

University of South Bohemia

Faculty of Science

Synthesis of high surface area polyimides

Master Thesis

BSc. Haudum Stephan

Supervisor: Assoc. Univ.-Prof. Dr. Ian Teasdale, JKU Linz
Co-Supervisor: Dipl.-Ing. Stephan Schaumüller, JKU Linz

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Annotation

Polyimides are high performance polymers with excellent features such as high chemical resistance and mechanical toughness. Recently the development of soluble highly porous, high surface area polyimides has been receiving growing attention and several scientists have reported new high surface area polyimides. The combination of the excellent features of polyimides with properties like high surface area and easy processability provides a unique polymer class with a manifold field of application.

The aim of this thesis was to synthesize and characterize soluble polyimides with high surface area and porosity, by following the concept of polymers of intrinsic microporosity (PIMs). This unique class of polymers combines high surface area with good solubility. This can be achieved by creating a rigid bulky polymer backbone which cannot pack efficiently, therefore creating void space, eventually leading to a non-covalent porous 3D system. The thesis includes the synthesis of novel rigid, bulky monomers and their polymerization with various comonomers, as well as post polymerization modifications by Diels Alder additions to maximize surface area.

All synthesized polymers were thoroughly characterized by nuclear magnetic resonance spectroscopy, size exclusion chromatography, and BET surface area measurements.

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Finally, I would like to express my deepest gratitude to my parents for providing me with un-failing support, patience, fortitude and continuous encouragement throughout my years of study. This achievement would not have been possible without them.

DECLARATION

I hereby declare that I have worked on my master thesis independently and used only the sources listed in the bibliography. I hereby declare that, in accordance with Article 47b of Act No. 111/1998 in the valid wording, I agree with the publication of my master thesis, in shortened form resulting from deletion of indicated parts, to be kept in the Faculty of Science archive, in electronic form in publicly accessible part of the STAG database operated by the University of South Bohemia in České Budějovice accessible through its web pages. Further, I agree to the electronic publication of the comments of my supervisor and thesis opponents and the record of the proceedings and results of the thesis defense in accordance with aforementioned Act No. 111/1998. I also agree to the comparison of the text of my thesis with the Theses.cz thesis database operated by the National Registry of University Theses and a plagiarism detection system.

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Haudum Stephan



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Table of Abbreviations

Abbreviation	Definition
6FDA	4,4'-(hexafluoroisopropylidene) diphthalic anhydride
Abs.	Absolute
AcOAc	Acetic anhydride
Anhyd.	anhydrous
BAPF	9,9-bis(4-aminophenyl) fluorene
BET	Brunauer-Emmett-Teller
BTDA	3,3', 4,4'-benzophenonetetracarboxylic dianhydride
DA	Diels Alder addition
DAHMSBI	6,6'-diamino -3,3,5,3',3',5'-hexamethyl-1,1'-spirobisindane
DATMPI	5(6)-amino-1(4'-aminophenyl)-1,3,3'-trimethylindane
DCM	Dichloromethane
DMAC	N,N-dimethylacetamide
DMF	N, N-dimethylformamide
DNHMSBI	6,6'-dinitro -3,3,5,3',3',5'-hexamethyl-1,1'-spirobisindane
DNTMPI	5(6)-nitro-1(4'-nitrophenyl)-1,3,3'-trimethylindane
DSC	Differential scanning calorimetry
EBPA	4,4'-(ethyne-1,2-diyl) diphthalic anhydride
Equiv.	equivalent
EtOH	Ethanol
GBL	Gamma butyrolactone
GPC	Gel permeation chromatography
HMSBI	3,3,6,3',3',6'-hexamethyl-1,1'-spirobisindane
HPLC	High performance liquid chromatography
IR	Infrared spectroscopy
kDa	Kilo Dalton
m-BAPF	9,9-bis(4-amino-3-methylphenyl)fluorene
MEPA	4-(methylethynyl) phthalic anhydride
M _n	number average molar mass
Mp	Melting point
MS	Mass spectrometry
NMP	N-methyl-2-pyrrolidone
NMR	Nuclear magnetic resonance
p.a.	Per analysis
PI	Polyimide
PIM	Polymer of intrinsic microporosity
Redest.	Re-distilled
SBF	Spirobifluorene
SBI	Spirobisindane
T _g	Glass transition temperature
TMPI	1,3,3'-trimethyl-1-phenylindane
TPCP	Tetraphenylcyclopentadienone
Wt. %	Weigh percent

1 Introduction

The aim of this work was to develop and synthesize soluble highly porous polyimides with large surface areas, also known as polyimide polymers of intrinsic microporosity (PIM PI). These polymers have been increasingly drawing interest, due to their outstanding features and wide field of possible applications. Chapter 2 provides the theoretical background of this work and is introducing in polyimides (2.1), polymers of intrinsic microporosity (2.2) and Diels Alder addition reactions (2.3). The aim and approach taken is described in chapter 2.4. Next, chapter **Fehler! Verweisquelle konnte nicht gefunden werden.** describes the experimental part and chapters **Fehler! Verweisquelle konnte nicht gefunden werden.** and **Fehler! Verweisquelle konnte nicht gefunden werden.** present the results and conclusion. Finally, all analytical data can be found in the appendix in chapter **Fehler! Verweisquelle konnte nicht gefunden werden.**

2 Background

Chapter 2.1 gives an overview of polyimides, their syntheses by polycondensation and sums up important applications. Chapters 2.2 and 2.3 provide an introduction into polymers of intrinsic microporosity (PIMs) and Diels Alder addition reactions.

2.1 Polyimides

Polyimides are a class of thermally and chemically stable polymers whose most important structural element is the imide bond. The first reported synthesis of a polyimide (PI) was in 1908^[1]. However, its further development and first commercialization was pioneered in the 1960s by DuPont^[2]. Since then there has been growing interest in this polymer class and nowadays there are many applications, especially in the high-performance sector. Figure 1 shows the general structure of a polyimide.

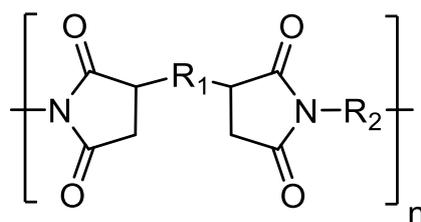


Figure 1: Structural formula of a polyimide.

Aromatic Polyimides are amongst the most thermally stable polymers. They can withstand temperatures up to 450 – 500 °C^[2] and have high glass transition (T_g) and melting (Mp) temperatures. Therefore, polyimides are often used in high temperature applications. Polyimides are chemically stable and even at elevated temperatures they can withstand radiation, moisture, caustic acids, salt solutions and many organic solvents^[3]. Furthermore they possess high tensile strengths (170-270 MPa) and elongation (> 3 GPa) values^[4]. However, due to their high thermal (high T_g and Mp) and chemical (solvent resistance) stability, processing of polyimides is challenging. Therefore, they are usually processed via its precursor polyamic acid. The improvement of processability of polyimides is a key factor and lots of research is done on this topic.

2.1.1 Synthesis

There are several ways how to synthesize PI, but the most widespread one is by the polycondensation of dianhydrides and diamines^[2], which is described in the following chapter. The general reaction scheme of the imide bond formation is shown in Figure 2.

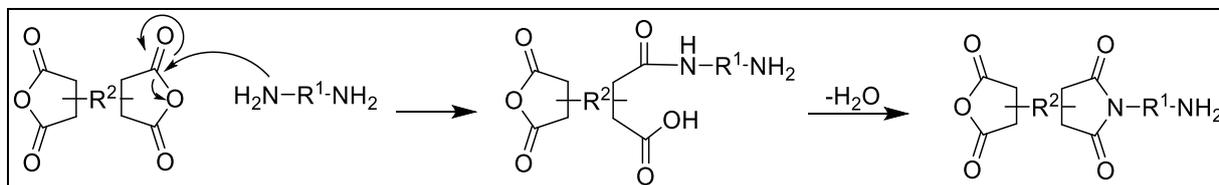


Figure 2: Reaction scheme of the imide bond formation, exemplary for one repetition unit.

At first a nucleophilic attack of the diamine leads to the formation of an amic acid and a subsequently elimination of water forms the final imide bond^[2]. Ongoing repetitions of those steps eventually lead to polyimides. The reaction rate of the first step depends strongly on the reactivity of the diamine and dianhydride monomers. Generally, the higher the basicity of the diamine and the higher the electrophilicity of the dianhydride, the faster the reaction is.^[2] Other important factors are monomer concentrations, steric hinderance and choice of solvent^[2]. The most common solvents are aprotic polar solvents like DMF, DMAC and NMP^[2]. Increasing concentrations of monomer, accelerate the reaction rate and lead to polymers with higher molecular weights^[2]. However, too concentrated solutions and too high molecular weights will increase the viscosity and might lead to stirring and homogenizing problems. Another key factor is the absence of water, since even small amounts can lead to hydrolytic degradation of the amic acid bond leading to low molecular weight polymers^[2].

The final imidization step occurs by cyclodehydration of the amic acid to form the imide bond. This can be carried out either by thermal or chemical dehydration. Thermal imidization is achieved by heating the polyamic acid solution to elevated temperatures above 165 °C under constant removal of water^[5]. The chemical imidization is performed using a chemical dehydration agent and a base, common are acetic anhydride and pyridine or triethylamine^[2,6]. The mechanism of the chemical cyclodehydration is shown in Figure 3^[2].

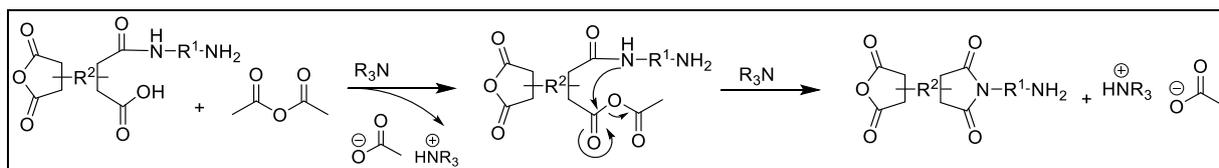


Figure 3: Reaction scheme of the cyclodehydration with acetic anhydride and a tertiary amine as base R₃N^[2].

The first step is the base catalyzed acylation of the carboxy group forming an anhydride intermediate. Next an intramolecular nucleophilic attack of the nitrogen on the carbonyl and loss of acetate leads to the formation of the imide bond^[2,6]. A side reaction that can occur during cyclodehydration is the formation of isoimides. This can be seen in Figure 4^[2].

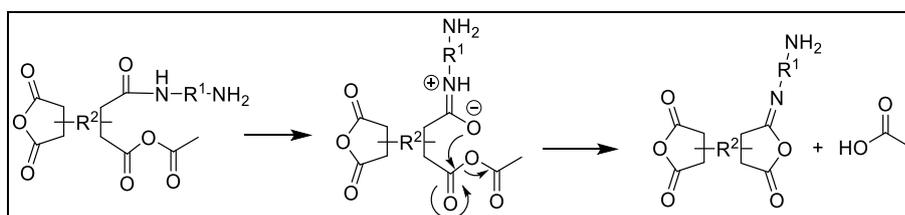


Figure 4: Reaction scheme of the isomerization to an isoimide^[2].

Those isoimides can be isomerized to the imide at elevated temperatures^[7]. However, the initial amount of iso imide formation strongly depends on the imidization conditions. It was found, that stronger bases (e.g.: triethylamine pKa 10.76 or triethylenediamine (DABCO) pKa 8.6)^[8] exclusively form imide bonds whereas weaker bases like pyridine (pKa 5.23^[8]) produces also isoimides^[8]. The reason for this is that stronger bases more effectively form acetate ions, which catalyzes isomerization of the isoimide to the imide group^[9].

2.1.2 Applications of Polyimides

Thanks to their excellent chemical and thermal stability and mechanical toughness, aromatic polyimides are often used in the high-performance sector. The first utilization of polyimides was as polymer film Kapton, developed by DuPont in the 1960s^[2]. Until now, Polyimides films are one of the most important fields of application. Due to its good insulation properties and thermal resistance polyimide films are widely used as wire coatings. Other utilizations are e.g. as bagging for composites, membranes, flexible circuits and sensors. Another well-known application is in aerospace, where thermal stability, flame retardancy, chemical and radiation resistance are important key factors. Other recent fields of applications are in flexible optoelectronic devices like flexible LEDs, flexible solar cells and in microelectronics where polyimides are used in sensors and micro-chips^[2].

2.2 Polymers of intrinsic microporosity

2.2.1 General information

Polymers of intrinsic microporosity (PIMs) is a concept that was firstly developed during the early years of 2000 at Manchester University UK^[10,11]. PIMs are polymers which have a high porosity and surface area without forming covalent networks. This is achieved by creating a rigid and bulky polymer backbone, which prevents rotational freedom and tight packing of the chains, resulting in the formation of void space and a microporous structure. Most commonly these systems are based on monomers with fused aromatic ring structures^[10,11] which are inflexible and introduce kinks (site of contortions) into the polymer backbone, hampering packing. Figure 5 shows the structure and Figure 6 the space filling model of PIM 1, reported by Budd, McKeown et al. in 2003^[11].

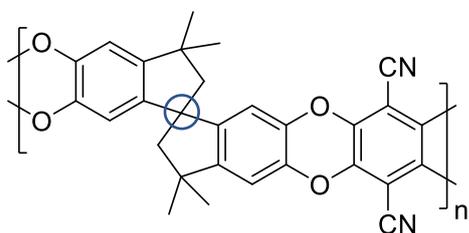


Figure 5: Structural formula of PIM 1 with the typical spiro center (encircled)^[10,11].

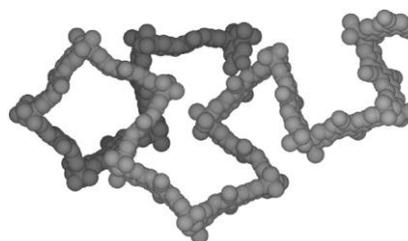


Figure 6: Space filling model of PIM, showing void space by insufficient packing of the polymer^[11]. Reproduced by permission of The Royal Society of Chemistry.

As can be seen, the repeating unit of PIM 1 is based on spirobisindane, which is bound via two ether bonds in a ladder fashion to the nitrile moiety. This was achieved by the nucleophilic aromatic substitution reaction (S_NAr) of 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl- spirobisindane with 2,3,5,6-tetrafluoroterephthalonitrile, as shown by Figure 7 ^[11].

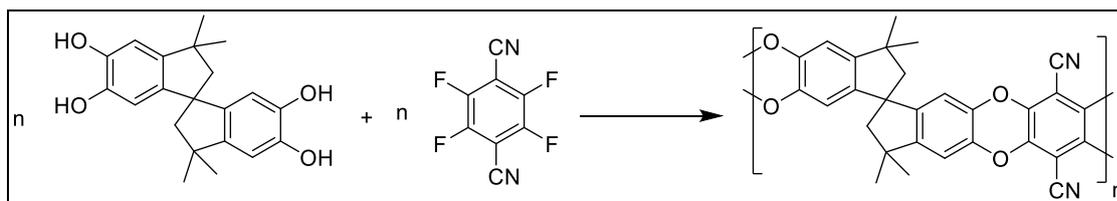


Figure 7: Reaction scheme of the nucleophilic aromatic substitution reaction of 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl- spirobisindane and 2,3,5,6-tetrafluoroterephthalonitrile to yield PIM 1^[11].

The used monomers introduce a kink into the polymer backbone and provide high rigidity/inflexibility via its ladder type ether bonds, thereby prohibiting rotational movements. All together this leads to poor packing of the polymer chains, resulting in void space and a microporous structure, as shown by the space filling model in Figure 6. With their polymer design, Budd, McKeown et al. could achieve a for polymers excellent BET surface area of $850 \text{ m}^2 \text{ g}^{-1}$ ^[11].

The most important advantage of PIMs over other microporous polymers and materials is their good solubility in common organic solvents^[11], which makes them easily processable. Therefore, there has been growing interest in this field and since the publication of PIM 1 various, variations of PIM 1 as well as new PIMs have been synthesized. The most prominent field of application for PIMs due to their outstanding features is gas separation membranes^[10,12]. Nevertheless, all other applications where high porosity is important can benefit from the properties of PIMs, such as adsorbent for separation processes, gas storage, gas or humidity sensors and metal organic frameworks ^[12,13].

2.2.2 Overview of PIMs

Up to now a wide variation of different PIMs has been reported. Generally four main types of monomers are used for the synthesis of PIMs: spirobisindane (SBI), spirobifluorene (SBF), Tröger's base and triptycene^[12] (see also Figure 11).

2.2.2.1 Spirobisindane and spirobifluorene based PIMs

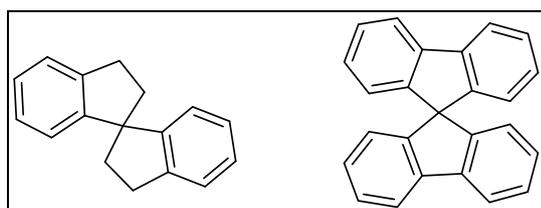


Figure 8: Basic structural formula of spirobisindane and spirobifluorene. The additional phenyl groups of spirobifluorene decrease rotational flexibility.

Via its spiro centers, spirobisindane and spirobifluorene monomers contain a site of contortion which introduces a kink into the polymer backbone and therefore effectively hampers chain packing. The rotational freedom and flexibility of the spiro center depends on the substituents and is decreasing with increasing bulkiness of its side groups ^[14]. Therefore, spirobifluorenes are usually less flexible than spirobisindanes (Figure 8) and higher surface areas can be achieved with the former^[14].

2.2.2.2 Tröger's base based PIMs

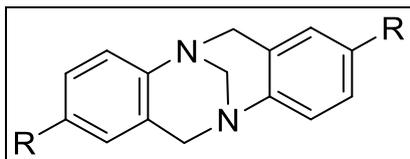


Figure 9: Structural formula of a Tröger's base, showing the characteristic nitrogen bridgeheads.

To further decrease flexibility, PIMs with Tröger's base monomers were introduced. Although they lack the kink produced by a spiro center, Tröger's base PIMs could achieve high surface areas, due to their highly inflexible V-shaped bridged bicyclic structure^[12,14]. Especially the combination of Tröger's base and spirobisindane/spirobifluorene monomers proved to be effective and surface areas of as high as $700 \text{ m}^2 \text{ g}^{-1}$ were reported^[12].

2.2.2.3 Triptycene based PIMs

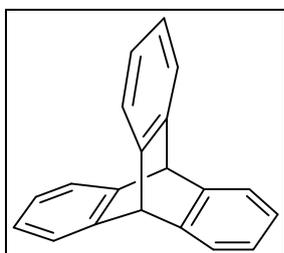


Figure 10: structural formula of triptycene.

The newest development in the area of PIMs is the use of triptycene moieties. Their Y-shaped bicyclic structure provides high rigidity and bulkiness, which can be even improved by alkyl groups at the bridge heads^[12,15]. Ghanem et al. reported in 2014 triptycene based polyimide PIMs PI KAUST-PI-1 and PI KAUST-PI-2 with excellent surface areas of $752 \text{ m}^2 \text{ g}^{-1}$ and $737 \text{ m}^2 \text{ g}^{-1}$ ^[15]. These are the highest reported BET surface areas for polyimides PIMs by 2018^[12,15].

2.2.2.4 Polyimide PIMs

Due to their synthetic flexibility and beneficial chemical and mechanical properties the interest in polyimide-based PIMs (PIM PI) is increasing and many different variants have been synthesized. Figure 11 gives an overview over the PIM PIs that have been reported until 2018, sorted according to the monomers used.

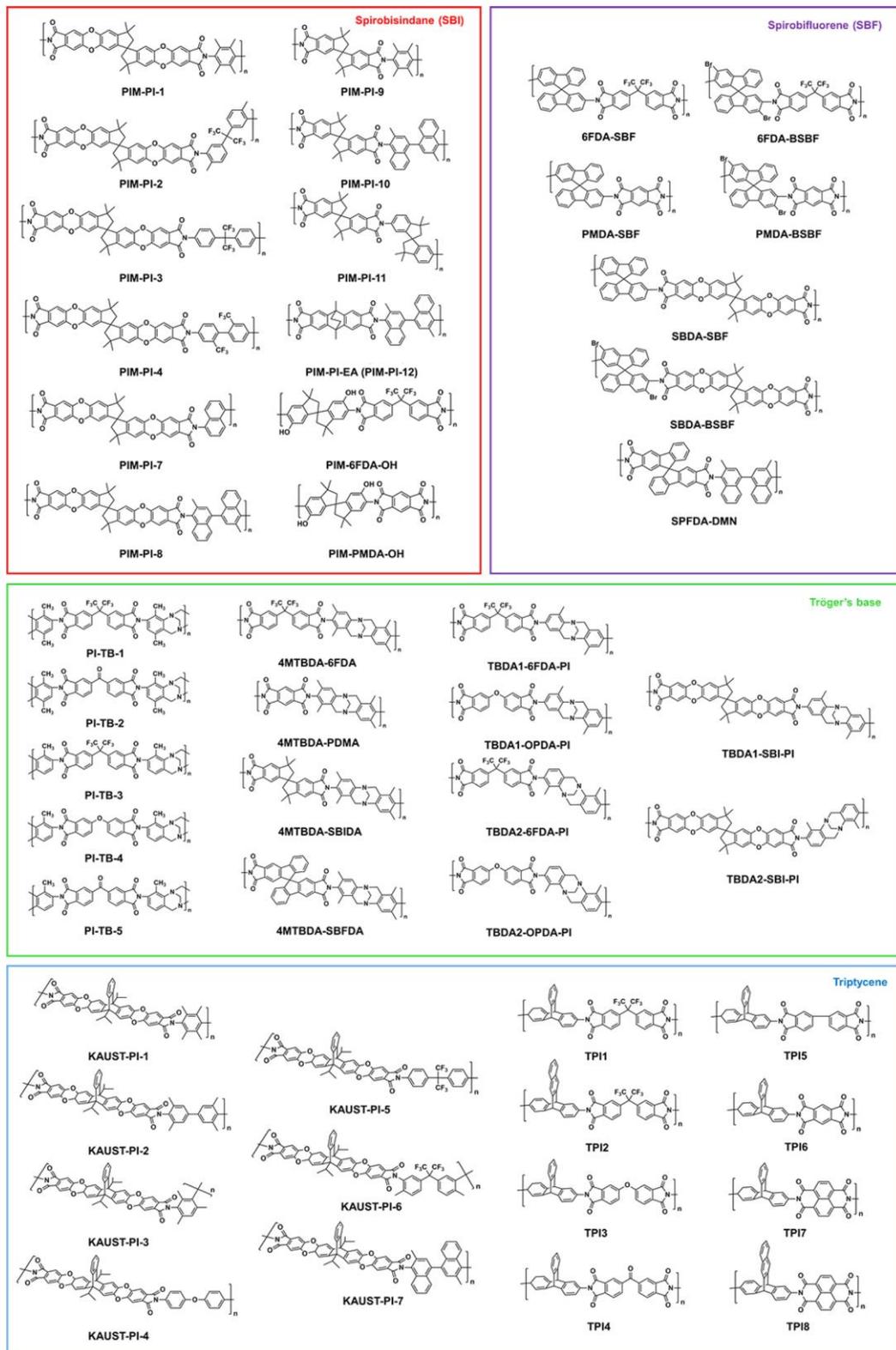


Figure 11: Overview of polyimide based polymers of intrinsic micro porosity that have been reported until 2018^[12]. Reprinted with permission from^[12]. Copyright 2020, American Chemical Society.

2.3 Diels Alder addition

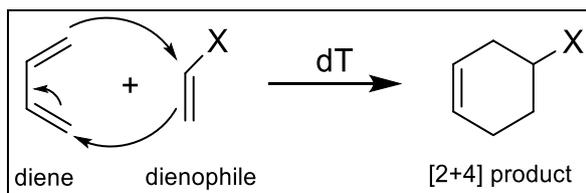


Figure 12: Reaction scheme of a Diels Alder reaction between a diene and a dienophile with an electron withdrawing group X at elevated temperature.

The Diels Alder addition (DA) is a [4+2] cycloaddition, named after its discoverers Otto Diels and Kurt Alder^[16]. It is a valuable tool in synthetic organic chemistry and provides excellent atom economy. During the reaction two σ – bonds are formed simultaneously between two π – systems associated with 4 and 2 atoms^[16,17] (hence the name [4+2]). Figure 12 shows the general reaction scheme of an Diels Alder addition between a diene and a dienophile with an electron withdrawing group X. The reaction takes place at elevated temperature, however, at even higher temperature, the reaction can reverse in a retro Diels Alder addition^[16,17].

One very interesting Diels Alder addition is the reaction of a phenyl substituted cyclopentadienone with an alkyne containing moiety, creating a newly formed benzene ring^[18]. The reaction in which the cyclopentadienone acts as diene and the alkyne group as dienophile, has been widely reported in literature^{[19] [20]}. Figure 13 shows the general reaction scheme of this type of cycloaddition. The reaction occurs through an intermediate, which cleaves of carbon monoxide (CO), therefore driving the equilibrium forward to the final product, giving excellent yield^[18]. Thereby this reaction provides an excellent method of introducing benzene groups into alkyne containing molecules.

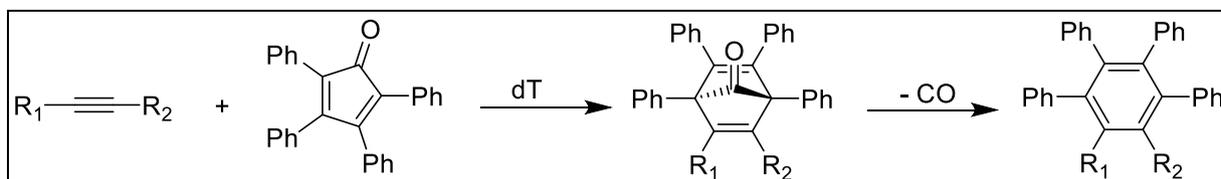


Figure 13: Reaction scheme^[19] of the reaction of an alkyne group with a phenyl substituted tetraphenylcyclopentadienone. Loss of the CO group of the intermediate drives the reaction forward to the product.

2.4 Aim and approach

The aim of the thesis and this project was to synthesize and characterize (aromatic) polyimide-based polymers with high surface areas. These should then be processed into thin films by spin coating in future work. Therefore, to ensure easy processability, these polyimides should be soluble in common organic solvents. This should be achieved by following the concept of PIMs and focusing on three key elements; side of contortion, bulkiness and rigidity. Figure 14 shows a graphical overview of the approach. Firstly, rigid monomers with a side of contortion should be synthesized to create basic polymers. Then, different bulky comonomers should be used to examine their effect on the surface area. Additionally, post polymerization modifications of alkyne functionalized polyimides by Diels Alder addition should be performed to introduce large, bulky side groups. Furthermore, crosslinking of alkyne functionalized polyimides should be done to examine the effect on rigidity/stiffness and surface area. However, to ensure solubility and processability this crosslinking process must be applicable after processing the polymer. This should be achieved by thermal cross linking.

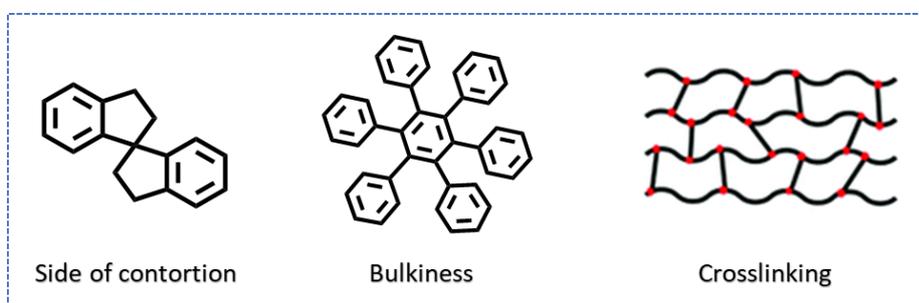


Figure 14: Graphical representation of the 3 main elements of the approach; side of contortion, bulkiness and crosslinking. By using these elements in combinations, the surface area should be maximized.

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