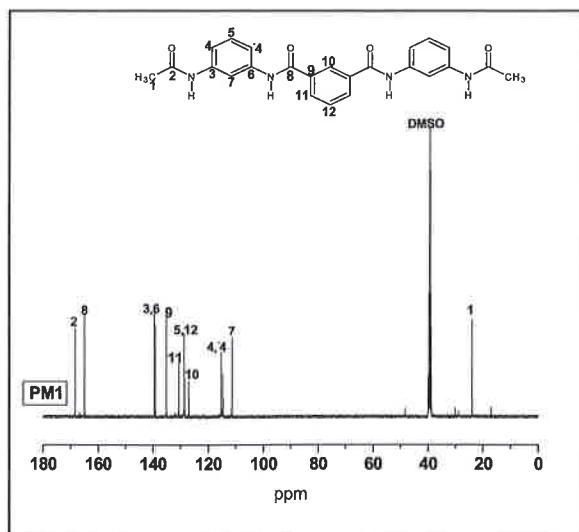


Figure C 2: ^{13}C NMR spectrum of PM 1 in DMSO- d_6

C 3: ^1H NMR of PM 2

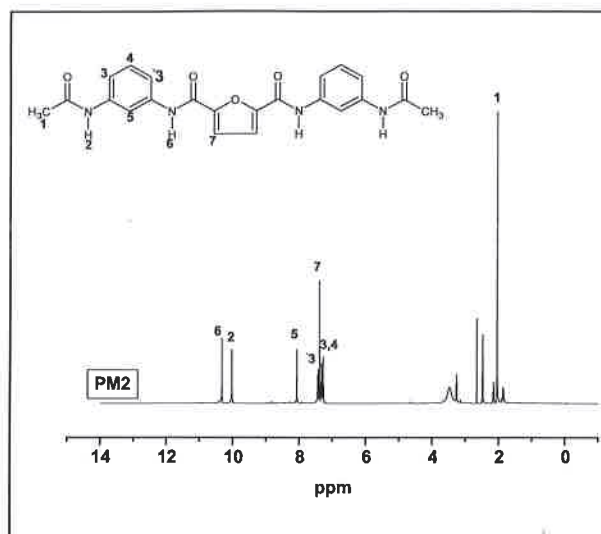


Figure C 3: ^1H NMR spectrum of PM 2 in DMSO-d_6

C 4: ^{13}C NMR of PM 2

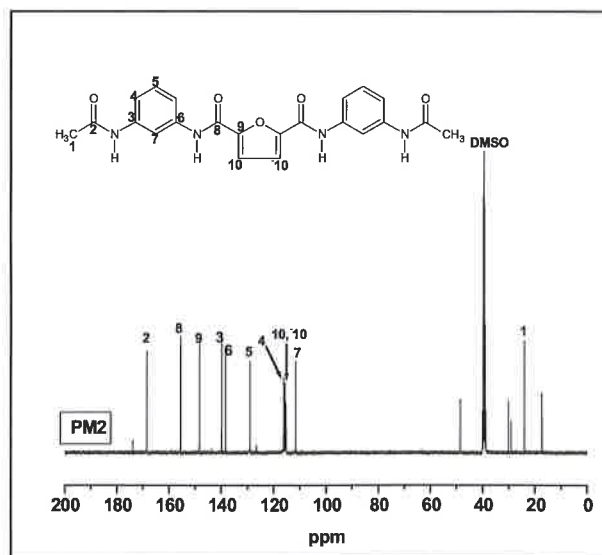


Figure C 4: ^{13}C NMR of PM 2 in DMSO-d_6