Organic photovoltaics

- Synthesis of a novel pendant side-chain conjugated perylene based polymer -





Master Thesis Nils Johannes Klitmøller

> Aalborg University Chemistry and Bioscience Fredrik Bajers Vej 7H

8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm

Copyright © Aalborg University 2015



Department of Chemistry and Bioscience Aalborg University http://www.aau.dk

AALBORG UNIVERSITY

Master Thesis

Title:

Synthesis of a novel pendant sidechain conjugated perylene based polymer

Theme: Organic photovoltaics

Thesis Period: Fall 2014 - Fall 2015

Candidate: Nils Johannes Klitmøller

Supervisor(s): Donghong Yu

Copies: 4

Pages: 56 (without appendix)

Date of Completion: October 2, 2015

Abstract:

The focus in this master thesis was developing a synthetic strategy for a novel perylene based monomer, capable of radical polymerization, resulting in side-chain conjugated homopolymers with possible photovoltaic properties, by π - π stacking of conjugated pendants. The monomer was synthesized through a 3-step process, followed by the fourth step, i.e., polymerization. Verification of the structure was done by ¹H NMR and ATR FT-IR spectroscopy, and characterization of the polymer and intermediates included solubility analysis, UV/VIS absorbance and fluorescence spectroscopy and simultaneous thermogravimetric analysis. The synthesis was successful, resulting in a completely insoluble bright orange homopolymer. The low solubility of the intermediates led to the additional synthesis of perylene diimides with four different alkylamine substitutions, the most soluble of which was the diimide of sec-butylamine. Further synthesis of the diimides towards a similar homopolymer was however unsuccessful, due to the severely reduced reactivity in the Diels-Alder cycloaddition of maleic anhydride, in step two.

The content of this report is freely available, but publication (with reference) may only be pursued by agreement with the author.



Institut for Kemi og Biovidenskab Aalborg Universitet http://www.aau.dk

AALBORG UNIVERSITET

Kandidatafhandling

Titel:

Syntese af en ny type sidekædekonjugeret perylen baseret polymer

Tema: Organiske solceller

Specialeperiode: Efterår 2014 - Efterår 2015

Kandidat: Nils Johannes Klitmøller

Vejleder(e): Donghong Yu

Oplagstal: 4

Sidetal: 56 (uden bilag)

Afleveringsdato: 2. oktober 2015

Abstract:

Fokuspunkterne i dette speciale var at udvikle en syntese-strategi for en ny type perylen baseret monomer, til radikale polymerisering. Den resulterende homopolymer med side-kæde konjugerede systemer har potentielle fotovoltaiske egenskaber via π - π kobling mellem enhederne. Monomeren blev syntetiseret gennem en 3-trins proces, efterfulgt af fjerde trin; polymerisering. Verificering af strukturen forløb vha. ¹H NMR og ATR FT-IR-spektroskopi. Karakterisering af polymeren og mellemstadier inkluderede opløseligheds bestemmelse, UV/VIS absorbans og fluorescens spektroskopi og simultan termogravimetrisk analyse. Syntesen lykkedes, hvilket resulterede i en uopløselig lys orange polymer. Den lave opløselighed af mellemprodukterne førte til yderligere syntese af perylen-diimider med fire forskellige alkylamin substituenter, den mest opløselige af slagsen var diimiden af sec-butylamin. Videre syntese af diimiderne mod en tilsvarende homopolymer fejlede dog, på grund af den stærkt reducerede reaktivitet i Diels-Alder cycloadditionen af maleinsyreanhydrid, i trin to.

Rapportens indhold er frit tilgængeligt, men offentliggørelse (med kildeangivelse) må kun ske efter aftale med forfatterne.

Contents

Preface			ix			
Li	st of	Abbrev	viations	xi		
1	Intr 1.1	roduction Thesis statement				
2	The	oretica	l considerations	7		
	2.1	2.1 Syntheses				
		2.1.1	The Diels-Alder cycloaddition	7		
		2.1.2	Nucleophilic acyl substitution	8		
		2.1.3	Free radical polymerization	9		
		2.1.4	Solubility modification	9		
3	Experimental design			11		
	3.1	Synth	esis of the perylene based polymer	11		
		3.1.1	Step 1 - benzo[g,h,i]perylene-1,2-dicarboxylic anhydride	11		
		3.1.2	Step 2 - N-(6-hydroxyhexyl)benzo[ghi]perylene-1,2-dicarboximi	de 12		
		3.1.3	Step 3 - N-(hexylprop-2-enoate)benzo[ghi]perylene-1,2-dicarbox	kimide 12		
		3.1.4	Step 4 - free radical polymerization	13		
	3.2	Synth	esis of the perylene dianhydride based polymer	13		
		3.2.1	Step 1 - N,N'bis(x)perylene-3,4:9,10-bis(dicarboximide)	13		
		3.2.2	Step 2 - N,N'bis(x)benzo[ghi]perylene-2,3:8,9-bis(dicarboximide	e)-		
			11,12-dicarboxylic anhydride	14		
4	Materials and analyses			15		
	4.1	Chem	icals	15		
		4.1.1	Solvents	15		
		4.1.2	Reagents	16		
	4.2	Analy	sis methods and materials	16		
		4.2.1	Nuclear magnetic resonance spectroscopy	16		
		4.2.2	Fluorescence spectroscopy	17		

		4.2.3	Absorption spectroscopy	17	
		4.2.4	Simultaneous thermal analysis	17	
		4.2.5	Fourier transform infrared spectroscopy	18	
		4.2.6	Quantitative solubility analysis	18	
5	Exp	erimen	ts and outcome	19	
-	5.1	Synth	esis of the pervlene based polymer	19	
		5.1.1	Step 1	19	
		5.1.2	Step 2	20	
		5.1.3	Step 3	21	
		5.1.4	Step 4	22	
	5.2	Synth	esis of the perylene dianhydride based polymer	22	
		5.2.1	Step 1	22	
		5.2.2	Step 2	24	
6	6 Results and discussion				
	6.1	Absor	ption spectroscopy	29	
	6.2	Fluore	escence spectroscopy	30	
	6.3	Fourie	er transform infrared spectroscopy	33	
	6.4	Quant	titative solubility analysis	35	
	6.5	Synth	eses	36	
		6.5.1	Compound PA	36	
		6.5.2	Compound PI	37	
		6.5.3	Compound PIV	39	
		6.5.4	Compound PPIV	41	
		6.5.5	Compounds PDx	42	
		6.5.6	Compounds $PDAx$	47	
7	Conclusion		53		
8	Futi	uture work		55	
р,		1			
В1	bliog	raphy		57	
Α	Analyses results				
	A.1	NMR	spectra	59	
		A.1.1	Perylene based monomer	59	
		A.1.2	Perylene dianhydride based monomer	60	
		A.1.3	Spectra of reagents	68	
	A.2	STA a	nalyses	69	
	A.3	ATR F	T-IK analyses	71	

Preface

This report is a master thesis for a MSc in chemical engineering at Aalborg University. It is directed for readers either studying in the field of chemical engineering and organic synthesis, or those interested in perylene based organic photovoltaics and chromophores. The prerequisites for reading the report is an understanding of scientific chemical terminology. A list of abbreviations for both reagents and synthesized compounds is available in the next section. Sources are referred to with a number in square brackets, [X], indicating their placement in the bibliography. In the bibliography the sources are listed by number as they appear in the report under IEEE citation standards. The Digital Object Identifier (DOI) for online sources has been added, where available. Pictures in the report are mainly my own work, but includes few public domain images with no copyright claim, and images with due citation.

The purpose of the project was initially to investigate the behavior and properties, of a pendant side-chain conjugated perylene based photovoltaic polymer. Modifications were done to enhance the solubility, but subsequent challenges with the synthetic procedure resulted in the focus being directed towards synthesis optimization and planning.

I would like to thank my supervisor, associate professor Donghong Yu, for guidance, inspiration and an ever-positive spirit when it comes to problem solving. I would also like to thank Ph.d. student Rasmus Guldbæk Brandt and postdoc Zhengkun Du, for help with practical issues, ideas and assistance with NMR measurements. I would also like to thank my parents and my girlfriend, for moral and financial support, when my SU ran out just before the finish line.

Aalborg University, October 2, 2015

Nils Johannes Klitmøller <klitmoeller@live.dk>

List of Abbreviations

The following list contains the *IUPAC* names and abbreviations for all the syntheses products in a numbered order.

Unmodified perylene monomer and polymer:

- 1. benzo[g,h,i]perylene-1,2-dicarboxylic anhydride *PA* (*Perylene Anhydride*)
- 2. N-(6-hydroxyhexyl)benzo[ghi]perylene-1,2-dicarboximide *PI (Perylene Imide)*
- 3. N-(hexylprop-2-enoate)benzo[ghi]perylene-1,2-dicarboximide *PIV (Perylene Imide Vinyl)*
- poly(N-(hexylprop-2-enoate)benzo[ghi]perylene-1,2-dicarboximide) *PPIV (Poly(Perylene Imide Vinyl))*

Modified perylene diimide monomers and polymers:

- N,N'bis(x)perylene-3,4:9,10-bis(dicarboximide) PDx (Perylene Diimide x)
- N,N'bis(x)benzo[ghi]perylene-2,3:8,9-bis(dicarboximide)-11,12-dicarboxylic anhydride PDAx (Perylene Diimide Anhydride x)
- 3. N¹-(6-hydroxyhexyl)N²,N³-bis(x)benzo[ghi]perylene-2,3:8,9:11,12-tris(dicarboximide) *PTx* (*Perylene Triimide x*)
- 4. N¹-(hexylprop-2-enoate)N²,N³-bis(x)benzo[ghi]perylene-2,3:8,9:11,12-tris(dicarboximide) *PTVx* (*Perylene Triimide Vinyl x*)
- poly(N¹-(hexylprop-2-enoate)N²,N³-bis(x)benzo[ghi]perylene-2,3:8,9:11,12-tris(dicarboximide *PPTVx (Poly(Perylene Triimide Vinyl x))*

x refers to the four possible alkyl group substituents with abbreviations by codenumber, being either 2.6 for 2-ethylhexyl, 4 for 1-methylpropyl, 8 for octyl or 12 for dodecyl.

Additional abbreviations, in alphabetical order:

2EHA	A 2-ethylhexylamine		
AC	Acryloyl chloride		
AHex	6-amino-1-hexanol		
ATR	Attenuated Total Reflectance		
BPOX	Benzoyl peroxide		
CA	<i>p</i> -chloranil		
CDCl ₃	Deuterochloroform		
COSY	Correlation Spectroscopy		
DCM	Dichloromethane		
DMA	Dimethylacetamide		
DMF	Dimethylformamide		
DSC	Differential Scanning Calorimetry		
FT-IR	Fourier Transformed-Infrared		
НОМО	Highest occupied molecular orbital		
ITO	Indium tin oxide		
LUMO	Lowest unoccupied molecular orbital		
MA	Maleic anhydride		
NMR	Nuclear Magnetic Resonance		
OPV	Organic Photovoltaics		
PAH	Polycyclic aromatic hydrocarbon		
R_f	Retention factor		
SATP	Standard Ambient Temperature and Pressure		
STA	Simultaneous Thermogravimetric Analysis		
TEA	Triethylamine		
TGA	Thermogravimetric Analysis		
TLC	Thin Layer Chromatography		
TMS	Tetramethylsilane		
ZA	Zinc acetate dihydrate		

Chapter 1 Introduction

Modern society is growing, expanding, consuming at a constantly increasing rate. The need for alternative energy sources is becoming more and more obvious, and harnessing the potential of solar energy is an important challenge to pursue. Efficiencies of solar cells have risen constantly over the past 40 years, yet solar cell devices only constituted 0.1% of the renewable energy contribution to global power production, as of 2004.[10] The organic branch of photovoltaics (OPV), as opposed to inorganic, have clear advantages in terms of processing simplicity, production cost and duration; they also have low weight and high versatility of the finished OPV.[1] The tradeoff is considerably lower efficiency compared to conventional silicon-based solar cells, cf. figure 1.2.



Figure 1.1: The basic principle of a photovoltaic cell comprised of two organic components, the donor and acceptor, sandwiched between two electrodes, ITO and Al. The arrows indicate charge separation, but also the potential opposite, charge recombination. Design idea from [10].

The principle in a state-of-the-art organic solar cell, is based on bulk heterojunctions of the donor and the acceptor, sandwiched between two electrodes often, semi-transparent indium-tin oxide (ITO), and aluminium (Al). The donor material is responsible for the photon absorption, and subsequent excitation, with creation of an exciton - an electron and electron-hole pair. The electron is excited from the highest occupied molecular orbital (HOMO), to the lowest unoccupied molecular orbital (LUMO), leaving behind the electron hole.[10] Charge separation of the electron hole and electron, must occur, in which the excited electron is relaxed into the lower LUMO level of the acceptor material, and the hole moves towards the ITO electrode. The electron moves towards the aluminium electrode, cf. figure 1.1. In a bulk heterojunction cell the crucial charge separation occurs at the interface.[10] Maximizing interfacial area is therefore of utmost importance in the architectural design. In bulk heterojunctions, phase separation is present between donor and acceptor, therefore morphological control on a micrometer or even nanometer scale is utilized to achieve high interfacial area. The inspiration



Figure 1.2: "Devices included in this plot of the current state of the art have efficiencies that are confirmed by independent, recognized test labs (e.g., NREL, AIST, Fraunhofer) and are reported on a standardized basis." - This plot is courtesy of the National Renewable Energy Laboratory, Golden, CO. Content updated June, 2015.

for this masters thesis therefore came from an idea to experiment with a different type of polymer for OPV. Many OPV polymers rely on a conjugated backbone for charge transfer, either by conventional means of interchanging linear double and single bonds remniscent of polyacetylene, or by aromatically conjugated moieties as seen in polythiophene, cf. figure 1.3. Being able to create an OPV polymer from a free radical (vinyl) polymerization is interesting, and opens new possibilities in terms of controlling the molecular architecture. If vinyl co-polymerization of donor and acceptor material is made possible, while maintaining the photovoltaic properties, control of the interface can be done on a molecular scale as compared to bulk heterojunction cells, greatly increasing the odds of charge separation. Vinyl polymerization therefore holds promise, as interfacial area can be greatly increased by, e.g., self-assembled block co-polymerization of donor and acceptor material. A free radical polymerization is also a very flexible and versatile polymerization, while being very tolerant towards impurities. The downsides are reduced control over molecular weight and polydispersity.[7]





With this is mind, designing a novel OPV monomer with a vinyl moiety is of significant interest, with added ease of polymerization and potential increase in post-processing abilities. With a vinyl polymerization, a conjugated backbone is however not possible, requiring a different means of conductivity. The design of the conductive property may be fulfilled by designing a pendant side-chain conjugated system of aromatic moieties capable of π - π stacking between the pendants of repeating units, resulting in a semi-conductive acceptor material without a conjugated backbone. Fullerene derivatives, and polycyclic aromatic hydrocarbons (PAH) have seen much use in OPV due to their high electron affinity, and therefore application as the electron accepting component.[10] One PAH that has a large size while still being acceptably soluble, is the five-membered ring, perylene as seen in figure 1.4.



Figure 1.4: The five-membered polycyclic aromatic hydrocarbon, perylene.

The perylene starting point can be modified to introduce an "anchor" to the vinyl moiety, and thus the subsequent backbone. There must be sufficient distance between perylene and the backbone to avoid steric hindrance. A polymer of the design in figure 1.5 fulfill these criteria.



Figure 1.5: The envisioned polymer, poly(N-(hexylprop-2-enoate)benzo[ghi]perylene-1,2-dicarboximide).

One considerable well-known downside of perylene based compounds are the inherently low solubilities in most organic solvents. Therefore modification of the above polymer to enhance solubility may be done by creating a perylene diimide moiety, with alkyl groups being responsible for solubility enhancement. Modifications by addition of different primary alkylamines to perylene-3,4,9,10-tetracarboxylic dianhydride, further synthesized to a similar polymer as seen above, is visualized in figure 1.6.



Figure 1.6: The four envisioned polymers based on modified perylene diimides, for high solubility. Note that R is identical in both top and bottom, so only symmetrically substituted diimides are produced.

1.1 Thesis statement

The scope of this thesis can be summarized with two main synthesis "branches"; each comprised of a design phase of the polymer, followed by synthesis trials with subsequent optimization and characterization. The first branch of syntheses will end with the perylene based homopolymer. The second branch will end with the four different perylene dianhydride based homopolymers, modified with four different primary alkylamines. The focus points can be summarized as follows:

• Designing the synthetic route for the perylene based polymer

- Optimization of the synthetic route through practical trials
- Verification of the desired structures
- Analysis and characterization of both intermediates and final polymer
- Designing the synthetic route for the perylene dianhydride based polymers
 - Optimization of the synthetic route through practical trials
 - Verification of the desired structures
 - Analysis and characterization of all intermediates and final polymers
- Developing strategies for further work and potential optimizations

Chapter 2

Theoretical considerations

In the following sections relevant theoretical background will be summarized. This includes a theoretical foundation for the synthetic procedures.

2.1 Syntheses

2.1.1 The Diels-Alder cycloaddition

The Diels-Alder reaction is commonly employed to form six-membered rings, from a diene and a dienophile. The diene is the electron-rich component, and the dienophile must be electron-poor, often by containing electron-withdrawing groups. In the case of cycloaddition of maleic anhydride, the dienophile, strong electron-withdrawing groups cause an electron-poor double bond, making it a good dienophile for a Diels-Alder reaction.[6]

In the case of cycloaddition of maleic anhydride to perylene the reactivity is however so low, that it is best done solvent-less in molten maleic anhydride to drive the equilibrium, as first described by Clar and Zander in 1957.[2] The reaction is a relatively unfavorable one, due to the fact that two of the aromatic rings must temporarily but simultaneously break aromaticity, causing a rise in aromatic stabilization energy.[6][11] This reaction, with formation of the intermediate cycloadduct, can be seen in 2.1.



Figure 2.1: The Diels-Alder cycloaddition of maleic anhydride to the bay area of perylene, with the intermediate cycloadduct.

In the reaction, p-chloranil (tetrachloro-1,4-benzoquinone), will rapidly aromatize the cycloadduct intermediate by hydrogen scavenging, to yield the benzo[g,h,i]perylene-1,2-dicarboxylic anhydride. When applying an identical reaction mechanism to perylene tetracarboxylic dianhydride however, the reactivity is considerably lowered. This is presumably due to the electron withdrawing effect of the dianhydride moieties, lowering the effective diene strength of the perylene core. The reactivity is lowered to such an extent that an identical reaction as with perylene, takes days instead of minutes.[5]

2.1.2 Nucleophilic acyl substitution

The second step in the synthesis could include nucleophilic acyl substitution of the formed anhydride, with a primary amine. In order to form the monomer as visualized in the introduction. Reaction with 6-aminohexanol would undergo a reaction as the type in figure 2.2, resulting in the compound N-(6-hydroxyhexyl)benzo[ghi]perylene-1,2-dicarboximide. This reaction is also called a nucleophilic addition elimination.



Figure 2.2: The nucleophilic acyl substitution reaction of a primary amine with a cyclic anhydride.

The reaction mechanism involves a nucleophilic attack on one carbonyl carbon, resulting in a ring opening intermediate, before elimination of water. [8]

The third step of the synthesis could be another nucleophilic acyl substitution, this time with acryloyl chloride reacting with the primary alcohol of the recently added 6-aminohexanol. The resulting compound would be N-(hexylprop-2enoate)benzo[ghi]perylene-1,2-dicarboximide. In this case the roles are switched, with the nucleophile being the alcohol of the perylene based compound, and the electrophile being the carbonyl carbon of the acid chloride.



Figure 2.3: The nucleophilic acyl substitution reaction of an acid chloride with a primary alcohol.

Due to the hydrochloric acid evolution, an alkaline presence is necessary to remove the byproduct. This can be obtained by performing the reaction in pyridine,

2.1. Syntheses

or by addition of a weak base like triethylamine.[9]

2.1.3 Free radical polymerization

An example of an initiator for a free radical polymerization, is benzoyl peroxide, which undergoes homolytic cleavage above 60° C. This results in two unstable benzoyl radicals which swiftly breaks down to CO₂ and two phenyl radicals, cf. figure 2.4.[3]



Figure 2.4: Homolysis of benzoyl peroxide, forming two benzoyl radicals which quickly degrade to carbon dioxide and a phenyl radical.

The phenyl radical is highly reactive, and will attack most vinyl double bonds, resulting in the propagation and polymer formation, as seen in figure 2.5.



Figure 2.5: Initiation and propagation of a compound R containing a vinyl group, by a phenyl radical from the homolysis of benzoyl peroxide.

2.1.4 Solubility modification

Good solubility is important in many aspects, and can negatively affect syntheses if the solubility is too low. With this in mind, a modified perylene moiety was envisioned based on perylene-3,4,9,10-tetracarboxylic dianhydride as seen in figure 2.6. The modification to the dianhydride is an additional nucleophilic acyl substitution, identical to the one in figure 2.2. In this disubstitution reaction with primary alkylamines, the reaction should be catalyzed by zinc salt of either chloride or acetate. Zinc salts ensure symmetrical di-addition of the alkylamine, by somewhat uncertains mechnisms most likely attributed to a dehydration effect, or as a solutizer by anhydride complexation.[4] The resulting compound will be a perylene



Figure 2.6: Perylene-3,4,9,10-tetracarboxylic dianhydride, the precursor for a perylene moiety, modified for increased solubility.

bis-dicarboximide, hereby referred to as a diimide. In terms of effective solubility enhancement, it may be expected that branched alkylamines will perform better than unbranched ones with otherwise equivalent molar weight. This can be determined by examining diimides substituted with, e.g., 2-ethylhexylamine versus n-octylamine. One of the crucial properties of the resulting diimide is the breaking of the π -stacking plane at the imide nitrogen. The alkyl "tails" of the diimide will therefore enhance the solubility by allowing the molecule to interact better with organic solvents.

Chapter 3

Experimental design

In the following chapter, experimental considerations and strategies will be presented, based on well-known methods from literature. The overall goal was to synthesize both a perylene based polymer, and a perylene dianhydride based polymer modified with differing alkyl groups for solubility enhancement. Note that only the optimized and most successful procedures are described in this chapter. Specific methods, materials and techniques varied to a big extent, and with varying levels of success. Each attempt can be seen in detail in chapter 5 on page 19.

3.1 Synthesis of the perylene based polymer

The *PIV* polymer will be synthesized through a 3-step process, outlined below, with the 4th step being the free radical polymerization, resulting in *PPIV*, or poly(*PIV*).

3.1.1 Step 1 - benzo[g,h,i]perylene-1,2-dicarboxylic anhydride

The synthesis of benzo[g,h,i]perylene-1,2-dicarboxylic anhydride (*PA*) will be done solventless with perylene dissolved in refluxing molten maleic anhydride (bp: 202°C) in the presence of tetrachloro-1,4-benzoquinone (*p*-chloranil), with a reaction time of approximately 20 minutes. No protective atmosphere will be needed.



Figure 3.1: Diels-Alder cycloaddition of maleic anhydride to perylene, oxidized by *p*-chloranil.

3.1.2 Step 2 - N-(6-hydroxyhexyl)benzo[ghi]perylene-1,2-dicarboximide

Synthesis of the imide N-(6-hydroxyhexyl)benzo[ghi]perylene-1,2-dicarboximide (*PI*), from *PA* in step 1 and 6-aminohexanol, will be carried out in refluxing DMA (bp: 165°C). The synthesis will require no catalyst nor protective atmosphere, and will be allowed to react for 12 hours.



Figure 3.2: Condensation of 6-aminohexanol with PA, through nucleophilic acyl substitution.

3.1.3 Step 3 - N-(hexylprop-2-enoate)benzo[ghi]perylene-1,2-dicarboximide

Synthesis of the monomer N-(hexylprop-2-enoate)benzo[ghi]perylene-1,2-dicarboximide (*PIV*) from reaction between *PI* in step 2 and acryloyl chloride (AC) will be carried out in DCM at room temperature, in the presence of triethylamine (TEA). The reaction will be protected with a N_2 purge, and allowed to react for approximately 24 hours.



Figure 3.3: Nucleophilic acyl substitution of *PI* and acryloyl chloride.

Column chromatography will be used to recover pure PIV.

3.1.4 Step 4 - free radical polymerization

Polymerization of pure *PIV* to yield poly(N-(hexylprop-2-enoate)benzo[ghi]perylene-1,2-dicarboximide) will be carried out in DMA at 80°C, initiated by 15% mol benzoyl peroxide. The reaction will be protected with a N₂ purge identical to that in step 3, with a reaction time of approximately 24 hours under stirring.



Figure 3.4: Vinyl polymerization of PIV initiated by benzoyl peroxide.

3.2 Synthesis of the perylene dianhydride based polymer

The plan to synthesize the finished polymer with all the perylene diimides of differing alkyl groups, would however be unsuccesful after the cycloaddition of maleic anhydride proved to be cumbersome. The remaining syntheses steps after step 2 will therefore not be described, as no insight was gained into these steps. It is assumed the steps would have been otherwise similar to those of the perylene based monomer.

3.2.1 Step 1 - N,N'bis(x)perylene-3,4:9,10-bis(dicarboximide)

The diimides, *PDx*'s, will all be synthesized in identical ways, by reaction of their 4 respective amine substituents with the starting compound perylene-3,4,9,10-tetracarboxylic dianhydride (PDA). The modifications will consist of the four primary alkylamine substituents: *sec*-butylamine, 2-ethylhexylamine, n-octylamine and n-dodecylamine, resulting in the diimides, (*PD4*), (*PD2.6*), (*PD8*) and (*PD12*), respectively. It will be carried out in refluxing DMA (bp: 165°C). Catalytic zinc

acetate dihydrate will be added in an equimolar amount to the PDA. A 5 hour reaction time will be allowed.



Figure 3.5: Condensation of the four primary alkylamines with PDA, through nucleophilic acyl substitution, catalyzed by zinc acetate.

3.2.2 Step 2 - N,N'bis(x)benzo[ghi]perylene-2,3:8,9-bis(dicarboximide)-11,12-dicarboxylic anhydride

The synthesis of the *PDAx*'s will be done very similar to that of the perylene based monomer, the main difference being reaction time. It will be carried out by dissolving the *PDx*'s in molten maleic anhydride at 145° C in the presence of tetrachloro-1,4-benzoquinone (*p*-chloranil), with a reaction time of approximately 4 days. No protective atmosphere will be used. Small amounts of various solvents will be added, to prevent maleic anhydride from subliming and depositing on the inside of the apparatus.



Figure 3.6: Long duration Diels-Alder cycloaddition of maleic anhydride to the *PDx* diimides, oxidized by *p*-chloranil.

Chapter 4

Materials and analyses

In this chapter all the materials, chemicals and methods of analyses will be described. Both apparatus for analyses and specific methods of analysis will be listed in the final section, 4.2.

4.1 Chemicals

In this section all chemicals and brands will be listed, for both solvents and reagents. All chemicals were used "as received" with no further purification or treatment.

4.1.1 Solvents

Dimethylacetamide (ReagentPlus[®] \geq 99.0%) Dichloromethane (CHROMASOLV[®] \geq 99.8%) Chloroform (GC 99.0%-99.4%) Ethyl acetate (CHROMASOLV[®] \geq 99.7%) Diethyl ether (ACS \geq 99.8%) Acetone (Puriss., $GC \ge 99\%$) 2-propanol (GC \geq 99.5%) Hexane (CHROMASOLV[®] \geq 97.0%) Heptane (CHROMASOLV[®] > 99.0%) Toluene (ACS \geq 99.7%), all of the above purchased from Sigma-Aldrich Chemie GmbH (Germany). Ethanol (Absolute, TechniSolv[®] \geq 99.5%) purchased from VWR Chemicals Prolabo, Bie & Berntsen. Xylene (mix of o, m, and p-dimethylbenzene) purchased from Merck Schuchardt OHG (Germany), through Bie & Berntsen (Denmark). Deuterochloroform, CDCl₃ (D, 99.8%) Cambridge Isotope Laboratories, Inc. (USA).

4.1.2 Reagents

Perylene (\geq 99%) Perylene-3,4,9,10-tetracarboxylic dianhydride (97%) *p*-chloranil (99%) Zinc acetate, dihydrate (ACS \geq 99.0%) 6-aminohexanol (97%) 2-ethylhexylamine (98%) sec-butylamine (99%) Octylamine (99%) Dodecylamine (was lost in the moving phase of the institute) Hydrochloric acid (ACS 37%) Acryloyl chloride ($\geq 97\%$) Triethylamine (\geq 99%), all of the above purchased from Sigma-Aldrich Chemie GmbH (Germany). Maleic anhydride, purchased from ICN Biomedicals, Inc. through Bie & Berntsen A-S (Denmark). Benzoyl peroxide (75%, remainder water) ACROS Organics (Belgium).

Other

TLC Silica Gel 60 sheets, purchased from Merck Millipore (Germany). 20 μ L Hirschmann Micropipettes, purchased from Sigma-Aldrich Chemie GmbH (Germany). Silica Gel 60 (63 μ m-200 μ m), purchased from AppliChem GmbH (Germany).

Qualitative filterpaper 413 (5-13 μ m) ashless, sizes 75-110mm, purchased from VWR International (USA).

4.2 Analysis methods and materials

In this section the analytical apparatus, and specific methods and settings will be listed for each analysis.

4.2.1 Nuclear magnetic resonance spectroscopy

¹H NMR analyses were performed on a Brüker AvanceTM III HD 600 (600MHz magnet). Only deuterochloroform (CDCl₃) solvent was used, and no solvent suppression in the measurement program. Chamber temperature was 298K, with TMS as internal standard at 0ppm. Standard 1D and 2D Correlation Spectroscopy (COSY) ¹H NMR measurements were performed.

4.2.2 Fluorescence spectroscopy

UV fluorescence analyses were conducted on a Varian Cary Eclipse fluorescence spectrophotometer in a Hellma[®] QS SUPRASIL[®] quartz glass cuvette, with 10mm light path and 1400 μ L chamber. Chloroform was the solvent in all cases. The most fluorescent samples were diluted to a higher degree. All samples showed such high fluorescence, that the internal Xenon flash lamp was set to low voltage. All the resulting compounds from the syntheses show fluorescence from exposure to a large interval of UV wavelengths. The procedure therefore consisted of 3 steps, where the first step was determining the maximum emission wavelength. All excitation measurements take place in the 200nm - 400nm range, while emission spectra are in the visible range of 400nm - 700nm.

The data acquisition for each sample was specifically done by running an initial emission plot from a fixed 340nm long wave excitation wavelength. The maximum visible emission wavelength was then noted and used as a fixed measure, while plotting the subsequent excitation spectrum. The found maximum excitation wavelength was then used to yield the final emission spectrum in visible light. All spectra with more than one data set consists of normalized values for ease of comparison.

4.2.3 Absorption spectroscopy

Ultraviolet to visible light absorption was measured on a Varian Cary 50 UV-VIS spectrophotometer, with a scan rate of 4800nm/min in a range of 800-260nm. Chloroform was the solvent in all cases, thus the native cut-off value of 260nm. Measurements were done in a Hellma[®] QS SUPRASIL[®] quartz glass cuvette, with 10mm light path and $1400\mu L$ chamber. Internal baseline subtraction was done with a clean chloroform solution in the cuvette, and all samples used the same baseline. All samples were diluted to yield a maximum absorption of approximately 0.6-0.9.

4.2.4 Simultaneous thermal analysis

Simultaneous thermal analyses, comprising differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), were conducted on a Perkin Elmer STA6000 Simultaneous Thermal Analyzer. The heating profile was consistent for all samples and consisted of heating from 40°C to 400°C at a heating rate of 10°C/minute, in an alumina crucible under a nitrogen purge of 20mL/minute. Sampling rate was 8 datapoints/second. Between 5-8mg samples were used in all cases. Baselines with empty crucibles were measured and subtracted from each individual measurement. The melting point of monomeric samples were determined as the onset of the melting endotherm, whereas the peak of the endotherm was chosen at the melting temperature for polymers.

4.2.5 Fourier transform infrared spectroscopy

Measurements were done in the solid state on a Varian 660-IR FT-IR Spectrometer, with a PIKE MIRacleTM Single Reflection ATR attachment (Attenuated Total Reflectance). 32 scans were done from 4000cm⁻¹ - 600cm⁻¹(2500nm - 16667nm, respectively) with a 1,9cm⁻¹ sampling rate, in transmittance percentage mode. Sample preparation consisted of multiple applications of material, each application being compacted onto the ATR crystal to insure uniform contact between crystal and sample. A zero sample measurement was performed and subtracted from each sample measurement.

4.2.6 Quantitative solubility analysis

High precision of this measurement was not required, only sufficient reliability to determine a pattern in solubility of the various compounds, to judge the evolution of the solubility between intermediates.

The measurement was done by preparing an approximately 12mL saturated solution of the specific compound in chloroform, in a 15mL centrifuge tube at room temperature (22°C). Low-tech filtration was performed by slowly forcing a small wad of cotton to the bottom of the tube, leaving a solid-free supernatant on top. 10mL supernatant was then transferred by Finnpipette as 2x5mL portions to a pre-weighed 1,2g aluminium pan, where the chloroform was left to evaporate for approximately 1 hour. The pan with dry crystallized solids were then weighed to 1 decimal precision on the milligram, and gravimetric and molar solubility was calculated.

Chapter 5

Experiments and outcome

In the following chapter the procedures for all attempts of the syntheses will be summed up and outlined. If a synthesis of the same compound is repeated in an identical fashion, only one subsection will be created, noting the amount of times the synthesis was repeated. As these are novel types of compounds, this was a trial-and error approach requiring many attempts and tweaks. This chapter will only briefly conclude on the success or failure of the syntheses, and not contain NMR and TLC results and discussions - these will be referred to, and can be found in chapter 6 on page 29.

5.1 Synthesis of the perylene based polymer

In this section all pilot experiments and attempts towards synthesizing the perylene based polymer will be listed.

5.1.1 Step 1

#Pilot synthesis of *PA*

20.04grams of MA (204mmol), 503mg perylene (1.99mmol) and 1.011g *p*-chloranil (4.11mmol) was mixed in a 3-neck flask, in an insulated sandbath at 220°C with magnetic stirring. Reaction time was approximately 20 minutes once reflux was obtained. A simple single-walled, short glass-tube was adequate heat dissipation for reflux.

Quenching was done in 75mL near-boiling xylene, followed by vacuum filtration. It was washed on the filter with extra xylene then diethyl ether. After drying in an oven, the product was suspended in 50mL water, then vacuum filtered once more and rinsed with ether on the filter. The product was then dried in a oven at 105°C, for a yield of 83% with 578mg. Reaction was assumed to have occurred from a visible change of fluorescence wavelength, and a change in TLC behaviour. Product is too insoluble in chloroform, and other solvents to show a ¹H NMR signal.

#2 synthesis of PA

Amounts were 47.53grams of MA (484mmol), 1.436g perylene (5.69mmol) and 2.824g *p*-chloranil (11.48mmol). Besides being carried out in a 2-neck flask in a heating mantle instead of a sandbath, and the chloranil being slowly added, the procedure was identical to the pilot attempt. This method proved much faster, with less temperature fluctuations, and more aggressive reflux. Due to the slow addition of chloranil, the *PA* was observed to precipitate upon formation. Quenching and purification was similar. The product was washed with water, ethanol, then ether. After drying at 105° C, the yield was 80.5% with 1.605g of *PA*. TLC results were similar to those in the pilot attempt.

5.1.2 Step 2

#Pilot synthesis of *PI*

452mg *PA* (1.29mmol) and 254mg (2.17mmol) Ahex was added to 40mL DMA in a roundbottom flask submerged into a 150 °C oilbath with magnetic stirring. Barely any reflux occurred. Reaction time was 20 hours. The product was slowly precipitated with 120mL water, vacuum filtered after cooling. It was washed on the filter with small amounts of water followed by methanol. After drying at 60°C, yield was 103% with 595mg of *PI*, indicating impurities. Change was confirmed with TLC, and structure was confirmed with ¹H NMR analysis, although signs of impurities were present.

#2 synthesis of PI

1.400g *PA* (3.99mmol) from "#2 synthesis of *PA*" was firstly suspended in 40mL DMA in a roundbottom flask, in a heating mantle. Once close to 100°C, 762mg Ahex (6.50mmol) was added, and immediate dissolution and color change was observed. Once refluxing, the reaction was left for 16 hours. Precipitation was similarly done in 120mL water, but after the initial vacuum filtering the solids were suspended in 100mL ethanol, followed by additional vacuum filtering and washing with ethanol and ether to achieve a higher purity. After drying at 110°C the yield was 91.7% with 1.639g *PI*. ¹H NMR analysis indicated a purer product than that of the pilot attempt.

5.1.3 Step 3

#Pilot synthesis of *PIV*

506mg *PI* (1.13mmol) was suspended in 25mL DCM in a 2-neck roundbottom flask, fitted with a septum for nitrogen purge, with magnetic stirring. After purging the vessel, 1.5mL TEA (1.088g, 10.76mmol) was added, followed by 1.5mL AC (1.677g, 18.55mmol) in 3 portions. After the final addition of AC, the solids dissolved completely. Reaction proceeded for 24 hours, under nitrogen purge.

Precipitation of the product proved to be challenging, as when done with acetone was unsuccessful, requiring evaporation of solvents, followed by dissolution in DMA and precipitation with water. This was unsuccessful as a colloid suspension was seemingly formed, incapable of being vacuum filtered. Through many attempts it was determined that precipitation with hexane from DCM was preferable. The product was then washed with ethanol to remove excess hexane, then suspended in a 2M HCl solution to protonate and dissolve remaining TEA. An additional vacuum filtering followed, and washing with water, ethanol then ether on the filter. After drying at 60°C, yield was 71% with 405mg of *PIV*. Both TLC and ¹H NMR analysis indicated an impure product, but successful synthesis.

#2 synthesis of PIV

1.423mg *PI* (3.18mmol) from #2 synthesis of *PI* was suspended in 75mL DCM in a 2-neck roundbottom flask, fitted with a septum for nitrogen purge, with magnetic stirring. After purging the vessel, 10.5mL TEA (7.291g, 72.06mmol) was added, followed by 3.605mL AC (4.034g, 44.57mmol). Reaction proceeded for 24 hours, under nitrogen purge.

Precipitation was successfully done in hexane, followed by vacuum filtering. The solids were suspended in a 2M HCl solution, and vacuum filtered once more. It was washed with water, ethanol, then ether on the filter. After drying, it was purified by flash column chromatography with 63μ m-200 μ m silica gel, eluted with dichloromethane under induced pressure with a hand-pump. The eluted product solution was concentrated in a rotavap, precipitated with triple the volume of hexane, vacuum filtered and washed with ethanol, then dried in an oven for 2 days at 110°C. The final yield was only 18.8% with 300mg of *PIV* in a bright orange color. Both TLC and ¹H NMR analysis showed a very pure product of the expected structure.

5.1.4 Step 4

#Pilot synthesis of *PPIV*

206mg *PIV* (0.41mmol) was dissolved in 60mL DMA in a 2-neck roundbottom flask under nitrogen purge with magnetic stirring. 60mL was the minimum volume for complete dissolution. 70mg BPOX (0.22mmol) was added, and the flask was lowered into a 70°C oilbath to initiate polymerization. 24 hours was given for reaction. No precipitation was seen after this duration, so precipitation was done with water. After filtering, 92mg solids are collected. ¹H NMR analysis shows no sign of polymerization.

#2 synthesis of PPIV

232mg pure *PIV* (0.46mmol) from "#2 synthesis of *PIV*" was dissolved in approximately 10mL DMA in a 2-neck roundbottom flask under nitrogen purge with magnetic stirring. 18mg BPOX (0.06mmol) was added, and the flask was lowered into an 80°C oilbath to initiate polymerization. After 24 hours, good precipitation was observed, and the precipitate was vacuum filtered in a 20mm glass-frit filter size #3, upon cooling down. It was washed with water and ethanol on the filter. Unreacted monomer, and potential oligomers were washed out with chloroform and the filtrate was analyzed separately. TLC analysis of the filtrate shows a change, with different fractions when compared to *PIV*. The *PPIV* was completely insoluble in all organic solvents. FT-IR analysis on the solid *PPIV* further shows a successful change, when compared to *PIV*.

5.2 Synthesis of the perylene dianhydride based polymer

In this section steps 1 and 2 of the synthesis towards the perylene-3,4,9,10-tetracarboxylic dianhydride (PDA) based polymer will be listed. Step 2 of the synthesis was never fully successful, therefore the subsequent steps, 3-5, were not attempted.

5.2.1 Step 1

Synthesis of PD4

3.046 PDA (7.76mmol) was suspended in 300mL DMA in a roundbottom flask in a heating mantle. 3.10mL *sec*-butylamine (2.244g, 30.69mmol) was added, along-side 1.716g zinc acetate dihydrate (7.82mmol), and the suspension was brought to reflux. After 3 hours all solids were dissolved. Time given for reaction was 5 hours.

Precipitation was done in 500mL water, followed by vacuum filtration. It was washed on the filter with extra water, then diethyl ether. It was only rinsed with sparing amounts of ethanol, due to the increased solubility. The solids were dried in an oven at 110°C for 1 hour, for a yield of 97.08% with 3.788g of dark red *PD4*. Both TLC and ¹H NMR analysis verified a successful synthesis.

Synthesis of PD2.6

This synthesis was carried out 4 times to provide more precursor for the next step, all with the identical tried and verified procedure, as the first synthesis described below. The amounts in the subsequent syntheses varied, but ratios and techniques were identical.

1.200g PDA (3.06mmol) was suspended in 120mL DMA in a roundbottom flask in a heating mantle. 2.00mL 2-ethylhexylamine (1.578g, 12.2mmol) was added, alongside 680mg zinc acetate dihydrate (3.10mmol), and the suspension was brought to reflux. After approximately 2 hours all solids were dissolved. Time given for reaction was 5 hours.

A dark red precipitate formed when quenched with 400mL water, followed by vacuum filtration. It was washed on the filter with extra water, ethanol then diethyl ether. The solids were dried in an oven at 110°C for 1 hour, for a yield of 98.9% with 1.860g of dark red *PD2.6*. Both TLC and ¹H NMR analysis showed a very pure product of the expected structure, with no variation in result of the different syntheses.

Synthesis of PD8

302 mg PDA (0.77mmol) was suspended in 35 mL DMA in a roundbottom flask in a heating mantle. 510μ L octylamine (399 mg, 3.09 mmol) was added simultaneously with 172 mg zinc acetate dihydrate (0.78 mmol), and the suspension was brought to reflux. All solids never seemed fully dissolved. Time given for reaction was 2 hours.

Precipitation was done with 150mL water, resulting in a seemingly brown precipitate, followed by vacuum filtration. It was washed on the filter with extra water, ethanol then diethyl ether. It was dried in an oven at 105°C for 1 hour, for a yield of 103% with 488mg dark brownish-red *PD8*. TLC and ¹H NMR analysis showed a successful reaction had occurred, with few impurities.

Synthesis of PD12

340mg PDA (0.87mmol) was suspended in 30mL DMA in a roundbottom flask in a heating mantle. 639mg solid dodecylamine (3.45mmol) and 200mg zinc acetate dihydrate (0.78mmol) was added, and the suspension was brought to reflux. All

solids appeared to be dissolved after only 30 minutes. Time given for reaction was 2 hours. Immediately after raising the flask from the heating mantle, solids were seen to precipitate.

Full precipitation was done with 100mL water, yielding a deep purple colored precipitate, followed by vacuum filtration. It was washed on the filter with extra water, ethanol and some diethyl ether. It was dried in an oven at 105°C for 1 hour, for a yield of 98.7% with 622mg dark brownish-red *PD8*. TLC and ¹H NMR analysis revealed a successful reaction but with a significant unidentified signal in the ¹H NMR spectrum.

5.2.2 Step 2

This step was attempted many times with different techniques, with varying levels of success, with the exception of the synthesis of *PDA8* and *PDA12* which were only attempted once.

Synthesis of PDA4

The different syntheses of this compound will be listed below, with #1 describing the most successful procedure. Each subsequent, and arbitrarily numbered, procedure will only list the differences and important notes, but not amount of reagents and details of the syntheses.

#1 Synthesis of PDA4

24,4g maleic anhydride, 365mg *PD4* (0.73mmol) and 605mg chloranil (2.46mmol) was simultaneously added to a 3-neck flask, and inserted into a 145°C insulated sandbath, with magnetic stirring. Approximately 5mL ethyl acetate was added to reduce sublimation of maleic anhydride. The flask was equipped with a single-walled, short glass-tube which was kept open. Otherwise the flask was closed. Reaction time was 100 hours. The reaction was ended by adding 50mL acetone, which dissolved the maleic anhydride. 200mL of water was slowly added, and the suspension was vacuum filtered. The solids were rinsed on the filter with additional water, ethanol, and diethyl ether. After drying in an oven at 110°C, 566mg of product was retrieved as a slightly lighter colored red solid. ¹H NMR analysis indicated conversion of approximately 37%mol. TLC analysis revealed an identical picture, with both compounds *PD4* and *PDA4* being visible.

#2 Synthesis of PDA4

This synthesis was identical to that of #1, but with a small amount of acetone, instead of 5mL ethyl acetate. Close to no conversion could be seen from NMR analysis.

5.2. Synthesis of the perylene dianhydride based polymer

#3 Synthesis of PDA4

Maleic anhydride was brought to reflux in a heating mantle, with *PD4*, chloranil and a couple milliliters of chloroform. Refluxing at 110°C. Reaction time was 30 minutes. No reaction could be seen.

#4 Synthesis of PDA4

Maleic anhydride, *PD4* and chloranil was brought to reflux in a 200°C sandbath. Nitrogen purge was used to prevent oxidative thermal degradation. However, the maleic anhydride decomposed to a tar-like substance. No product could be recovered.

Synthesis of PDA2.6

The different syntheses of this compound will be listed below, with #1 describing the most successful procedure. Each subsequent, and arbitrarily numbered, procedure will only list the differences and important notes, but not amount of reagents and details of the syntheses. The ¹H NMR spectra of all procedures after #1 can be found in A.1.2 on page 63 in the appendix.

#1 Synthesis of PDA2.6

22.2g maleic anhydride was melted in a 3-neck flask in a heating mantle, after which 424mg *PD2.6* (0.69mmol) and 980mg chloranil (3.99mmol) was added. Reflux was obtained in a single-walled, short glass-tube. It was brought to reflux for 20 minutes, after which it was quenched with 75mL near-boiling xylene and vacuum filtered. It was rinsed with 200mL water, 100mL ethanol, then 100mL diethyl ether. After drying in an oven at 100°C, 343mg was recovered. ¹H NMR analysis indicated conversion of approximately 32%mol. TLC analysis showed the presence of *PDA2.6*.

#2 Synthesis of PDA2.6

In this synthesis maleic anhydride was attempted dried by boiling in a open vessel initially, before addition of *PD2.6* and chloranil. Nothing else was added, and the mixture was refluxing for 1 hour. It was quenched with xylene. The NMR analysis showed potential thermal decomposition with many small emergent signals.

#3 Synthesis of PDA2.6

This synthesis was identical to that of #2, the only difference being that it was quenched with water, and had slightly more maleic anhydride to *PD2.6*. The NMR analysis indicated decomposition, but different to that of #2.

#4 Synthesis of PDA2.6

This synthesis relied on standard dissolution of both maleic anhydride and *PD2.6* in DMA. No reaction occurred, and the NMR spectrum showed only *PD2.6*.

#5 Synthesis of PDA2.6

This procedure relied on a lower temperature, achieved by submersion in an oilbath at 130°C. The ratio of maleic anhydride to *PD2.6* was 60, and a small amount of acetone was added. Additional fresh maleic anhydride was added each day, for a total reaction time of 5 days. The NMR spectrum showed only trace amounts of potential *PDA2.6*.

#6 Synthesis of PDA2.6

This procedure similarly employed an oilbath at 130°C. The difference from #5 was that this synthesis was quenched with water. No conversion could be seen from NMR results.

#7 Synthesis of *PDA2.6*

This synthesis relied on refluxing maleic anhydride in a heating mantle with *PD2.6*. Reaction time was half an hour, and it was quenched with water. Close to no conversion could be seen.

#8 Synthesis of PDA2.6

In this procedure maleic anhydride was kept at approximately 170°C with a heating mantle. A small amount of DMA was added along with *PD2.6*. Reaction time was approximately 2 hours. Some conversion could be seen in NMR signals, but with emergent peaks, most likely from degradation.

#9 Synthesis of PDA2.6

In this procedure, maleic anhydride was kept at approximately 200°C for 1 day in a heating mantle. The maleic anhydride solidified to a tar-like substance. No product was recovered.

Synthesis of PDA8

27.01g maleic anhydride was melted in a 3-neck flask in a heating mantle, after which 485mg *PD8* (0.79mmol) and 906mg chloranil (3.68mmol) was added. Reflux was obtained in a single-walled, short glass-tube. It was brought to reflux for 20 minutes, after which it was quenched with 75mL near-boiling xylene and vacuum filtered. It was rinsed with 200mL water, 100mL ethanol, then 100mL diethyl ether. After drying in an oven at 100°C, 260mg was recovered. TLC analysis indicated no presence of *PDA8*.

Synthesis of PDA12

20.05g maleic anhydride was melted in a 3-neck flask in a heating mantle, after which 620mg *PD12* (0.85mmol) and 1.039g chloranil (4.23mmol) was added. Reflux was obtained in a single-walled, short glass-tube. It was brought to reflux for 20 minutes, after which it was quenched with 75mL near-boiling xylene and vacuum filtered. It was rinsed with 200mL water, 100mL ethanol, then 100mL diethyl ether. The *PD12* was hardly soluble in MA, and after drying in an oven at 100°C, 449mg product was recovered. TLC analysis indicated no presence of *PDA12*.

Chapter 6

Results and discussion

A discussion of the results of the syntheses, analyses and so forth can be found in this chapter. The sections are ordered by analyses not immediately essential to characterization of the compounds, followed by a section for each individual compound with respective crucial analyses.

6.1 Absorption spectroscopy

The absorbance of the perylene based compounds can be found in figure 6.1. There is not much difference between the compounds, with only subtle changes to the shoulders of the main peak at 340nm.



Figure 6.1: Absorbance spectra of compounds PA, PI, PIV in chloroform.

Similarly, the perylene dianhydride based monomers show no effective difference in absorbance.



Figure 6.2: Absorbance spectra of the *PDx* diimide compounds in chloroform. Note that the Y-axis has been reduced to a maximum of 0.7 for better resolution of the series.

6.2 Fluorescence spectroscopy

All the compounds show fluorescence under UV light. Figure 6.3 illustrates this for compounds *PA*, *PI*, *PIV* and perylene.



Figure 6.3: Perylene (P), PA (1), PI (2) and PIV (3) dissolved in chloroform, fluorescing under long-wave UV light.

The optimum excitation and emission wavelength for each compound in the perylene based monomer series, is seen in table 6.1. The emission spectra of com-

6.2. Fluorescence spectroscopy

Table 6.1: Peak excitation and subsequent emission wavelength in chloroform of compounds *PA*, *PI*, *PIV* and perylene. Only the anhydride exhibits two dominant emission peaks. All wavelengths are in nanometers.

	$\lambda_{ex,max}$	$\lambda_{em,max}$
Perylene	322	473
PA	335	525
PI	343	523
PIV	310	522

pounds *PA*, *PI*, *PIV* and perylene can be seen in figure 6.4, when excited by their respective optimum UV excitation wavelengths. Note that emission intensity has been modified for each data set, so the spectra are comparable in size. This is done due to the aforementioned fact that concentration varies, so intensity maxima are otherwise incomparable.



Figure 6.4: Emission spectra of compounds *PA*, *PI*, *PIV* and perylene in chloroform. The UV excitation wavelength varied between 338nm and 350nm depending on the compound, as can be seen in table 6.1. Peak intensity values are normalized to 100 for all series.

A hypsochromic shift in fluorescence is observed from perylene to the anhydride (*PA*), aswell as a small emergent peak at 490nm. Loss of the latter occurs when forming the dicarboximide (*PI*). The change in fluorescence is corresponding to the visibly changed fluorescent color of the compounds, with no apparent difference between *PI* and *PIV*. A similar table of maximum excitation and emission wavelength, for the diimide compounds (PDx) can be seen in table 6.1. The starting compound perylene-3,4,9,10-tetracarboxylic dianhydride (PDA) has likewise been included in this series. Figure 6.5 shows the fluorescence emission profiles for the PDx compounds.

Table 6.2: Peak excitation and subsequent emission wavelengths in chloroform of the *PDx* compounds, and PDA for reference. All wavelengths are in nanometers.

	$\lambda_{ex,max}$	$\lambda_{em,max}$
PDA	259	521
PD4	258	575
PD2.6	257	576
PD8	257	576
PD12	258	576
	I	
PDA	PDI4 P	DI2.6 PDI8



Figure 6.5: Emission spectra of all the *PDx* compounds and perylene-3,4,9,10-tetracarboxylic dianhydride (PDA) in chloroform. The UV excitation wavelength was approximately 258nm, as can be seen in table 6.2. Peak intensity values are normalized to 100 for all series.

Interestingly, the difference in fluorescence of the PDx compounds is close to none, except for the profile of PD4, showing a stronger shoulder at 550nm.

6.3 Fourier transform infrared spectroscopy

Only compounds of the perylene based synthesis route will be included in this section. FT-IR spectra of *PD2.6* and *PD4* can be found in the appendix in A.3 on page 71.



Figure 6.6: Transmittance ATR FT-IR of PA. The three most important attributes have been marked.

In the spectrum of *PA* in 6.6 the three most important attributes are, from left, the C=O bond stretching of the two carbonyls of the anhydride at 1750cm⁻¹. This band is visible in all the compounds. Next band at 1200cm⁻¹ is the C-O stretching of the anhydride group. The last band at 800cm⁻¹ is assumed to be the bending of aromatic C-H bonds and C=O bending of the anhydride carbonyls, this double band is also visible in all the compounds. In the spectrum of *PI* in 6.7 below, the C-O stretching at 1200cm⁻¹ has disappeared by replacement with an dicarboximide group, while a new broad band has appeared around 3450cm⁻¹ originating from the stretching of the O-H bond in the newly introduced alcohol group. Similarly, a band originating from aliphatic C-H stretching has been introduced at 2900cm⁻¹.



Figure 6.7: Transmittance ATR FT-IR of PI. The four most important attributes have been marked.



Figure 6.8: Transmittance ATR FT-IR of *PIV*. The seven most important attributes have been marked and numbered.

Compound *PIV* in figure 6.8 creates a spectrum with many important bands, numbered 1 through 7 for ease of reference. 1 is the aliphatic band as also seen in *PI*, 2 at 1750cm⁻¹ is the newly introduced ester bond from the condensation

reaction of acryloyl chloride and the alcohol group seen in the spectrum of *PI*. *3* is the familiar anhydride group and *4* is C=C stretching from the vinyl end-group at 1600cm^{-1} . *5* at 1200cm^{-1} is C-O stretching from the newly formed ester bond, and *6* is potentially C-H bending of the vinyl protons at 950cm^{-1} . *7* is the recurring aromatic proton and carbonyl bending. In the spectrum of *PPIV* in figure 6.9, the most important observations are the apparent, and expected, disappearance of the C=C stretch at 1600cm^{-1} and the disappearance of the vinyl proton signal at 950cm^{-1} . These two properties indicate a successful polymerization of the vinyl moieties.



Figure 6.9: Transmittance ATR FT-IR of PPIV. The four most important attributes have been marked.

The carbonyl stretching of the ester group is still visible just to the left of the anhydride carbonyl stretch, in the *PPIV* spectrum, as is the C-O stretch at 1200cm⁻¹.

6.4 Quantitative solubility analysis

The solubility of the various compounds can be seen in table 6.3. The solubility of the compounds appeared to be highest in chloroform, when compared to DMF, DMA, ethanol, acetone, toluene, ethyl acetate and diethyl ether. Benzo[g,h,i]perylene-1,2-dicarboxylic anhydride, *PA*, was omitted from measurement, due to its severely low solubility, completely hindering measurement with this technique. The solubility of the perylene based compounds show an interesting evolution, from effectively zero for *PA* to a hardly soluble *PI*, ending in a big increase in solubility for *PIV*, mainly due to the ester group. If the evolution of the solubility can be extrap-

	Molar weight	Solubility	Molar solubility
	g/mol	g/liter	mM
Perylene	252.31	4.1	16
PA	350.37	${\sim}0$	~ 0
PI	447.52	0.7	1.6
PIV	502.57	48	94
PD4	502.56	22	43
PD2,6	617.77	5.8	9.4
PD8	617.77	1.8	3.0
PD12	726.99	2.4	3.4

Table 6.3: The gravimetric and molar solubility of the various compounds at 22°C in chloroform. Determined from dry weight of evaporated saturated solutions. Perylene is included as a reference.

olated with some reliability to the perylene dianhydride based compounds, one might expect the solubility of the monomer modified with *sec*-butylamine (PTV4) to be very high.

The difference in solubility of the *PDx* compounds indicate that if the imideadjacent carbon atom is secondary, i.e. in the case of *PD4*, a large increase in solubility can be expected. This may be due to disruption of the tight π - π stacking plane of the perylene moieties, since a branching so close to the imide will have a stronger disrupting effect.

6.5 Syntheses

This sections contains a discussion of the results of the syntheses with relevant ¹H NMR and TLC analyses. There are subsections for each individual compound with respective crucial analyses.

6.5.1 Compound PA

The solubility of benzo[g,h,i]perylene-1,2-dicarboxylic anhydride (*PA*) was too low to reveal a signal in ¹H NMR. However, all attempts at synthesizing *PA* were successful, given the positive ¹H NMR spectra of the subsequent synthesis steps, and the clear change in fluorescence, as seen from figure 6.3 on page 30 in section 6.2. TLC results further establishes the change in structure. *PA* is a reddish-brown solid as seen from picture 6.10.



Figure 6.10: Solid benzo[g,h,i]perylene-1,2-dicarboxylic anhydride.

Both the pilot and the second synthesis of *PA* had an identical outcome. TLC analysis of *PA*, when compared to the starting point, perylene, shows an unambiguous reaction, as seen from figures 6.12 and 6.11, showing samples from both syntheses.





Figure 6.11: TLC test of (from left) perylene and *PA* from the pilot synthesis, under illumination by long-wave UV light. Eluent is chloroform-ethyl acetate (10:1).

Figure 6.12: TLC test of (from left) perylene and *PA* from the second synthesis, under il-lumination by long-wave UV light. Eluent is chloroform-ethyl acetate (10:1).

PA has an R_f of 0.62 with a chloroform-ethyl acetate eluent of 10:1. As seen from the TLC plates, perylene was easily distinguishable from *PA*, both in terms of fluorescent color and retention. No perylene was visible in the *PA* samples, indicating complete purification, and a clean product. Furthermore, residue from chloranil should be completely washed out with diethyl-ether. Likewise will maleic anhydride be removed in the water suspension. *PA* does not appear to melt, but rather decompose above 350°C, as seen from the STA results in section A.2 on page 69 in the appendix.

6.5.2 Compound PI

N-(6-hydroxyhexyl)benzo[ghi]perylene-1,2-dicarboximide is only sparingly soluble in chloroform, at 0.7g/liter, cf. table 6.3 on the facing page. It is a dark orange

solid, as seen in figure 6.13. Both the pilot, and second synthesis of *PI* was a success, as proven by the ¹H NMR spectrum in 6.14.



Figure 6.13: Solid N-(6-hydroxyhexyl)benzo[ghi]perylene-1,2-dicarboximide. Identical in appearance in both syntheses, this sample is from the second synthesis.

The fluorescent color under long-wave UV light had changed again to a slightly green appearance, with the change from *PA* which had a yellow appearance, as seen in 6.3 on page 30. This convenient change in emitted light made tracking the changes upon reaction easy.



Figure 6.14: ¹H 500MHz NMR spectrum of N-(6-hydroxyhexyl)benzo[ghi]perylene-1,2dicarboximide from the second synthesis, in CDCl₃, at 298K. Each signal has been assigned to numbered carbon atoms. Note that the spectrum has been fragmented for easier viewing, but still includes all signals, with the exception of the chloroform signal at 7.27ppm. Total integral sum: 18.15.

The NMR spectrum showed clearly defined signals, with an integral sum of

18.15 for the 18 protons not obscured by the water in the sample. The remaining 4 protons are assumed to reside in the signal containing the water at 1.6ppm, as seen from the shifts of pure 6-aminohexanol in a separate spectrum, cf. figure A.14 on page 68 in the appendix. Judging from the NMR spectrum the compound is of high purity, disregarding the water. But an important fact is that impurities of unreacted *PA* will not yield a visible NMR signal, as concluded in 6.5.1. Impurities of *PA* should however be visible in the TLC analysis, and can be seen in figures 6.15 and 6.16.





Figure 6.15: TLC test of (from left) *PA* and *PI* both from the second synthesis, under illumination by long-wave UV light. Eluent is chloroform-ethyl acetate (10:1).

Figure 6.16: TLC test of (from left) *PA* and *PI* both from the second synthesis, under illumination by long-wave UV light. Eluent is chloroform-ethyl acetate-acetic acid (5:5:1).

PI has an R_f of 0.09 with a chloroform-ethyl acetate eluent of 10:1, and a 0.13 R_f with a chloroform-ethyl acetate-acetic acid eluent of 5:5:1. As the TLC test showed, no apparent residue of *PA* was present, verifying the purity of *PI* from the second synthesis. *PI* has a melting point of 235°C, seen in A.2 on page 69.

6.5.3 Compound PIV

Compound N-(hexylprop-2-enoate)benzo[ghi]perylene-1,2-dicarboximide has a solubility in chloroform, of approximately 48g/liter, cf. table 6.3 on page 36. It is a bright orange solid after purification by column chromatography, as can be seen in figures 6.17 and 6.18. Both the pilot synthesis, and the second synthesis was successful as determined from both NMR and TLC results. The melting point of pure *PIV* is 198°C, as determined from the STA analysis in A.2 on page 69.



Figure 6.17: Solid crude monomer, N-(hexylprop-2-enoate)benzo[ghi]perylene-1,2-dicarboximide. From the second synthesis, before purification by column chromatography.



Figure 6.18: Solid monomer, N-(hexylprop-2-enoate)benzo[ghi]perylene-1,2-dicarboximide. From the second synthesis, after purification by column chromatography.

The fluorescence under UV light had not visibly changed from *PI* to *PIV*, but the change in solubility and polarity had a big effect on retention in TLC results. Figures 6.19 and 6.20 show the appearance of *PIV* prior to column cromatography, and after, respectively. The TLC result of the crude *PIV* from the pilot synthesis and the second synthesis was identical.





Figure 6.19: TLC test of (from left) *PI* and crude *PIV* both from the second synthesis, under illumination by long-wave UV light. Eluent is chloroform-ethyl acetate (10:1).

Figure 6.20: TLC test of (from left) *PA*, *PI* and purified *PIV* all from the second synthesis, under illumination by long-wave UV light. Eluent is chloroform-ethyl acetate (10:1).

The R_f of *PIV* was 0.55 with a chloroform-ethyl acetate eluent of 10:1. Only a slight potential impurity of unreacted *PI* is visible in the purified *PIV* sample. The ¹H NMR spectrum of *PIV* additionally confirms the structure, cf. 6.21, with only water being a significant impurity. As in the spectrum of *PI*, the four protons of the central -CH₂- groups overlap with the water signal at 1.6ppm. Adding these four protons brings the integral sum to the expected total of 25.



Figure 6.21: ¹H 500MHz NMR spectrum of the monomer N-(hexylprop-2enoate)benzo[ghi]perylene-1,2-dicarboximide from the second synthesis, in $CDCl_3$, at 298K. Each signal has been assigned to numbered carbon atoms. Note that the spectrum has been fragmented for easier viewing, but still includes all signals, with the exception of the chloroform signal at 7.27ppm. Total integral sum: 21.06.

The NMR spectrum of *PIV* is nicely defined with some subtle shifts from that of *PI*. All aromatic protons see a decrease in chemical shift, and coincidental overlap of aromatic protons 1+10 and 2+9. An additional noticeable change in chemical shift is that of -CH₂- group #16, going from a shift of 3.75ppm to 4.2ppm, as expected with the introduction of an adjacent ester group. The introduced vinyl protons show classic behaviour, with both trans (17 and 18a) and cis (17 and 18b) coupling being visible. The slight geminal coupling (18a and 18b) is visible in zoomed portions of the spectrum, and can be seen in figure A.1 on page 59 in the appendix.

6.5.4 Compound PPIV

The polymer of *PIV*, poly(N-(hexylprop-2-enoate)benzo[ghi]perylene-1,2-dicarboximide) is a light orange colored solid, completely insoluble in organic solvents and water. It has a melting point of 272°C as determined from STA analysis, as found in figure A.18 on page 70 in the appendix.



Figure 6.22: Solid polymer from the second synthesis, poly(N-(hexylprop-2-enoate)benzo[ghi]perylene-1,2-dicarboximide).

The polymerization was unsuccessful in the pilot synthesis, but successful in the second synthesis. As concluded in the previous section, the *PIV* from the pilot synthesis was impure but otherwise identical to that of the second synthesis prior to purification. The presence of impurities may have hindered the polymerization in itself, or the failure was due to the higher degree of dilution in the pilot polymerization. It was considerably more dilute than compared to the second attempt - 3.4g/L versus 23.2g/L. The dilution was done under the notion that all solids had to be dissolved, most of these solids turned out to be impurities, however. In the second attempt, the higher concentration, and much higher purity resulted in the solid in figure 6.22.

As the polymer is insoluble, characterization is made difficult, with only FT-IR results revealing the polymerization by proving the absence of a vinyl group, the presence of which is detectable in *PIV*. This was shown to be the case, verifying the polymerization, in 6.3. Furthermore, the melting point was increased from that of *PIV*, and also showed a broader melting endotherm, typical of a polymer.

6.5.5 Compounds PDx

In general the synthesis of all the diimides, *PDx*, was straight forward. The yield was high (+90%) in all cases and the reaction was simple. All the *PDx* compounds were of similar color, being a dark red solid as seen in figure 6.23.



Figure 6.23: The appearance of all the *PDx* compounds were identical to the human eye. This particular image is of solid N,N'bis(1-methylpropyl)perylene-3,4:9,10-bis(dicarboximide), *PD4*.

The four *PDx* compounds were combined in a TLC analysis to compare retention, cf. 6.24.



Figure 6.24: TLC test of *PDx* compounds (from left) *PD12, PD8, PD2.6* and *PD4*. Illumination is by long-wave UV light. Eluent was chloroform-ethyl acetate (10:1).

The R_f values for *PD12*, *PD8*, *PD2.6* and *PD4* in chloroform-ethyl acetate eluent of 10:1, are 0.66, 0.64, 0.65 and 0.61, respectively. The four *PDx* compounds will be described below. As mentioned in section 5.2.1 on the outcome of the syntheses, *PD2.6* was synthesized numerous times, but with no variation in the procedure or the outcome. Therefore, the multiple syntheses will be treated as one.

Compound PD2,6

The synthesis of PD2.6 was confirmed by ¹H NMR analysis, and the signals assigned by ¹H 2D COSY, the assignment being shown in figure 6.25.



Figure 6.25: ¹H 500MHz NMR spectrum of N,N'bis(2-ethylhexyl)perylene-3,4:9,10bis(dicarboximide), in CDCl₃, at 298K. Protons have been numbered and assigned via a ¹H 2D COSY spectrum. The mirror symmetry plane is added to indicate equivalence of the signals on either side. Note that the spectrum has been fragmented for easier viewing, but still includes all signals, with the exception of the chloroform signal at 7.27ppm. Total integral sum: 42.03.

With a very precise integral sum of 42.03 for the 42 protons present, the spectrum is very accurate. The ¹H 2D COSY spectrum can be found in figure A.2 on page 60 in the appendix. *PD2.6* has a melting point of 349°C, with mass loss from temperatures just above melting.

Compound PD4

PD4 was the final *PDx* compound to be synthesized, but showed the most promise in terms of solubility and further synthesis. With a solubility of 22g/L it is approximately four times more soluble than *PD2.6*. The NMR result of *PD4* can be seen in figure 6.26.



Figure 6.26: ¹H 500MHz NMR spectrum of N,N'bis(1-methylpropyl)perylene-3,4:9,10-bis(dicarboximide), in CDCl₃, at 298K. Note that the spectrum has been fragmented for easier viewing, but still includes all signals, with the exception of the chloroform signal at 7.27ppm. Total integral sum: 26.28.

Based on the ¹H 2D COSY assignment of *PD2.6*, parallels can be drawn to assign the signals of *PD4*. The only unexpected difference is the apparent non-equivalence of the $-CH_2$ - groups on the alkyl modifications, showing two signals at 2.0 and 2.3ppm with septet splitting. The integral sums up to 26.28 as expected for the 26 protons in *PD4*. The compound does not have a melting point, but instead appears to decompose above 350° C.

Compound PD8

This compound was only synthesized once, due to the superior properties of *PD2.6*. The synthesis was however successful, as seen in the NMR spectrum below in 6.27.



Figure 6.27: ¹H 500MHz NMR spectrum of N,N'bis(octyl)perylene-3,4:9,10-bis(dicarboximide), in CDCl₃, at 298K. Note that the spectrum has been fragmented for easier viewing, but still includes all signals, with the exception of the chloroform signal at 7.27ppm.

PD8 had such a low solubility, that advantages over perylene in itself was very minor.

Compound PD12

Compound *PD12* was only synthesized once, as *PD8*. Similar to *PD8* the solubility was so low, that a potential complete monomer might even have a lower solubility than the perylene based monomer. The NMR spectrum of *PD12* can be seen in figure 6.28.



Figure 6.28: ¹H 500MHz NMR spectrum of N,N'bis(dodecyl)perylene-3,4:9,10-bis(dicarboximide), in CDCl₃, at 298K. Note that the spectrum has been fragmented for easier viewing, but still includes all signals, with the exception of the chloroform signal at 7.27ppm.

The spectrum is very similar to that of *PD8* and *PD2.6*, and serves to verify the structure. Aside from the impurity at 1.29ppm the compound appears to be pure.

6.5.6 Compounds PDAx

Due to the low solubility of *PD8* and *PD12*, *PD2.6* and *PD4* were the chosen compounds in focus for troubleshooting the synthetic strategy, and therefore the former will not be as clearly described. The reactivity of the *PDx* compounds towards cycloaddition was somewhat similar, and severely decreased. Presumably this is due to the two electronegative dicarboximide groups, lowering the important electron density at the bay area of the perylene core. This in turn lowers the diene behaviour of the bay area, making cycloaddition of a dienophile less favorable. Even after prolonging the reaction time to 4 days at above 120°C, the majority of the *PDx* compounds are still not converted.

Compound PDA2,6

The most successful synthesis was the one numbered #1, in 5.2.2 on page 25 in *'Experiments and Outcome'*. Ironically, this was the first attempt at the synthesis, and the procedure was almost identical to that of the maleic anhydride addition to perylene. It was carried out in refluxing maleic anhydride with a 20 minute reaction time. The NMR spectrum, cf. 6.29, shows a molar conversion of 32%.



Figure 6.29: ¹H 500MHz NMR spectra of the incomplete synthesis #1, of *PDA2.6*, and pure *PD2.6* for comparison, in CDCl₃, at 298K. The spectrum is an excerpt of the aromatic protons, including the $-CH_2$ - group adjacent to the imide at 4.2ppm.

The new aromatic signals are as expected one singlet and two doublets, each with 2 protons. The integral of the -CH₂- group reveals a ratio of 2:1 of *PD2.6* to *PDA2.6*. A similar comparison of the lower region of the spectrum can be found in figure A.5 on page 63 in the appendix. The TLC analysis was mostly identical in all the attempts where *PDA2.6* was present in a detectable degree. A TLC analysis comparing pure *PD2.6* to *PDA2.6* can be seen in figure 6.30, where *PDA2.6* takes on a blue fluorescent color.

6.5. Syntheses





Figure 6.30: TLC test of (from left) *PD2.6* and *PDA2.6*, under illumination by long-wave UV light. Eluent is chloroform-ethyl acetate (10:1).

Figure 6.31: TLC test of (from left) *PD2.6* and *PDA2.6*, under illumination by long-wave UV light. Eluent is chloroform-ethyl acetate-acetic acid (5:5:1).

The R_f value of *PDA2.6* is effectively 0 in chloroform-ethyl acetate 1:1. However with a chloroform-ethyl acetate-acetic acid eluent of 5:5:1, the R_f of *PDA2.6* rises to 0.44, and to 0.84 for *PD2.6*, cf. figure 6.31. There is an unidentified fraction remaining at the zero point of the TLC plate after *PDA2.6* has been eluted upwards, but of a different fluorescent color.

The various synthesis attempts has proven that keeping the reaction at the reflux temperature of maleic anhydride for more than 30 minutes, will end in thermal degradation. Dehydration of the maleic anhydride, prior to adding *PD2.6* appears to have no effect. In general, the synthesis is very uncooperative, with a procedure being successful one day, and unsuccessful the next. This shows that strict parameter control is necessary.

Compound PDA4

PDA4 was the compound faring the best in addition of maleic anhydride to the *PDx* compounds. The most successful synthesis was #1. This synthesis employed 145°C reaction temperature with some ethyl acetate present, and a 4 day reaction time. The NMR spectrum shows the presence of the added anhydride, removing 2 aromatic protons, and adding a singlet to the signal of two doublets, cf. figure 6.32.



Figure 6.32: ¹H 500MHz NMR spectra of the incomplete synthesis of *PDA4* from synthesis #1, in $CDCl_3$ at 298K. The spectrum is an excerpt of the aromatic protons, including the -CH- group adjacent to the imide at 5.3ppm.

The ratio of the integrals of the -CH- group adjacent to the imide at 5.3ppm reveals a molar conversion of approximately 37%. Similarly to *PDA2.6, PDA4* is easily detectable in TLC analysis, due to the acquired blue fluorescence and low R_f value.

6.5. Syntheses





Figure 6.33: TLC test of (from left) *PD4* and *PDA4*, under illumination by long-wave UV light. Eluent is chloroform-ethyl acetate (10:1).

Figure 6.34: TLC test of (from left) *PD4* and *PDA4*, under illumination by long-wave UV light. Eluent is chloroform-ethyl acetate-acetic acid (5:5:1).

The R_f value of *PDA4* is again 0 in chloroform-ethyl acetate 1:1, and 0.38 in 5:5:1 chloroform-ethyl acetate-acetic acid eluent. While *PD4* has an R_f value of 0.80 in the latter.

From the results of the syntheses, it appears that the presence of ethyl acetate has a beneficial effect on the reaction. Whereas the presence of acetone or chloro-form appears to have no benefit, other than keeping the subliming maleic anhydride in check. Synthesis #4 attempted to maintain reflux of maleic anhydride to a prolonged duration, with a nitrogen atmosphere to prevent oxidation. This failed, and the outcome was similar to the burned attempt of *PDA2.6* synthesis #9, with no recoverable product. As with the synthesis of *PDA2.6*, strict parameter control is necessary to make this reaction occur.

Compound PDA8

The product and TLC analysis plates were lost in the moving phase of the institute, so no results will be described of this otherwise unsuccessful synthesis. The TLC analysis showed no presence of *PDA8* at an R_f of zero, in chloroform-ethyl acetate 1:1 eluent, as would be expected.

Compound PDA12

The product and TLC analysis plates were lost in the moving phase of the institute, so no results will be described of this otherwise unsuccessful synthesis. The TLC analysis showed no presence of *PDA12* at an R_f of zero, in chloroform-ethyl acetate 1:1 eluent, as would be expected.

Chapter 7 Conclusion

The pendant side-chain conjugated polymer based on perylene was successfully synthesized through a 4-step process, from perylene as the precursor. The first step was designed to be a Diels-Alder cycloaddition of maleic anhydride to perylene, resulting in benzo[g,h,i]perylene-1,2-dicarboxylic anhydride, compound PA. The second step was a nucleophilic acyl substitution reaction of 6-aminohexanol on PA, resulting in the dicarboximide N-(6-hydroxyhexyl)benzo[ghi]perylene-1,2dicarboximide, PI. The third step was an additional nucleophilic acyl substitution reaction of the acid chloride, acryloyl chloride with the primary alcohol of PI, resulting in the monomer N-(hexylprop-2-enoate)benzo[ghi]perylene-1,2-dicarboximide, *PIV*. The fourth step was the free radical polymerization of the vinyl group of *PIV* initiated with benzoyl peroxide, resulting in the homopolymer poly(N-(hexylprop-2-enoate)benzo[ghi]perylene-1,2-dicarboximide), PPIV. The compounds were successfully synthesized, as proven by both ¹H NMR and ATR FT-IR analyses. The syntheses were optimized after pilot-syntheses, and reaction times were considerably decreased, by application of a heating mantle instead of a sandbath for some of the steps. Precipitation and purification steps were likewise optimized. Characterization of the polymer, *PPIV*, was limited due to its insolubility in most organic solvents. An important observation was the polymerization being apparently hindered by impurities in the monomer, requiring purification by column chromatography of the latter, prior to polymerization. Most of the impurities present in the monomer were most likely attributed to the high amount of acryloyl chloride and triethylamine used in the synthesis, due to the extremely low solubility of PI, at just 0.7g/liter in chloroform at SATP, also resulting in a very low yield of the subsequent step.

The solubility of the intermediate compounds of the perylene based polymer synthetic route, led to the desire to enhance the solubility by utilizing different perylene diimides, synthesized from perylene-3,4,9,10-tetracarboxylic dianhydride

and various primary alkylamines. The most successful of these diimides in terms of solubility, was the one modified with sec-butylamine. Compared to the diimides of 2-ethylhexylamine, octylamine and dodecylamine, the solubility was 4, 12 and 9 times higher, respectively, and due to the low molar weight, the molar solubility was 5, 14 and 13 times higher. This first step was successful, with a high yield, as verified by ¹H NMR analysis of all four diimides - N,N'bis(x)perylene-3,4:9,10bis(dicarboximide), PDx. The design of the synthesis route was initially similar, after addition of the alkylamines to the dianhydride. The second step of the synthetic route, corresponding to step 1 of the perylene based polymer synthesis, was a big challenge due to the electron affinity of the two dicarboximide groups, reducing the electron density at the diene area of the perylene diimide core. This resulted in reduced reactivity towards cycloaddition with maleic anhydride, the dienophile. Extension of the reaction time, and variation of different parameters had mixed results. In the case of N,N'bis(2-ethylhexyl)benzo[ghi]perylene-2,3:8,9bis(dicarboximide)-11,12-dicarboxylic anhydride, PDA2.6, the most successful synthesis was comprised of a 20 minute reaction time in refluxing maleic anhydride, with a somewhat identical procedure as the reaction of perylene with maleic anhydride. There was no apparent benefit to extending the reaction time, in this case. In the case of N,N'bis(1-methylpropyl)benzo[ghi]perylene-2,3:8,9-bis(dicarboximide)-11,12-dicarboxylic anhydride, PDA4, however, the most successful synthesis had an elapsed time of 4 days at 145°C in the presence of approximately 20% ethyl acetate. The maximum molar conversion of PD2.6 and PD4 to PDA2.6 and PDA4 in these syntheses, was approximately 32% and 37%, respectively, as estimated by ¹H NMR analysis.

In summary, the perylene based polymer was successfully synthesized, analyzed and the synthetic route optimized, proving that the envisioned polymer can indeed be synthesized. The perylene dianhydride based polymer was not successfully synthesized beyond step two, but ideas to synthesize the final polymers will be covered in the next chapter, 8.



Figure 7.1: The synthesized and purified compounds, from left: PA, PI, PIV, PPIV and PDx.

Chapter 8

Future work

For all the compounds, characterization of the photovoltaic properties would be of interest, to determine whether or not they are promising. The perylene based polymer was successfully synthesized, and the synthetic route optimized. Proof of conjugation and conductivity of the the perylene pendants would be the next obvious goal. The perylene dianhydride based polymer, however, needed optimization of the synthetic route. The Diels-Alder cycloaddition of maleic anhydride (MA) in step two, was the incomplete step. Ideas to optimize this synthetic step could be:

- Addition of 2 equivalents of zinc acetate to the perylene diimides, acting as a potential solutizer
- Using very large quantities of MA: in excess of 100gram per gram diimide
- Modifying MA prior to cycloaddition, for more aggressive dienophilic behavior

Point one relies on the uncertain theory of the reaction mechanism of catalytic zinc acetate in the nucleophilic acyl di-substitution. If the zinc acetate indeed acts as a solutizer, it may aid the interaction between MA and the diimide. Point two simply rests on the observation that the diimides are scarcely soluble in molten MA, unless refluxing. Higher ratios of MA may simply drive the equilibrium towards the products. Point three is based on the notion to modify MA beforehand, with electronegative substituents, withdrawing electrons and thus "exposing" the reactive end, acting as the dienophile. Such moieties could be based on maleimide. The reactivity of the maleimide moieties in figure 8.1, would be interesting to investigate. N-chloromaleimide is the most simple version, in which the chlorine substituent may be electron withdrawing, raising the reactivity of the dienophilic region.



Figure 8.1: From left: Maleimide, N-chloromaleimide, N-phenylmaleimide and 1-[4-(hydroxymethyl)phenyl]-1H-pyrrole-2,5-dione.

N-phenylmaleimide may be even more reactive, but further syntheses steps must be kept in mind. Therefore 1-[4-(Hydroxymethyl)phenyl]-1H-pyrrole-2,5dione may be the most promising compound, if the dienophilic behavior is higher than that of maleic anhydride. It can be synthesized by reaction of MA and 4aminobenzyl alcohol, followed by cycloaddition to the bay area of the perylene diimides. The resulting compound could be reacted with acryloyl chloride, followed by polymerization, resulting in an analogous compound to the ones envisioned in this project.

Purification of the *PDAx* compounds through column chromatography would most likely be necessary. From the R_f values found through the TLC analyses, elution of unreacted perylene diimide could be done with chloroform or DCM. Subsequent elution of the newly formed anhydride could be done with an acetic acid containing eluent.

Bibliography

- [1] Eva Bundgaard and Frederik C. Krebs. "Low band gap polymers for organic photovoltaics". In: Solar Energy Materials and Solar Cells 91.11 (2007). Low Band Gap Polymer Materials for Organic Solar Cells, pp. 954 –985. ISSN: 0927-0248. DOI: http://dx.doi.org/10.1016/j.solmat.2007.01.015. URL: http://www.sciencedirect.com/science/article/pii/S0927024807000451.
- [2] E. Clar and M. Zander. "927. Syntheses of coronene and 1:2-7:8-dibenzocoronene". In: *Journal of the Chemical Society* (0 1957), pp. 4616–4619. DOI: 10.1039/ JR9570004616. URL: http://dx.doi.org/10.1039/JR9570004616.
- [3] Jonathan Clayden et al. Organic Chemistry. ISBN: 0-19-850346-6. Oxford University Press, 2001, pp. 1023–1027,1384.
- [4] H. Langhals. "Cyclic Carboxylic Imide Structures as Structure Elements of High Stability. Novel Developments in Perylene Dye Chemistry". In: *Heterocycles* Vol 40, No. 1 (1995), pp. 477–500. DOI: 10.3987/REV-94-SR2.
- [5] Heinz Langhals and Susanne Kirner. "Novel Fluorescent Dyes by the Extension of the Core of Perylenetetracarboxylic Bisimides". In: *European Journal of Organic Chemistry* 2000.2 (2000), pp. 365–380. ISSN: 1099-0690. DOI: 10.1002/ (SICI) 1099-0690(200001) 2000: 2<365:: AID-EJ0C365>3.0.CO; 2-R. URL: http://dx.doi.org/10.1002/(SICI)1099-0690(200001)2000: 2<365:: AID-EJ0C365>3.0.CO; 2-R.
- [6] Jr. L.G. Wade. *The Diels-Alder Reaction of Anthracene with Maleic Anhydride*. 1998.
- Krzysztof Matyjaszewski and James Spanswick. "Controlled/living radical polymerization". In: *Materials Today* 8.3 (2005), pp. 26 –33. ISSN: 1369-7021. DOI: http://dx.doi.org/10.1016/S1369-7021(05)00745-5. URL: http://www.sciencedirect.com/science/article/pii/S1369702105007455.
- [8] Dana W. Mayo, Ronald M. Pike, and David C. Forbes. *Microscale organic laboratory: With multistep and multiscale syntheses*. 5th. John Wiley and Sons Inc., 2009, pp. 347–348.

- [9] McMurry and Simanek. *Fundamentals of Organic Chemistry*. 6th. BROOKS/COLE CENGAGE Learning, 2007, pp. 312–313.
- [10] Holger Spanggaard and Frederik C. Krebs. "A brief history of the development of organic and polymeric photovoltaics". In: Solar Energy Materials and Solar Cells 83.2–3 (2004). The development of organic and polymer photovoltaics, pp. 125 –146. ISSN: 0927-0248. DOI: http://dx.doi.org/10.1016/ j.solmat.2004.02.021. URL: http://www.sciencedirect.com/science/ article/pii/S0927024804000923.
- [11] J.I. Wu et al. "On the aromatic stabilization energy of the 4N Pi electron pyrene". In: *Molecular Physics* 107.8-12 (2009), pp. 1177–1186. DOI: 10.1080/00268970902784918. eprint: http://dx.doi.org/10.1080/00268970902784918.
 URL: http://dx.doi.org/10.1080/00268970902784918.