Functionalized Polyisocyanides

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Polyisocyanides are unique synthetic polymers. They are one of the few polymers containing a backbone that consists of an all-carbon skeleton in which every carbon belongs to a different monomer unit and bears a side group. Consequently, the carbons in the polyisocyanide backbone have a limited rotational freedom, which makes the polymer relatively rigid, especially when the carbons are substituted with bulky substituents. Chapter 2 of this thesis describes the history and development of polyisocyanide chemistry. A scheme is proposed, which classifies the different polyisocyanides presented in the literature on the basis of their thermodynamic and kinetic parameters and lays down a foundation for the future design of well-defined rigid polyisocyanides.

Peptide derived polyisocyanides are a class of polyisocyanides that can be extremely well-defined and very stiff due to the resultant hydrogen bonding network in the side-arms of the polymers (see Figure 1). This thesis describes the synthesis, characterization and application of peptide derived polyisocyanides in which the monomer units are decorated with a functional group (F, Figure 1). Due to the well-defined character of the polyisocyanide the functional groups are arranged in four columnar stacks along the backbone (see Figure 1 for one array).

Perylene bisimides (PBIs) have been investigated as one of the functional groups attached to the polyisocyanides. As an introduction to Chapters 4-6, Chapter 3 also gives a literature overview on the assemblies and properties of PBIs and their application in optoelectronics, in particular photovoltaics. PBIs are widely studied in the field of optoelectronics because of their good thermal and photochemical stability, high electron affinity, high optical density, and high fluorescence quantum yield. In well defined perylene assemblies such as crystals, extremely high electron mobilities have been measured. The intrinsic properties of PBIs make them interesting for use as functionality in the side-arms of polyisocyanides, to create polymers with highly-defined photoactive PBI arrays.
Chapter 4 describes the synthesis and characterization of PBI functionalized polyisocyanides 1 and 2 (Figure 2). In both polymers the backbone is stabilized by hydrogen bonding between the amide functions of every $n^{th}$ and $(n+4)^{th}$ monomer unit, as was revealed by infrared spectroscopy. Absorption, CD, and fluorescence spectroscopies conducted on polymer 1 revealed that the PBIs are weakly excitonically coupled (strong exciton-phonon coupling) in a chiral fashion, with the $n^{th}$ and $(n+4)^{th}$ PBIs stacked in an H-aggregated fashion. For polymer 2 interpretation of the photophysical data was more difficult. Absorption and fluorescence spectroscopy indicated weak exciton coupling between the PBIs, probably also in an H-aggregated fashion. The CD signal did not originate from excitonically coupled PBIs, but is more likely the result of a helical shape induced in the prochiral PBI planes of 2. Moreover, the CD signal of 2 varies in different solvents and the signal in tetrachloroethane is lost when the solution is heated to higher temperatures. The conformation of polymer 1, in contrast, is very stable even upon going to higher temperatures. Atomic force microscopy studies on the two polymers adsorbed on surfaces revealed rigid fiber-like structures. Polymer molecules of 2 are relatively short compared to those of 1, which was attributed to the slow polymerization of the bulky monomeric precursor of 2. Light scattering data on 1 could be fitted to a rod-like model and revealed similar dimensions for the polymer as those determined by AFM.

Chapter 5 reports on experimental and computational studies on polymer 1 that provide evidence that these ultrastiff polymers are ideal scaffolds for precisely organizing chromophoric arrays into functional 2D wires. Extensive molecular modeling dynamics refined previous models and revealed a $4_1$ helix in which the chromophores overlap along the polymer backbone. The calculated and spectroscopically observed architectures predict that this unique polymer is in a highly favorable orientation, ideal for electron transport. This was confirmed by transient absorption spectroscopy studies, which indicate extremely high exciton migration rates and charge densities.

Chapter 6 describes the preparation and characterization of photovoltaic cells composed of either polymer 1 or polymer 2 as electron acceptor material and regioregular polythiophene (P3HT) as electron donor material. The photovoltaic cells do not match the state of the art power efficiencies of organic solar cells, but their performance is good when compared to photovoltaic systems of similar blends and much better when compared to cells incorporating PBI monomers instead of a PBI functionalized polyisocyanide. The improved power efficiencies of organic solar cells with polymer 1 instead of monomeric PBIs was further investigated by KPFM. KPFM measurements on the photovoltaic cells of polymer 1 and P3HT in dark and light revealed that a photovoltaic effect indeed occurs, but that topologically polyisocyanide 1 and P3HT could not be distinguished. On more diluted samples of polymer 1 and P3HT on silicon, the two polymer materials could be distinguished by their different surface potentials in the KPFM images. Upon turning on the light a photovoltaic effect between the two materials was measured. The increase in the surface potential difference between the two materials that was observed is comparable to that found in systems with P3HT.
and monomeric PBI, however, the charging of polyisocyanide 1 in the thin layer was much more homogenous than that of the monomer islands. This result shows that blends of polymer 1 and P3HT form well-interpenetrated networks with improved charge transport compared to blends incorporating monomeric PBI.

In Chapter 7 the synthesis and isolation of micrometer long polyisocyanides of copolymer 3, which contains fluorescent PBI units, has been described (Figure 3). The isolation of long polymers was achieved by the fractionation of the reaction mixture on a GPC column. Preliminary results show that it is possible to follow the reptational movements of these polymers in a non-fluorescent polyisocyanide matrix with fluorescence microscopy. The direct visualization of the motion of a single chromophoric polymer makes it possible to verify polymer physics theories, such as the reptation theory.

In Chapter 8 of this thesis the subject changes to polyisocyanides with nucleobases as a functional group. Nucleobase functionalized polyisocyanides are promising candidates as synthetic mimics of DNA. They can possibly act as a reaction template for other polymerization reactions (mimicking DNA replication) or can form new biohybrid structures with DNA. Examples of DNA mimics in literature are described showing DNA-mimics that can strongly bind DNA and RNA and that are interesting for applications such as bio-recognition and therapeutics.

Polyisocyanides functionalized with adenine (polymer 4 and 5, Figure 4) have been prepared. First steps in the synthesis towards thymine functionalized polyisocyanides have also been undertaken. Only short adenine functionalized polyisocyanides were formed due to fast precipitation of the polymer during polymerization. The polymers are therefore not ideally suitable as a template for other polymerization reactions or as a DNA mimic.
Block copolymers of polystyrene and adenine functionalized polyisocyanide 5 could be prepared, due to the enhanced solubility induced by the presence of the polystyrene. From the $^1$H NMR spectrum it was estimated that circa 13 isocyanide units were incorporated into the block copolymer, when the adenine protecting compound succinimide was added to the polymerization reaction.

The block copolymers were found to give vesicular structures in water as was demonstrated by TEM and SEM. When thymine functionalized block copolymers (PEG$_{45}$-PT$_{10}$) were added to the aggregates, modified structures were formed as seen by TEM and SEM suggesting interactions between the adenine and thymine functionalized block copolymers. When aggregates of the adenine block copolymer were formed in the presence of single stranded thymine DNA, vesicular structures with holes were observed.

This thesis shows that the synthesis of functionalized polyisocyanides can lead not only to exciting optoelectronic materials on the one hand and biologically interesting materials on the other hand, but also to unique tools for studying fundamental concepts in photovoltaics and polymer physics.
Polyisocyanides zijn polymeren, waarvan de ruggengraat volledig uit koolstofatomen bestaat. Uniek is dat elk koolstofatoom, met daaraan een zijgroep, een afzonderlijke repeterende eenheid vormt. Het gevolg hiervan is dat de dichtheid van de zijgroepen rondom de polymere ruggengraat hoog is en dat de koolstofatomen weinig rotatievrijheid hebben ten opzichte van elkaar. Polyisocyanides zijn daarom relatief rigide, in het bijzonder wanneer de zijgroepen aan het koolstofatoom groot in omvang zijn.

In hoofdstuk 2 van dit proefschrift wordt de geschiedenis van de ontwikkeling van de chemie van polyisocyanides beschreven en wordt een schema gepresenteerd waarin tot op heden in de literatuur beschreven polyisocyanides worden geclassificeerd op basis van hun thermodynamische en kinetische parameters. Het schema geeft inzicht in de parameters die van belang zijn bij het ontwikkelen van goed gedefinieerde rigide polyisocyanides.

Met name de klasse van polyisocyanides die van aminozuren zijn afgeleid zijn zeer goed gedefinieerd en rigide dankzij het netwerk van waterstofbruggen dat wordt gevormd door de amidegroepen in de zijarmen van het polymer. In Figuur 1 is ter illustratie de structuur van een van alanine afgeleide polyisocyanide met functionele groep F afgebeeld, waarbij de waterstofbruggen tussen elke nde en (n+4)de monomere eenheid zijn weergegeven.

Dit proefschrift beschrijft de synthese, karakterisatie en toepassing van polyisocyanides die zijn afgeleid van aminozuren en waarvan elke monomere eenheid een functionele groep draagt. In deze polymeren zijn de functionele groepen in 4 ketens rondom de polymere ruggengraat georganiseerd (zie Figuur 1).

![Figuur 1: Structuur van een van aminozuren (L-alanine) afgeleid polyisocyanide, waarbij aan elke monomere eenheid een functionele groep (F) is bevestigd. In de afbeelding zijn alleen de zijgroepen van elke vierde monomere eenheid getoond, die onderling waterstofbruggen vormen. Rondom de polymere ruggengraat zijn 4 van deze waterstofgebrugde ketens aanwezig.]

Eén van de functionele groepen, die onderzocht zijn als zijgroep van polyisocyanides, is het peryleen bisimide (PBI). Als inleiding op het beschreven werk in de hoofdstukken 4-6, wordt in hoofdstuk 3 een literatuuroverzicht gegeven over PBIs. Daarbij wordt ingegaan op de (foto)fysische eigenschappen, de eigenschappen van PBI aggregaten en polymeren en de toepassing van deze PBI systemen in optisch elektronische toepassingen zoals zonnecellen. PBIs krijgen in het onderzoeksgebied van de optische elektronica veel aandacht vanwege hun goede thermische en fotochemische stabiliteit, hun hoge elektronaffiniteit en hun hoge optische
Hoofdstuk 4 beschrijft de synthese en karakterisering van polymeren 1 en 2 die PBI als functionele groep hebben (Figuur 2).

| Figure 2: Polymeren 1 en 2 |

In beide polymeren wordt de ruggengraat gestabiliseerd door waterstofbruggen tussen de amidegroepen van elke n\textsuperscript{de} en (n+4)\textsuperscript{de} zijarm, zoals werd aangetoond met infraroodspectroscopie. Absorptie-, circulair dichroïsme (CD), en fluorescentspectroscopie aan polymer 1 lieten zien dat de PBIs onderling een chirale interactie vertonen met een zwakke exciton koppeling, maar een sterke exciton-phonon koppeling, waarbij elke n\textsuperscript{de} en (n+4)\textsuperscript{de} PBI zijn georiënteerd zoals in een H-aggregaat. Voor polymer 2 bleek het interpreteren van de fotofysische data ingewikkelder. Absorptie en fluorescentspectroscopie wezen ook hier op een zwakke exciton koppeling tussen de PBIs, waarschijnlijk ook op H-aggregaatachtige wijze. Het waargenomen CD signaal lijkt niet te worden veroorzaakt door exciton gekoppelde PBIs, maar eerder door een geïnduceerde chiraliteit in het prochirale vlak van de PBIs.

Een aanwijzing hiervoor is ook dat het CD-signaal van polymer 2 varieert in verschillende oplosmiddelen en dat het signaal in tetrachloorethaan verdwijnt wanneer de oplossing wordt verwarmd. De conformatie van polymer 1 daarentegen, is bij hoge temperaturen wel stabiel. Afzonderlijke polymerevezels van polymer 1 en 2, opgebracht op een vlak oppervlak van mica, konden zichtbaar worden gemaakt met atoomkrachtmicroscopie (AFM). Daarbij bleek dat de polymereketens van 2 relatief kort zijn (ca. 110 nm) vergeleken met die van polymer 1 (ca. 180 nm), wat kan worden toegeschreven aan de langzame polymerisatie van het volumineuze isocyanide, dat de uitgangsstof is van polymer 2. Data verkregen uit lichtverstrooiingsexperimenten zijn in overeenstemming met een buisvormig model, waarvan de dimensies overeenstemmen met de afmetingen uit de AFM experimenten.

In hoofdstuk 5 worden modelstudies en experimenten met polymer 1 beschreven die aantonen dat de rigide polyisocyanides ideale kapstokken zijn om chromoforen in functionele 2D ketens te organiseren. Met behulp van uitgebreide moleculaire dynamica studies zijn eerdere berekeningen aan polyisocyanide modellen verder verfijnd en werd een 4i helix aangetoond, waarin de PBIs langs de polymere ruggengraat een met elkaar overlappende structuur vormen. Berekeningen en spectroscopische waarnemingen geven aan dat polymer 1 een veelbelovend systeem is voor elektronengeleiding. Dit werd bevestigd door transiënte absorptie spectroscopie studies, waarmee zeer hoge exciton migratiesnelheden en hoge ladingsdichtheden zijn gevonden.

In hoofdstuk 6 wordt de vervaardiging en de karakterisatie van zonnecellen beschreven, die zijn gemaakt met een actieve laag van polymer 1 dan wel 2 als n-type (elektronen accepterend) materiaal en regioregulair polythiofeen (P3HT) als p-type (elektronen donerend) materiaal. De vermogensefficiëntie van de geprepareerde zonnecellen is weliswaar minder dan die van de best
beschikbare organische zonnecellen die, maar is goed te noemen in vergelijking met zonnecellen die zijn gemaakt van vergelijkbare mengsels en zeer goed wanneer ze vergeleken worden met zonnecellen die gemaakt zijn van een mengsel van PBI monomer en P3HT. De betere vermogensefficiëntie van polymeer 1 ten opzichte van PBI monomer is verder onderzocht met behulp van Kelvin-probe krachtmicroscopie (KPFM). Met behulp van KPFM metingen aan de active laag van polymeer 1 en P3HT in het licht en in het donker kon een duidelijk fotovoltaïsch effect worden waargenomen. In de KPFM afbeeldingen kon echter geen onderscheid gemaakt worden tussen het n-type materiaal (polymeer 1) en het p-type materiaal (P3HT). Op meer verdunne preparaten van polymeer 1 en P3HT op een oppervlak van silicium, kon met KPFM wel onderscheid gemaakt worden tussen de twee materialen op basis van hun structuur en het verschil in oppervlaktepotentiaal. Wanneer het oppervlak werd verlicht, werd een fotovoltaïsch effect zichtbaar door een toename van het potentiaalverschil tussen de twee materialen. Dergelijke effecten zijn ook door andere waargenomen voor mengsels van monomeer PBI en P3HT op een oppervlak, maar de opname van negatieve lading door PBIs in polymeer 1 bleek veel homogener dan in de monomeeraggregaten. De resultaten laten zien dat mengsels van polymeer 1 en P3HT goed gemengde netwerken vormen waarin ladingstransport op efficiëntere wijze plaatsvindt dan in mengsels met monomeer PBI.

Figuur 3: Polymeer 3

In hoofdstuk 7 is de synthese en isolatie van micrometer lange polymeren van fluorescent copolymeer 3 beschreven (Figuur 3). De lange polymeren konden worden geïsoleerd door het reactiemengsel te scheiden met behulp van gelpermeatiechromatografie (GPC). De eerste resultaten geven aan dat het mogelijk is met behulp van fluorescentiemicroscopie de slangachtige bewegingen van individuele polymeermoleculen in een niet fluorescente polyisocyanide matrix te volgen. Dit maakt het mogelijk om theorieën uit de polymeerfysica, zoals de “reptation” theorie, te verifiëren met behulp van de directe waarnemingen van polymeerbewegingen.

Tenslotte wordt in hoofdstuk 8 onderzoek beschreven, waarbij nucleobasen zijn gebruikt als functionele groep in de zijarmen van polyisocyanides. Deze polyisocyanides kunnen mogelijkerwijs interessant zijn als DNA-analogen. Hierbij kan gedacht worden aan toepassingen zoals het templaten van andere polymerisatiereacties (zoals in DNA replicatie) of het vormen van biohybride structuren met DNA. In de literatuur zijn ook verschillende voorbeelden bekend van DNA-analogen, die sterke binding met DNA en RNA vertonen en die dienst kunnen doen in biologische herkenningsprocessen en als medicijn.
Samenvatting

In dit hoofdstuk zijn de synthesen van polyisocyanides met als functionele groep adenine (polymeer 4 en 5, Figuur 4) beschreven, evenals de eerste synthesestappen in de richting van polyisocyanides met thymine zijgroepen. De gevormde polyisocyanides met adenine groepen bleken erg kort te zijn doordat de polymeren vroegtijdig in de polymerisatiereductie precipiteren. De korte polymeren werden niet interessant genoeg verondersteld voor toepassing als polymerisatie template of als DNA analoog anderszins.

Figuur 4: Polymeren 4 en 5

Blokcopolymeren van polystyreen en polymeer 5 werden daarom gesynthetiseerd, waarbij geen onmiddellijke precipitatie plaatsvond, dankzij het goed oplosbare polystyreenblok aan de initiatior. Uit het $^1$H NMR spectrum werd opgemaakt dat het blokcopolymer bestond uit een blok van ongeveer 13 isocyanide eenheden wanneer de reactie werd uitgevoerd in de aanwezigheid van succinimide. In water bleken de blokcopolymeren vesiculaire structuren te vormen, zoals werd aangetoond met transmissie en scanning elektronen microscopie (TEM en SEM). Het toevoegen van thymine gefunctionaliseerde blokcopolymeren (PEG$_{45}$-PT$_{10}$) resulteerde in andersoortige structuren, wat er op kan duiden dat er interacties zijn tussen de adenines en de thymines van de twee soorten blokcopolymeren. Wanneer de aggregaten werden gevormd in de aanwezigheid van enkelstrengs thymine DNA, werden vesiculaire structuren met gaten waargenomen.

Dit proefschrift laat zien dat het synthetiseren van gefunctionaliseerde polyisocyanides niet alleen kan leiden tot nieuwe optisch elektronische en biologisch interessante materialen, maar ook tot “moleculair gereedschap” waarmee fundamentele concepten uit de zonnecelchemie en de polymeerfysica kunnen worden bestudeerd.
Chapter 1

Outline of thesis

Peptide derived polyisocyanides have been shown to be unique polymers because of their well-defined structure and their extreme rigidity.\textsuperscript{[1]} They can be several micrometers long and their chemistry allows the use of different functionalities at the periphery of the polymer.\textsuperscript{[2-4]} This thesis describes the investigations undertaken to apply these qualities to the creation of photoactive and conductive polymers on the one hand and DNA / RNA mimics on the other hand.

Chapter 2 is a literature survey on all work involving polyisocyanides until August 2006. A scheme is proposed, which classifies different polyisocyanides in the literature on the basis of thermodynamic and kinetic parameters. The scheme aims to give support for the design of well-defined rigid polyisocyanides.

Chapter 3 is an introduction to chapters 4-6 and gives a literature overview (dated March 2007) on perylene bisimides (PBIs), aggregates and polymers of PBIs, and their applicability in photovoltaic systems. In Chapter 4 the synthesis and characterization of PBI functionalized polyisocyanides are described. A full characterization of the polymers is given comprising standard spectroscopic characterization methods, elastic light scattering and atomic force microscopy. Chapter 5 contains the results of a modeling study on the morphology and spectroscopic features of the PBI functionalized polyisocyanides. The study gives insight in the electronic properties of the polymers and is backed up by photophysical experiments. Finally, chapter 6 deals with the application of the PBI functionalized polyisocyanides in photovoltaic (PV) cells. In the first part of the chapter, the preparation and characterization of PV cells are described. The second part elaborates on the characterization of the photovoltaic blend by Kelvin probe force microscopy (KPFM). The KPFM study reveals photovoltaic activity in sub-monolayer blends containing PBI functionalized polyisocyanides.

In Chapter 7 there is a change of topic; the chapter reports on the synthesis of micrometer long rigid and fluorescent polyisocyanides and the first results on the fluorescence microscopy studies of their reptational motion in polymer gels.

Finally, Chapter 8 describes the synthesis of nucleobase functionalized polyisocyanides, block copolymers thereof, and the aggregation behavior of these block copolymers.
Chapter 2

Polyisocyanides: Stiffened foldamers*

2.1 Introduction
In search for new materials in the field of electronics, biosensing, and catalysis, materials that not only possess the structural integrity and flexibility of many natural occurring materials but also their functionality are considered to be of great potential. Nature teaches us that the creation of well-defined structures is always accompanied by a loss of entropy, which needs to be compensated for by either an increase in favorable enthalpic interactions or a gain in entropy of the environment (e.g., hydrophobic interactions usually lead to an increase in entropy due to release of water molecules). In well-known robust biological architectures, such as the α-helix and the β-sheet, the entropic loss these peptide segments encounter upon folding is repaid by favorable steric, hydrophobic, electrostatic, and hydrogen-bonding interactions within the secondary structure. Foldamers, which have been studied as artificial mimics of these biomolecular structures, can adopt well-defined secondary arrangements stabilized by non-covalent interactions. They are dynamic in nature and can be influenced by changing the environment, such as pH, salt concentration, solvent and temperature. Polymers, such as polyacetylenes and polyisocyanates can be considered as polymeric foldamers since they are able to arrange themselves into well-defined dynamic helices under specific circumstances. The formation of well-defined polymeric foldamer structures is a challenge since entropy can be expected to play a substantial role: the longer the polymers become the larger the chance of a structural mismatch. Helically locked polymers constitute a special class of foldamers, that is, they can be considered as kinetically locked foldamers as a result of, for instance, steric hindrance or hindered rotation (atropisomerism) or the presence of strong hydrogen bonding networks. Helical polymers are considered to be stable when their helical inversion barrier exceeds ~85 kJ/mol. Examples of such polymers are sterically restricted poly(methacrylate ester)s, polychlorals, binaphtyl based polymers, polysilanes with steric bulk, and polyisocyanides.

This chapter will focus on the latter class of polymers, which were the first to be reported to possess a stable helical conformation. Their preparation, structure, and the use of these polymers in the creation of functional materials will be discussed.

2.2 Preparation
Polyisocyanides, also known as polyisonitriles or polyiminomethylene, are prepared by the polymerization of isocyanides. The driving force for this polymerization reaction is the

transformation of a formally divalent carbon atom in the monomer to a tetravalent carbon atom in the polymer, yielding a heat of polymerization of 81.4 (kJ/mol) (Figure 1A).\textsuperscript{[16]}

One of the special characteristics of polyisocyanides is the fact that every carbon atom in the polymer backbone bears a substituent. A consequence of this architectural novelty is that the side chains experience a large steric hindrance forcing the polymer to adopt a non-planar conformation (\textit{vide infra}). Many polymerization procedures are available for isocyanides,\textsuperscript{[17-19]} however, the most successful methods involve the use of a group 10 metal complex, of which the most widely applied is a Ni(II)-complex.\textsuperscript{[13, 16]} For the polymerization of aryl isocyanides in addition to Ni(II), a heteronuclear Pd-Pt catalyst has also proven to be very successful.\textsuperscript{[20, 21]}

In a comparative study of several metal acetylacetonates (acac) for the polymerization of ethyl isocyanide, Nolte et al. showed that Ni(acac)\textsubscript{2} is by far the most efficient catalyst.\textsuperscript{[22]} Ni(II) complexes also enabled the polymerization of the sterically encumbered poly(tert-butyl isocyanide), which subsequently could be resolved into the left- and right-handed helical form by chromatography using poly((S)-sec-butyl isocyanide) on glass as the stationary phase (Figure 2).\textsuperscript{[15, 23]} These experiments confirmed the helical structure of polyisocyanides, which had been earlier suggested by Millich.\textsuperscript{[24]}

For the polymerization of isocyanides a so-called ‘merry-go-round’ mechanism has been proposed (Scheme 1B).\textsuperscript{[25]} In this mechanism, a square planar tetrakis isocyanide nickel(II) complex is formed, which is activated by the addition of a nucleophile, usually an amine (step a). After first complexing directly to the Ni(II) center, this amine rapidly migrates to one of the coordinating isocyanide ligands to form a nucleophilic carbene-like species (step b), which subsequently attacks one of its neighboring isocyanide ligands (step c). The resulting vacant position on the Ni(II) center concomitantly is reoccupied by an isocyanide monomer from solution. The polymerization reaction propagates in the direction in which the initial attack took place.
place and results in one particular helical sense for the polymer chain formed. Consequently, for an achiral monomer and initiator, an equal amount of left- (M-) and right-handed (P-) helical polyisocyanides will be generated. When a chiral bias is present in the form of a chiral isocyanide monomer\[^{17, 25}\] or a chiral initiator,\[^{26}\] one helical sense will be preferred over the other.

**Figure 2:** Formation of left-handed (M) and right-handed (P) helices upon polymerization of tert-butyl isocyanide by a Ni(II) catalyst. The helices can be separated by chromatography using a chiral support.

The *merry-go-round mechanism* proved to be useful in explaining and predicting a number of features and properties of polyisocyanides,\[^{10}\] however, more recent work by Deming and Novak revealed that some aspects of the mechanism are probably more complex. ESR, cyclic voltammetry, and bulk magnetic susceptibility measurements indicated that a Ni(I) species is also present under the polymerization conditions and that the reaction is strongly dependent on the presence of O\(_2\). The polymerization was found to be optimal under 1 atmosphere of air, while under nitrogen the polymerization is slow and at high oxygen concentrations the isocyanide is converted into an isocyanate. Initially it was proposed that the isocyanide acts as a reductant when an excess of 10 equivalents is added to NiCl\(_2\), causing the formation of an inactive nickel(I) catalyst, which is reactivated by oxidation with O\(_2\).\[^{27}\] In order to overcome this deactivation they developed the electron deficient \(\eta^3\)-allylnickel trifluoroacetate 1 as a polymerization catalyst (Scheme 1). The allyl group acts as an internal initiator for the polymerization and the trifluoroacetate anion as a group to remove electron density from the nickel to promote nucleophilic attack on the isocyanide. The catalyst proved to be a highly active system and, in a non-coordinating solvent, displayed living chain-growth behavior.\[^{27, 28}\]
More detailed kinetic and mechanistic investigations employing this type of Ni-catalyst revealed that Ni(I), not Ni(II), is most likely the active species.\[29\] A mechanism was formulated in which Ni(I) is formed upon reduction by the isocyanide. Under atmospheric conditions, oxygen then acts as a spin trap for the formed isocyanide radical allowing the Ni(I) to remain active. If conducted under N\(_2\), after every insertion the Ni(II) species is reformed, therefore giving a slower reaction. This was in line with the observation that under N\(_2\) the polymerization was found to be first order in monomer, whereas under O\(_2\) the rate was zero order in monomer.\[29, 30\] The mechanistic details are depicted in Figure 3.

**Figure 3:** Catalytic cycles of the isocyanide polymerization under N\(_2\) and O\(_2\) with Ni(I) being the active species.
The living character of catalyst 1 also allowed the preparation of block copolymers from two different isocyanide monomers.\textsuperscript{[28]} Using a variety of catalysts based on 1, such as the chiral catalysts 2 and 3 \textsuperscript{[31, 32]} and the catalyst intermediates 4 and 5 with polybutadiene as an initiator (Scheme 1), a series of diblock and triblock copolymers of isocyanide and butadiene could be synthesized.\textsuperscript{[33, 34]} The latter block copolymers were prepared by first polymerizing butadiene followed by the polymerization of the isocyanide. A similar approach for the formation of block copolymers of two different types of polymer blocks was reported by Cornelissen et al. They utilized the polystyrene-nickel initiator complex 6 for the synthesis of polystyrene–polyisocyanide block copolymers such as 7 and 8 (Scheme 2). The nickel carbene catalyst was formed by the nucleophilic attack of a polystyrene amine on the stable nickel tert-butyl isocyanide complex. By using the same technique, block copolymers of type 9, consisting of a polyisocyanide connected to a series of carbosilane dendritic wedges, were prepared.\textsuperscript{[35-37]} For the previous cases, the nickel catalyst is only active for the polymerization of the polyisocyanide block of the block copolymer. More recently it was found that a polypeptide initiated nickel complex generated by reaction of N-carboxy anhydrides of amino acids (NCAs) with 2,2’-bipyridylnickel(0)(1,5-cyclooctadiene) can polymerize isocyanides, thereby forming rod-rod block copolymers of normal polypeptides and polyisocyanopeptides (10).\textsuperscript{[38]}
The alternative polymerization catalysts, \( \mu \)-ethynediyl Pd-Pt complex 11 and also \( \mu \)-ethynediyl Pd-Pd complex 13 (although this latter catalyst is less efficient), were discovered by Takahashi and coworkers (Scheme 3).\(^{20, 21}\) They found that this catalyst polymerizes aryl isocyanides, but not alkyl isocyanides, under reflux conditions in THF. The isocyanides exclusively insert into the Pd-carbon bond, however, the platinum plays an essential role since only a single insertion of isocyanide was observed for mononuclear complexes 12 in the presence of an excess of isocyanide. The Pd-Pt catalyzed polymerization proved to be living in nature as was illustrated by the low polydispersity of the obtained polymers and the ability of the catalyst to form block copolymers. Even after work-up the Pd end group remains connected to the polymer and polymerization can be continued. A mechanism was proposed involving the cationic intermediate 14 which, upon nucleophilic attacks of the isocyanide gives migratory insertion of the bound isocyanide. Chain termination occurs by nucleophilic attack of a chlorine ion on the Pd center leading to insertion of the last isocyanide.\(^{21}\) Initiators 15(Scheme 3), with two and three Pd-Pt \( \mu \)-ethynediyl units, were used to synthesize multi-armed polyisocyanides.\(^{39, 40}\)
2.3 Conformation

Millich et al. found that the polymerization of the optically active α-phenylethyl isocyanide in the presence of acid treated glass yields polymers with a high optical rotation per repeat unit.[41] On the basis of this observation, combined with Debye-Scherrer X-ray patterns and space-filling molecular models,[42] they proposed that in a polyisocyanide chain the transition dipoles of the absorbing imine chromophores are coupled and therefore lead to a highly organized helical polymer backbone containing four repeat units per turn and a pitch of 4.1–4.2 Å.[43]

The presumed helical conformation of polyisocyanides was confirmed on the basis of CD-spectroscopy by Nolte et al. when poly(tert-butyl isocyanide), which has no chiral centers, was resolved into (+)- and (−)-rotating fractions.[15, 23] Theoretical studies on the conformation of tert-butyl isocyanide oligomers using consistent force field conformational calculations indicated that a helical conformation was favored with an increasing number of monomer units. The average dihedral angle N=C–C=N in the hexamer was found to be ±78.6°, corresponding to 3.75 monomer units per helical turn.[44, 45] The same calculations for a hexadecamer of the tert-butyl isocyanide resulted in a dihedral angle of 84.3°, corresponding to 3.60 units per helical turn. Substitution of the tert-butyl group by a methyl-, ethyl-, or isopropyl group was calculated to give a smaller dihedral angle and more units per helical turn. In the case of poly(methylisocyanide), calculations revealed that the methyl group was too small to lead to a fixed dihedral angle and hence no atropisomerism (stereoisomerism due to hindered rotation around a single bond) was proposed to be possible.

In the late 1970s, Kollmar and Hoffmann carried out molecular orbital calculations by using an extended Hückel approach on a series of polyisocyanides,[46] namely RNC, with R = H, CH₃, and C(CH₃)₃. They concluded that N lone-pair repulsion between the nitrogen atoms that are the second nearest neighbors in the polymer chain (Figure 4) play a dominant role and as a result the polyisocyanide backbone must adopt a conformation that is not planar. In the case of isocyanides with bulky R substituents, the electronic repulsion between nitrogen atoms is of minor
importance and the non-planar conformation is mainly dictated by the steric interactions between the side groups. According to their calculations, the helical angle that is adopted by the polyisocyanide backbone varies from a fairly broad range of helical conformations for the R = H polymer, to a narrow range around the 4-fold helix as the steric bulk of the substituent increases to R= C(CH₃)₃. For intermediate steric bulk (e.g., R = CH₃), the authors found two helical minima with different degrees of helicity.

The influence of the steric bulk of the substituent on the conformation of polyisocyanides was experimentally corroborated by Yamada et al. who found that polyisocyanides derived from phenylalanine readily lose their initial helical conformation in solution when the carboxyl group is protected as an ethyl ester. Increasing the bulk of the ester to a tert-butyl ester significantly increased the stability of the helical conformation of the polyisocyanide.\[47\]

An alternative conformation for polyisocyanides was postulated on the basis of calculations by Clericuzio et al.\[48\] The repulsion between the N lone pairs in the planar all-anti conformation of polyisocyanides is absent in the so-called “syndio” conformation in which dimeric sections are alternatively (E,E) and (Z,Z) (Figure 5). On the basis of both ab initio and molecular mechanics (MM) calculations, this conformation was found to be by far the most stable one among a number of different possible geometries for polyisocyanides. The syndio conformation is non-helical but highly symmetrical and has a regularly alternating configuration of side chains on C=N bonds, and an alternating 180°±90° conformation of the backbone N=C–C=N angles (Figure 5). The driving force for this conformation seems to lie partly in the large preference for E,E trans-planar diiminic units; the rotation around the N=C–C=N central bond in the E,E ethane diimine (as calculated by ab initio) shows a (s-cis)-(s-trans) energy difference of ~ 34 kJ/mol in the flexible rotor approximation.

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**Figure 4:** Illustration of the different repulsive interactions driving the all-anti imine functions in a polyisocyanide chain out of planarity.

**Figure 5:** The two proposed most stable conformations proposed for polyisocyanides.
The proposed syndio-conformation was confirmed to be very likely for oligo(phenylisocyanide)s. NMR spectroscopic investigations demonstrated that the 1,3-diphenyl-1,2,3-tri(phenylimino)propane has a planar diimine unit with the third imine located at a 90° dihedral angle from the planar s-trans portion. For polymers of this compound, i.e., poly(phenylisocyanide), it was observed that in halocarbon solvents or tetrahydrofuran solution the conformation slowly changed from a helix to a random coil.

In addition to the above computational approaches suggesting possible alternative conformations for polyisocyanides different from the helical one, Green et al. pointed out that polyisocyanides, especially those with small pendant groups, adopt a quite irregular conformation. They emphasized the difference in the Mark-Houwink exponent \( a \) between several polyisocyanides, obtained by viscosity measurements. The Mark-Houwink exponent gives an indication about the rigidity of molecules: if \( a < 1 \), the polymers have a random-coil character and if \( a > 1 \), the polymers have a rigid-rod character. The Mark-Houwink exponents for poly(\( \alpha \)-phenylethyl isocyanide) (18) in toluene, \( \beta \)-phenylethyl isocyanide in tetrahydrofuran, and racemic 2-octyl isocyanide in toluene were found to be \( a = 1.36, 0.68, \) and \( 1.75 \) respectively. These results suggest that the structure of the pendant groups strongly affect the chain dimensions. With light scattering experiments Green et al. showed that even the relatively stiff poly(\( \alpha \)-phenylethyl isocyanide) 18 had only a limited persistence length of \( \sim 3 \) nm. In addition, a large chemical shift dispersion in the \(^{13}\)C NMR spectrum of all carbon atoms, including the backbone carbon, was found for this polymer and this dispersion was even stronger for polyisocyanides lacking an \( \alpha \)-substituent, such as 16 and 17. Since a broad chemical shift dispersion was also observed for polymers from achiral monomer units, Green et al. suggested that this stereo-irregularity is associated with a syn-anti isomerism about the C=N bond (Figure 6D).

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* Polyisocyanopeptides, however, possess a much longer persistence lengths (see Section 2.4).
Figure 6: A, B, C) Signals for the imine carbon in the polymer backbone in the $^{13}$C NMR spectra for polyisocyanides lacking an α-substituent (A and B) and with an α-substituent (C). D) Stereoisomeric possibilities for a triad in a polyisocyanide.\[^{51}\]

The carbon nuclei may be sensitive to sequences longer than the triads depicted in Figure 6D. These results indicate that the conformational data for polyisocyanides proposed from interpretation of CD spectroscopy\[^{56-65}\] are difficult to reconcile with the structural disorder revealed by the high-field $^{13}$C NMR data. Millich and Baker\[^{41}\] previously suggested the possibility of blocks with different syn-anti isomerism of the imino group together with the possibility of helix reversals as illustrated in Figure 7. Block 1 is obtained by rotation of block 2 around the short axis (similar for 3 and 4), which corresponds to syn-anti isomerism of the imino group, while blocks 1 and 3 and blocks 2 and 4 have opposite helix senses. In the case of achiral monomers, 1 and 4, and 2 and 3, are mirror images, whereas for chiral monomer units they are diastereomers.

Figure 7: Schematic drawing of the different polymer conformations for polyisocyanides as illustrated by Millich and Baker. The blocks 1–4 correspond to structures with different imine conformations and different helicity.
Takahashi et al. showed that polymerization conditions can have an influence on the stereoregularity of the resulting polymer. Polyisocyanide 20 prepared by polymerizing 19 with NiCl$_2$ in methanol at room temperature revealed a lower specific rotation ($[\alpha]_{D}^{20} = +354$ and CD ($\Delta\varepsilon_{364} = +3.9$) than polymer 21 ($[\alpha]_{D}^{20} = +1070$ and $\Delta\varepsilon_{364} = +13.0$), which was prepared by polymerization of 19 with the Pd-Pt catalyst 11 in refluxing THF (Figure 8). By annealing polymer 20 in refluxing THF for 15 hours the specific rotation and CD intensity increased to values of $[\alpha]_{D}^{20} = +1038$ and $\Delta\varepsilon_{364} = +11.6$, whereas no increase was observed for polymer 21.

More information on the conformational changes was obtained by $^{13}$C NMR spectroscopy. A rather broad signal for the imino carbons of the backbone (width at half height: $W_{1/2h} = 208$ Hz) was observed in the $^{13}$C NMR spectrum of polymer 20 in contrast to the much sharper signal for polymer 21 ($W_{1/2h} = 133$ Hz). After annealing polymer 20 in deuterated toluene at 80 °C for 15 h, a similar sharp signal as for 21 was found. Comparable results were obtained for others polymers, including achiral ones and thus the $^{13}$C NMR signal distribution for the imino backbone carbon cannot be explained by stereochemical means. The authors therefore proposed, in line with the work of Green et al., that the initial stereoirregularity in the polymers formed by the nickel catalyzed polymerization is associated with the existence of both syn- and anti-isomers of the imino groups in the backbone. The irregular conformation can be transformed into the thermodynamically stable stereoregular form by syn-anti isomerization of the imino group at high temperatures. The polymerization at high temperature with the Pd-Pt catalyst 11 immediately led to the stereoregular conformation.

Figure 8: Reaction scheme for the polymerization of 19 by NiCl$_2\cdot6$H$_2$O and the Pd-Pt catalyst 11.

Yashima et al. further observed that polyisocyanides are not necessarily always present in a stable locked structure, but that some have more dynamic conformations. They provided evidence for a reversible transition between two conformational states of poly(4-carboxyphenylisocyanide) 22 under the influence of optically active amines and amino alcohols such as 23 and 24 (Scheme 4).
Based on their observations they suggested that apart from the aforementioned imino syn-anti isomerism these changes are caused by backbone (s-trans)-(s-cis) isomerism (Figure 9). Initially a $4_1$ helix is formed that rapidly loses its regular helix structure to form an irregular structure with s-trans, s-cis, and (s-cis)-(s-trans) domains (step 1). This structure will then slowly transform into the stable all s-trans structure at 30 °C resulting in sharper peaks in the $^1$H-NMR spectrum (step 2). It is proposed that the s-trans structure can give a helical arrangement upon binding chiral amines by directing the random twist around the C–C bonds in a single direction (step 3). In water, a helix could also be induced that after removal of the optically active amines, maintained its helical conformation at ambient temperatures but at elevated temperatures the helix unfolded readily. It was postulated that a combination of hydrophobic and chiral ionic interactions in water where responsible for the helix formation and the memory effect because, in DMSO, induced helices were unable to maintain their helical structure.[68]

In Summary, it can be concluded that two important structures for polyisocyanides have been proposed: (i) a helix structure that is close to the $4_1$-helix initially suggested by Millich et al., which is most likely for polymers with bulky sidearms and (ii) the syndio structure as was calculated by Clericuzio et al., which seems to be most favorable for polyisocyanides with small side-groups. In addition to these two distinct structures, Yashima et al. calculated a $12_1$-helix for their induced helices[67] and Young et al., aside from a $4_1$-helix, also calculated a $3_1$-helix.[69]
Irregularities that have been observed in polyisocyanides are mainly explained by syn-anti isomerism of the imino side-groups and by (s-cis)-(s-trans) isomerism of the carbon backbone. This latter isomerism leads to structures that are intermediates between a 41-helix and the syndio structure. Other possible explanations for observed irregularities are helix inversions as discussed by Millich and the existence of two types of helical pitches coexisting within one polymer as was calculated by Kollmar and Hoffmann for polyisocyanides with intermediate bulk.

2.4 Stiffening the helix

In principle, stable, regular polyisocyanides can be formed by polymerization reactions that are under (i) thermodynamic control (driving force=ΔG_{AB}) or (ii) kinetic control (driving force =ΔG_A^+−ΔG_B^−) (Figure 10). The different possibilities are depicted in Figure 10, for a polymerization of monomer M to a polymer with monomer units in conformations P-M_A and P-M_B, which might correspond to structures that differ in helicity, backbone syn-anti or imine cis-trans isomerism (only two are considered for simplicity). If the barrier between two conformations ΔG_{AB}^+ is sufficiently small (at a certain temperature), the different conformations are kinetically accessible and the polymer structure is under thermodynamic control. The thermodynamically formed conformations are situated on the left side of Figure 9c. Polymerization reactions under thermodynamic control can yield well-defined polymers when the free energy of the most stable conformation is sufficiently lower than that of competing conformations (high ΔG_{AB}). In the case of cooperativity, only small energy differences are already sufficient[^12].
Only recently has the literature provided some clear examples of regular well-defined polyisocyanides formed under thermodynamic control at elevated temperatures. Polymerization of aryl isocyanides using the Pd-Pt catalyst as reported by Takahashi et al. is typically done in refluxing THF. \[20, 21, 70, 71\] Several observations indicate that this type of polymerization is under thermodynamic control. Firstly, as previously mentioned, polymers formed by NiCl$_2$ at room temperature can be converted to a better defined regular conformation.
at higher temperature, while polymerization of the monomer in refluxing THF with the Pd-Pt catalyst at ~66 °C leads directly to the thermodynamic, regular structure.\textsuperscript{[66]} Secondly, from a detailed study on the helix-sense-selective polymerization using chiral oligomer complexes derived from isocyanide 20,\textsuperscript{[70]} it appeared that the rate constants for propagation are virtually identical, independent of whether the monomer that is incorporated has the same or the opposite chirality as the one constituting the initiating oligomer. This observation rules out the possibility of kinetic control. Finally, a non-linear relationship was observed between the excess of chiral monomer and the induced helical sense in the polymerization.\textsuperscript{[72]} This is indicative of a thermodynamically driven “majority rules” mechanism of the type observed in the polymerization of polyisocyanates.\textsuperscript{[73, 74]} It appeared, however, that only achiral isocyanides with substantial steric bulk could be polymerized with an ongoing helix sense from a chiral oligomer complex, whereas less bulky achiral isocyanides showed little preference for a single screw sense.\textsuperscript{[70]} In this case it remains the question whether, for the bulky isocyanides, the kinetics rather than the thermodynamics play a role in the helix-sense-selective polymerization.

Yashima showed that polymerization of phenyl isocyanide derivative 25 (Scheme 5) bearing an L-alanine residue can be performed under both kinetic and thermodynamic control.\textsuperscript{[75]} Whereas the polymerization with NiCl\textsubscript{2} in toluene or CCl\textsubscript{4} yielded the kinetic product with a positive Cotton effect, the polymerization in THF or, even more so, in toluene at 100 °C yielded the thermodynamic product, which gave a negative Cotton effect. Under kinetic control, in apolar solvents, hydrogen bonding is thought to play a role in the transition state. In contrast, in polar solvents or at high temperature, hydrogen bonding is suppressed and the thermodynamic product is formed. The role that hydrogen bonding plays was confirmed by the fact that for the polymer of phenyl isocyanide 26, which is incapable of hydrogen bonding, a negative cotton effect was observed independent of the polymerization conditions. Remarkably, apart from being manifested by CD spectroscopy, the helix sense of the polymers in self-assembled layers on HOPG could be visualized by AFM (Figure 11).
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Figure 11: Schematic pictures and AFM images of left- and right-handed helices of 25 prepared by two different polymerization methods. Left image: polymer prepared in refluxing toluene and subsequently annealed in toluene at 100 °C. Right image: polymer prepared in CCl₄.[73]

A special case of a thermodynamically formed helix is the previously discussed poly(4-carboxyphenylisocyanide) 22. The polymer does not form a regular structure by itself, but only on complexation with an optically active amine, therefore allowing one helix sense to become thermodynamically more favorable than the other. Interestingly, in water the helix structure was retained even without chiral amines present, meaning that the thermodynamically formed structure was kinetically trapped.[68]

Polymerization is under kinetic control when the transition state energy $\Delta G_A^\ddagger$ for the incorporation of a monomer into the desired configuration P-Mₐ is sufficiently smaller than that for other configurations P-Mₜ, that is $(\Delta G_A^\ddagger - \Delta G_I^\ddagger)$ is large. When the formed structure has reached thermodynamic stability, that is $\Delta G_{AB}$ is large, with P-Mₐ being the lower energy conformation (in this case the polymer could also be formed under thermodynamic control) or when the structure is kinetically trapped, that is $\Delta G_{AB}^\ddagger$ is large, stable well-defined polymers are formed (Figure 10).

Polymerizations of bulky monomer catalyzed by Ni(II) at room temperature are believed to be under kinetic control, although in many cases it is not very clear to what extent regular polymers are formed as has been discussed in section 2.2.

One of the most striking examples of kinetic control is the earlier mentioned polymerization of tert-butyl isocyanide, which yielded a mixture of $M$- (left handed) and $P$- (right handed) helices but no mixed $M$-$P$-polymers, as was shown by isolating the two polymers by column chromatography using a chiral support.[15, 23] The bulkiness of the tert-butyl group steers the kinetic control and provides kinetic stability to the formed polymers. Phenyl isocyanide was reported to kinetically give a 41-helix during polymerization, however, because of the lack of steric bulk in the side-chain, this helical structure is not stable and subsequently unfolds into a random coil polymer.[50] The initial formation of a helix illustrates the important role of the nickel catalyst in providing kinetic control over the reaction, presumably by the merry-go-round mechanism. Deming and Novak also showed that in the polymerization of less bulky isocyanides no complete stereo control is obtained. For a racemic mixture of methylbenzylisocyanide, $R$ and $S$ isomers partially mix up in the same helix.[76]
For bulky monomers, the occurrence of kinetic control in the Ni(II) mediated polymerization of isocyanides was nicely illustrated by an inhibition experiment.\[58, 77\] Achiral monomers, which rapidly polymerize, were copolymerized with a slowly polymerizing bulky chiral isocyanide. Instead of imposing its own helix sense (say \( P \)) on the achiral monomer it was found that the chiral isocyanide promoted the formation of a polymer with an opposite screw sense (say \( M \)). This intriguing result was explained by kinetic inhibition of the formation of one helix type by the bulky chiral monomer. Whereas the achiral isocyanides will normally form both \( M \) and \( P \) helices, one of the two helices is inhibited in the copolymerization (say \( P \)) because of the incorporation of the slowly polymerizing chiral monomer. A variation on this experiment was performed by Amabilino et al.,\[78\] who showed that diastereomers of polymers 27 and 28 could be formed by kinetically inhibiting the growth of the normally occurring helix by the addition of the slowly polymerizing isocyanide 30, of the same chirality, as the co-monomer.

**Scheme 6**

Work of the same authors also revealed that, apart from steric bulk, other interactions between the monomers can also influence the polymerization in a well defined way.\[79, 80\] Polyisocyanides 27—29, containing phenylbenzoate groups, are derived from promesogenic monomers (Scheme 6), which are able to induce cholesteric and chiral smectic C phases in nematic and smectic C liquid crystals, respectively.\[79, 80\] Upon polymerization, in most cases, the handedness of the polymers was the same as that of the monomer induced LC phases. The long range chiral induction by the stereogenic center in the tail was explained by the stereoselective interaction of the incoming monomer with the growing polymer in a similar fashion as observed in the LC phase. It is the rigid nature of the phenyl benzoate group that allows the transfer of chirality from the side chain to the isocyanide functionality. The CD signal related to the imine backbone was shown to diminish rapidly and invert in sign when the chiral center in the alkyl tail was placed further away from the promesogenic group. More evidence for the role of non-covalent interactions on the stereoselectivity was obtained by performing polymerizations at various concentrations and in different solvents.\[80\] Variable temperature CD measurements revealed that polymer 27 has a stable conformation up to at least 55 °C. When, however, a nitro-group was introduced onto the phenyl ring in close proximity to the stereogenic center, the polymer was found to adopt a less stable conformation, as was demonstrated by the dramatic and irrecoverable loss of optical activity at 55 °C. This observation confirms that the formed polyisocyanide is a kinetically-determined product.\[81\]
In a more recent publication of these authors, the influence of the length and the rigidity of the rod-like spacer located between the isocyanide and the chiral center of 31 was studied (Scheme 7). The chiral induction through spacers A—G was investigated in detail and it was concluded that some semi-rigid twisted conformation must be adopted by the spacer in order to be able to effectively transfer the chiral information into a helical polymer backbone. The phenyl benzoate spacer A proved to do this most efficiently whereas no chiral induction was observed for flexible spacer C. A 21 Å long teleinduction was observed for spacer G.\cite{82, 83}

![Scheme 7](image)

Cornelissen et al. showed the potency of peptide substituents in the formation of stable polyisocyanide helices in a paper in 2001 (Figure 12).\cite{1} It was found that the helical conformation of a polyisocyanide can be effectively stabilized if a well-defined hydrogen bonded network is present between the peptide side chains at positions \( n \) and \( (n+4) \), which are stacked above each other at a distance of \( \sim 4.6 \) Å (Figure 12b). Although polyisocyanides derived from peptides had been previously described by the authors,\cite{65, 84, 85} they did not recognize at that time the presence of the hydrogen bonds between the peptide side chains and did not utilize this to stiffen the helix of polyisocyanides with functional groups (\textit{vide infra}). The stepwise addition of 32a to the Ni(II)-catalyst revealed the kinetic nature of the polymerization, which involves a helical templating effect of the growing polymer on the incoming monomers. From the point on that eight monomers were added to the catalyst a steep increase in the CD signal was observed. At the same time hydrogen bonding interactions between the amide protons became visible in \( ^1 \)H-NMR spectroscopy.\cite{86}
Polyisocyanide 43, derived from trialanine, contains two amide groups per side chain and is able to fold into a β-sheet-like architecture, mimicking the interactions present in naturally occurring β-helices.\cite{87} Detailed infrared (IR) and $^1$H NMR spectroscopic investigations showed that nearly all amide groups present in polymers 34–43 participated in hydrogen bonding, in a similar way as observed in the x-ray crystal structure of 32a (Figure 13A–B). Ordered arrays of hydrogen bonds along the polymeric backbone, however, were not observed for polyisocyanide 37, which is derived from alanine glycine.\cite{1, 88} It is remarkable that in contrast to 37, polyisocyanide 36, derived from glycine-alanine, did give a well-defined helical structure suggesting that the steric bulk in the second amino-acid is of great importance, as because it stabilizes and directs the hydrogen bonding network. Analogous to the denaturation of proteins, the hydrogen bonds in these polymers can be disrupted leading to the unfolding of the helix. This unfolding is, however, only possible with strong acids such as trifluoroacetic acid (TFA) and not with hydrogen bonding solvents (e.g., methanol and DMSO) demonstrating the robust character of the hydrogen bonding arrays.\cite{1, 85} Powder X-ray diffraction (PXRD) experiments showed that, in the solid state, the rigid polyisocyanopeptides are organized in a pseudo-hexagonal arrangement. The acidified samples, which were studied for comparison, in contrast, only gave broad signals pointing to a decreased level of organization in the polymer structure.

The peptide-derived polyisocyanides are stable in solution at room temperature, and as a result of their rigidity, it was possible to visualize the individual macromolecules by atomic force
microscopy (AFM) (Figure 13C).\textsuperscript{[1, 88, 89]} By measuring the contour lengths and by a careful analysis of the curvatures it was possible to determine the molecular weight, the polydispersity, and the persistence length of the polymers. The persistence length was found to be 76 nm, highlighting that these polymers are more rigid than double stranded DNA.\textsuperscript{[89]} An accurate value of 1.6 nm for the height of the fibers was obtained by AFM measurements under chloroform vapor,\textsuperscript{[90]} which corresponds well with the polymer chain derived from molecular modelling and PXRD measurements.\textsuperscript{[1]}

\textbf{Figure 13:} A) Crystal structure of 32a. B) Schematic representation of the proposed orientation of the peptide side chains in 34a. C) AFM-micrograph of 34a prepared with 1/30\textsuperscript{th} equivalent of Ni(ClO\textsubscript{4})\textsubscript{2}\cdot6H\textsubscript{2}O. D) AFM-micrograph of 35a prepared with 1/32\textsuperscript{th} equivalent of TFA.

The assignment of the helical sense of peptide-derived polyisocyanides by CD spectroscopy is hampered by the overlap of signals arising from the polymer backbone and the side chains. For an L-alanine based polyisocyanide containing a spectator group (i.e. a diazo chromophore) in the side chains, a right-handed (\(P\)) helical geometry was found.\textsuperscript{[91]} Since the helical sense in polyisocyanides is kinetically controlled, this handedness was tentatively assigned to all L-alanine derived polyisocyanides. Selected properties of polyisocyanodipeptides (34–43) are presented in Table 1.\textsuperscript{[92]} When hydrogen bonds are present (e.g. 34, 35, and 40), a positive optical rotation and a strong positive Cotton effect around \(\lambda = 315\) nm indicate the presence of a right-handed (\(P\)) helix. When this is not the case (e.g., 35), the Cotton effect appears at lower wavelength, has the opposite sign, and has a lower intensity (Table 1). From IR and NMR spectroscopic studies it was concluded that polyisocyanides 34, 35, and 43 retain their hydrogen bonded helical conformation for significant periods of time\textsuperscript{[93]} even when they are dissolved in water after removal of the methyl ester functions. The thermal denaturation of these watersoluble polymers was also studied in water. It was demonstrated using variable temperature (VT) CD spectroscopy that the denaturation process proceeds in a cooperative fashion.\textsuperscript{[1]}
Previously Millich\^{19} had found that acid-coated glass can act as a catalyst for the polymerization of isocyanides, although not very efficiently. Metselaar et al. recently reported that the TFA initiated polymerization of isocyanopeptides leads to extremely long polymers with lengths up to 14 \mu m (Figure 13D).\^{89, 94} For the polymerization of 33a at a TFA concentration of 1 mM, kinetic studies revealed a large entropy of activation ($-170$ J mol$^{-1}$K$^{-1}$), which indicates a very high degree of organization in the transition state.\^{86} At higher acid concentrations, instead of polymerization, conversion of the monomer to the corresponding formamide was observed. Based on this result a polymerization mechanism was proposed in which a helical oligomer is first formed and acts as a template for the incorporation of subsequent monomer units through a supramolecular complex (Figure 14). In the case of high acid concentrations the template is disrupted and destroyed. The reaction is highly stereospecific since the addition of the enantiomeric monomer 33b completely blocked propagation of the polymerization of 33a, even when present in only 1%. The diastereomer 32a, but not 32b, could be incorporated into the growing polymer, although 32a itself, without 33a present, could not be polymerized with TFA. These subtle differences demonstrate the critical effect of the configuration of the first chiral center of the monomer on the polymerization reaction and the high stereospecificity of the transition state. The fact that 32a itself cannot be polymerized with TFA was attributed to the inability of 32a to form a helical template due to larger steric repulsion between the monomeric units in the helix. When a Ni(II) catalyst was used all monomer combinations could be readily polymerized.

\begin{table}
\centering
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
Compound & \([\alpha]\ (deg \cdot dm^{-1} \cdot cm^{-1}) & \Delta \epsilon(\lambda) & Screw & H-bonds \\
& Monomer & Polymer & (l/mol cm) & sense & \\
\hline
34a & 33 & 338 & 5.6 (313) & \(P\) & Yes \\
35a & -5.6 & 487 & 5.8 (307) & \(P\) & Yes \\
36 & 19.2 & 196 & 5.1 (321) & \(P\) & Yes \\
37 & 5.7 & -32 & -1.5 (290) & \(P\) & No \\
38 & 164 & 580 & 6.5 (304) & \(P\) & Yes \\
& & & -0.45 (345) & & \\
39 & 75 & -700 & 1.22 (270) & \(M\) & No \\
40 & -58.1 & 205 & 8.6 (310) & \(P\) & Yes \\
& & & 0.17 (355) & & \\
41 & -12.0 & -33 & -1.3 (263) & \(P\) & No \\
42 & 14 & -610 & -5.5 (300) & \(M\) & unclear \\
43 & 2.4 & 188 & 2.5 & \(P\) & Yes \\
\hline
\end{tabular}
\caption{Table 1}
\end{table}
Wezenberg et al. showed that polyisocyanides 44 and 45 derived from β-amino acids also form well defined rod-like polymers (Scheme 8). The kinetically formed polymer, however, turned out to be unstable and transformed into a more stable structure, which possessed a better defined hydrogen bonding pattern as was concluded from IR and temperature-dependent CD studies. The precise structure of the transformed polymer remained unclear.

**Figure 14:** Mechanism of the acid initiated polymerization of 33a, showing the helical template formation and the subsequent polymerization (Route A). The side reaction to the corresponding formamide, which occurs at high TFA concentrations is shown in Route B.

Scheme 8
2.5 Functionalized polyisocyanides

As was discussed in the previous sections, polyisocyanides possess a unique polymer backbone that can adopt a very stable rigid conformation when bulky side chains or additional stabilizing interactions between the repeat units, like $\pi-\pi$ stacking and hydrogen bonding, are present. Polyisocyanides, therefore, are very attractive scaffolds to arrange functional groups in well defined arrays, thus creating new materials with special properties. Many of the functionalized polyisocyanides have already been described in excellent reviews, for example by Cornelissen et al. and very recently by Suginome et al., \cite{13, 14, 16, 19} and will not be discussed here.

The bioinspired sugar (46–48)\cite{57, 96, 97} and cholesterol (49)\cite{98} derived polyisocyanides and polymers from isocyanides functionalized with ionic side groups (50–53)\cite{60, 99-101} have all been reported (Scheme 9). Amphiphilic isocyanide 50 forms vesicles in water and the isocyanide functions could be polymerized leading to the cross-linking of the bilayer.\cite{100} Iyoda et al. have shown that it is also possible to polymerize isocyanides with extremely bulky groups using Pd-Pt complex 11 as the catalyst. Dendronized polyisocyanides 54 were synthesized with a polymerization degree exceeding 100.\cite{102} Using such an approach, polyisocyanides bearing even polystyrene side groups (55) could be synthesized with a polymerization degree of circa 50.\cite{103}
Polyisocyanides also have been used as well-defined templates in catalysis, crystal growth, and for the transfer of chirality (Scheme 10). Polymeric catalysts have been prepared from polyisocyanide 56, by the coordination of Rh-catalysts to the phosphor ligands in the side chains.\textsuperscript{[104-106]} The stability and catalytic activity of the rhodium complex of 56 towards the hydrogenation of cyclohexene was found to be better than that of the monomeric rhodium complex. The catalytic activity was also better than the activity of analogous polymers with a flexible polystyrene backbone. The latter result was ascribed to the rigidity of the polyisocyanide, which makes the catalytic centers more accessible.

The water stable peptide derived polyisocyanide 57a was used as a supramolecular template for the crystallization of CaCO\textsubscript{3}. The formation of unusually shaped calcite was found to be controlled by nucleation and adsorption processes involving 57a.\textsuperscript{[93, 107]} The fact that less control over the crystallization process was obtained when polymer 57b was used demonstrated the
specificity of the interaction between 57a and the growing crystal. Single polymer chains of 57a were visualized on a graphite surface by AFM by complexing the polymer to positively charged amino alkanes.\cite{108} By varying the length of the aminoalkanes the apparent stiffness of the polymers on the surface could be influenced.

Polyisocyanide 58 with a stable, induced helix in water (see section 2.3),\cite{68} was found to be able to induce helicity in another oppositely charged polyelectrolyte based on a polyacetylene.\cite{109} The inter polymer complexation proved to be dependent on both the pH and the salt concentration. This helix replication strategy opens numerous possibilities for the growth of ordered helical assemblies.

![Scheme 10](image)

Scheme 10

Much research has been focused on the use of polyisocyanides as scaffolds for the creation of well defined molecular wires with special magnetic, optical, or electronic properties. Polyisocyanides 59, functionalized with crown ethers of different sizes, were reported to yield architectures containing four arrays of cofacially stacked rings connected to the polymer backbone (Scheme 11).\cite{62, 110} The polymers appeared to be able to function as ion channels when incorporated within bilayer membranes.

Persoons and coworkers studied polyisocyanide 60 and related compounds, which are functionalized with non-linear optically active (NLO) side groups.\cite{111-115} In solution, a first hyperpolarizability exceeding $5000 \times 10^{-30}$ electrostatic units was measured. Electric field-induced second-harmonic generation measurements revealed a larger non-linear response for the polymer than for the monomer. The second order non-linear response might be further optimized in structures with a smaller angle (60° for this structure) between the polymer backbone and the chromophores.\cite{111} Langmuir Blodgett films of polymer 60, showed stable second harmonic generation without the need of poling.\cite{114} This observed NLO effect is thought to originate from the highly defined orientation of the side chains obtained at the air-water interface.

Polyisocyanides 61 and 62 were designed as macromolecular ferromagnets,\cite{116} however, no evidence for ferromagnetism or any other short-range ordering among the unpaired spins was observed.
A chiral redox responsive polyisocyanide bearing ferrocenyl groups (63) has been reported by Takahashi and coworkers (Scheme 11)\(^\text{[117]}\). Redox cycles of this polymer proved to be completely reversible. CD measurements revealed that, upon oxidation at 1V and 1.5V, the intensity of the positive Cotton effect at 360 nm decreased to 40% of the initial value and the negative Cotton effect at 250 nm disappeared. The CD signal could be restored by reduction at 0.2 V. The same behavior was observed by chemical oxidation and reduction of the ferrocenyl groups. Upon oxidation, the helical backbone is believed to be transformed into a disordered structure by the electrostatic repulsion of the ferrocenium ions.

In the group of Amabilino, polymer 64 containing tetrathiafulvalene (TTF) units has been designed and synthesized with the objective of constructing a chiral redox polymer\(^\text{[118]}\). The polymer has three univalent and two wide mixed-valence redox states, which are fully interconvertible (Figure 15). The different redox states of the polymer, in contrast to the monomer, exhibited clearly distinguishable chiroptical properties as was shown by CD spectroscopy measurements and therefore can act as a multistate redox-switchable organic system.

\textbf{Scheme 11}
One of the early examples of polyisocyanides bearing electron acceptor and donor groups was reported by Oostveen and Drenth.\cite{119, 120} They synthesized polyisocyanides bearing pyridinium iodide in their side chains. In these polymers the pyridinium functions act as electron acceptors and the iodide ions as electron donors (Figure 16). A large bathochromic shift was observed in the charge-transfer (CT) spectra of copolymer 65, which was attributed to intercalation of the iodide ions in the cavities created by the co-monomers leading to strong CT interactions. Similarly, copolymer 66, with both short and long side-chains was found to effectively bind donor molecule 67 leading to electron transfer from the donor to acceptor as confirmed by EPR measurements. This electron transfer was, however, not observed between the monomeric species. In an attempt to create a polymeric photoconductor, polymer 68, which has side-groups capable of internal charge transfer, was synthesized.\cite{121} Unfortunately, the polymer was hardly soluble and no conductivity measurements could be performed.
A polyisocyanide-based light harvesting system has been constructed by Hong and Fox.\cite{122,123} Using the nickel catalyst 1, developed by Deming and Novak, a living polymerization reaction allowed the formation of homo, di-, and triblock copolymers incorporating acceptor and donor blocks (Scheme 12). From fluorescence spectroscopic studies it was concluded that the stiff polyisocyanide backbone was able to spatially define the chromophores thereby preventing excimer formation as often observed in more flexible polymers functionalized with chromophores. This is remarkable since the chromophores are connected to the backbone by a relatively flexible ethyl spacer.

Directional singlet energy migration to the acceptor-donor interface was observed in block copolymers 69 and 70. This resulted in electron transfer at the block interface in the case of 70 and exciplex formation in the case of 69. The energy wasting exciplex formation observed in 69 was suppressed in triblock copolymer 71, which contains an intervening pentamethylphenyl block between the two blocks present in 69. For block copolymer 70, transient absorption spectroscopy revealed the formation of a radical ion pair with a lifetime of 1.1 µs.

Extending the field of chromophore functionalized polyisocyanides, the group of Takahashi reported the porphyrin functionalized polyisocyanides 72–75 and related compounds, prepared by using Pd-Pt catalyst 11.\cite{124-127} The degree of polymerization was varied between 2 and 200 and block copolymers of type 74 with various block lengths and low polydispersities, mostly below 1.1, were prepared. Photophysical studies revealed that the porphyrins in the stacks are excitonically coupled in a face-to-face manner. It was found that exciton-exciton annihilation rate constants were independent of the length of the polymer indicating a fast exciton migration through the stacks. In the di- and triblock copolymers 74 and 75 energy transfer from the zinc...
Polyisocyanides: Stiffened foldamers

porphyrin to the free base porphyrins was observed. The rate constants for the excitation energy transfer process appeared to be the same for different block lengths of the free base and zinc porphyrins, again pointing to a fast exciton migration.\textsuperscript{[126]}

The achiral porphyrins moieties were also incorporated in different ratios as the middle block in a triblock copolymer, namely, between two blocks of chiral isocyanide 19 functionalized with a (L)-menthyl group. The included porphyrins were used as spectator functions to determine the helical sense of the poly(aryl isocyanide)s.\textsuperscript{[128]}

\begin{equation}
\begin{aligned}
69: & R^1=R^2=A, R^3=B \\
70: & R^1=R^2=C, R^3=B \\
71: & R^1=A, R^2=D, R^3=B
\end{aligned}
\end{equation}

Scheme 12
Using the well-defined polyisocyanopeptide as a scaffold, De Witte et al. synthesized the helical porphyrin functionalized polyisocyanides 76 and 77. AFM measurements revealed that the polymers had an average length of 87 nm, which corresponds to an average degree of polymerization of 830. Resonance light scattering measurements demonstrated that at least 25 porphyrins in a stack were interacting with each other and that the slip angle between the porphyrins in a stack was $30^\circ$. The presence of a chiral interaction between monomer $n$ and $(n+4)$ in this slipped conformation and between the neighboring porphyrins in the helix $(n$ and $(n+1))$ could be observed by CD spectroscopy (Figure 17). Upon addition of the bifunctional ligand 1,4-Diazabicyclo[2.2.2]octane (DABCO), polymer 77, which bears zinc porphyrin units, could be switched to a conformation in which the porphyrin stacks possess the opposite helicity whereas the helicity of the polymer backbone remains the same.

![Figure 17: A) Illustration of the slip angle between porphyrin n and (n+4) in polymer 76 and B) the CD-spectrum of 76 in CHCl₃.](image)

Based on the same polyisocyanopeptide backbone, the groups of Nolte and Rowan prepared the thiophene functionalized polyisocyanides 78–80 and perylene functionalized polymers 81 (Scheme 13). Thiophene polyisocyanide 78, with only one alanine unit in the backbone, appeared to be less soluble than polymer 79, which contains two alanine units. For 78 only short polymers were observed by AFM measurements, whereas longer ones with lengths up to 300 nm were found for 79. IR, fluorescence, and CD spectroscopy studies showed that the latter polymer contained a better defined backbone structure (with a well-defined stabilizing hydrogen bond array) than the former of which the CD spectrum resembled that of the less well-defined polymer 35 derived from alanine-glycine. The prepared polymers could be interesting compounds for the preparation of electron conducting nanowires, which would be obtained after a second topochemical polymerization of the thiophene side groups. In a different approach the monomer from which 78 is prepared, was polymerized using polystyrene nickel initiator complex 6 to yield block copolymer 80. In both water and organic solvents this block copolymer formed polymersomes, which are vesicles derived from amphiphilic polymers. In water, chemical oxidation resulted in cross-linking of the thiophene groups giving rise to electron conducting polymersomes. Catalytically active nanoreactors could be prepared in water by the inclusion of enzymes in the interior of the polymersome. The polymersome bilayer proved to be permeable to substrate molecules and the building up of a fluorescent product, formed by the enzymes inside the polymersome, could be observed by fluorescence microscopy. Giant vesicles with sizes up to 100 μm were prepared from 80, namely by electroformation.
The perylene functionalized polyisocyanides 81 were synthesized for use as a synthetic antenna system with the possible application as n-type material in organic photovoltaics.\cite{132, 133} During the polymerization, a color change from yellow to red was observed due to the intramolecular stacking of the perylenes, which occurs on formation of the rigid backbone. According to AFM measurements, the formed polymer fibers were up to 1 μm in length, incorporating circa 10,000 monomer units (Figure 18). A Cotton effect in the CD spectrum in the absorption region of the perylene chromophores revealed the helical organization of the perylenes around the helical polymer backbone.

Figure 18: Color change during polymerization of 81b (left and front cover) and AFM picture of the polymer molecules on mica.

Fluorescence and UV-Vis spectroscopic studies on 81a proved the occurrence of excimer-like species in the close packed perylene arrays. Using a setup combining single-molecule confocal fluorescence and atomic force microscopy, two species resulting from the polymerization reaction could be distinguished: (i) ill-defined oligomer species displaying monomer-like fluorescence (light gray spots (<590 nm), Figure 19B), which were too small to be observed by
AFM (Figure 19A). The oligomeric character of the species was revealed by their step-wise blinking and bleaching (Figure 19C) and the fact that their fluorescence spectrum was monomer-like (Figure 19D); (ii) well-defined polymers that could be observed by AFM, showing emission arising from multiple, and independent, excimer-like sites (dark gray spots (> 590 nm), Figure 19B). A continuous intensity decrease and an excimer-like emission spectrum, typical for a polymer, was observed for these species (Figure 19E–F). Unfortunately, since polymer 81a was found to be only sparingly soluble in solvents such as toluene and chloroform, application in a device was impossible. Therefore polymer 81b, exhibiting similar photophysical properties, but with improved solubility in the aforementioned solvents was synthesized. A photovoltaic cell with an active layer of 81b as electron acceptor and regioregular polythiophene (P3HT) as electron donor was prepared, displaying a 20-fold improved power output compared to a cell with an active layer of a perylene monomer homologue and P3HT.

Figure 19: A) AFM and B) confocal fluorescence (dark gray: $\lambda > 590$ nm, light gray: $\lambda < 590$nm) images from the same 3.8$\times$3.8 $\mu$m$^2$ area of a diluted solution of polymer 81a spin-coated on glass (bar = 500 nm; polymers are encircled. Fluorescence intensity trajectory for the C) green and D) red emissions in B. Emission spectra integrated over the whole time ($t=0–25$s) window for the E) green emissions and F) red emissions.
2.6 Conclusion

It is clear that the field of polyisocyanide chemistry originating more than 30 years ago is still thriving. This is primarily due to the unique nature of the polymers, which are only now becoming fully appreciated. It is of interest to note that the initial polymerization catalyst, namely, acidic glass, was followed by the development of the nickel and the Pd-Pt catalysts, and has now been rediscovered and improved, closing as it were the circle, resulting in polymers with lengths ~15–20 μm long and molecular weights in excess of 20,000,000 Dalton. The helical architecture of the polymers, in combination with the functional side-arms, which are precisely positioned along the polymer backbone, results in unique molecules stiffer than DNA. These can act as, for instance, nanowires along which excitons can migrate with ease. It can be foreseen that these polymeric foldamers will continue to raise the interest of chemists and physicists eventually leading to applications as functional materials in opto-electronic and other devices.
Perylene bisimides and their photophysical properties

Perylene bisimides (PBIs) are widely studied in the field of optoelectronics because of their good thermal and photochemical stability, high electron affinity, high optical density, and high fluorescence quantum yield. In addition, high electron mobilities have been measured in perylene crystals.\[^{135, 136}\] This chapter will give an introduction into PBIs, their (photo)physical properties, properties of aggregated and polymeric PBI systems, and their application in optoelectronics, in particular photovoltaics.

### 3.1 Absorption characteristics

The absorption spectra of the PBIs are dominated by the vibrational transitions (~525 nm: 0→0, ~489 nm: 0→1, ~458 nm: 0→2, ~431 nm: 0→3) of the π-π* transition (HOMO-LUMO, $S_0$-$S_1$) along the long axis of the perylene. The π-π* transition along the short axis ($S_0$-$S_2$) is forbidden and appears with low intensity at ~370 nm. The n-π* transitions at lower wavelengths are not observed because of their low oscillator strength.\[^{137}\] The color of the perylene is hardly influenced by the environment, in other words, little solvatochromism is observed.\[^{138}\] The substitution pattern of the imides only marginally influences the position of the absorption peaks. Substitution of the bay area (positions 1,6,7,12) of the perylene (Figure 1), however, does affect the positions of the absorption maxima and can lead to bathochromic (red) shifts of 50 nm for electron donating substituents such as phenoxy groups.\[^{138-141}\] The bulk of the phenoxy groups causes a twisting between the two naphthalene units in the perylene plane and as a result the $S_0$-$S_2$ transition becomes more accessible and therefore more visible in the absorption spectrum.

![Figure 1: PBI core and numbering of the carbon atoms.](image)

### 3.2 Aggregates and physical properties

For applications such as photovoltaic devices and field effect transistors (FETs) it is a challenge to synthesize materials in which the PBI moieties are ordered in such a way that energy and electron transport is possible. Most of the research on photovoltaics and FETs aims at structures in which the perylenes are aggregated in a cofacial fashion with high orbital overlap and exciton coupling. High electron mobilities\[^{135, 136}\] and also fast exciton transport over large distances\[^{142}\] have been measured in such cofacial systems (\textit{vide infra}).
Several approaches to obtain well organized perylene structures for application in solar cells and FETs have been described in the literature including studies on perylene crystals, aggregates, liquid crystals, and polymer architectures. The last two structures have the advantage that stable films can be formed by cheap processing methods such as drop casting and spin coating. Struijk et al. reported high structural ordering in the liquid crystalline phase of the mesogenic derivative 1 of PBI. The compound forms smectic layers wherein the perylene moieties are oriented in a slightly rotating columnar stack. By pulse radiolysis time resolved microwave conductivity (PR-TRMC) measurements, a charge (electron) mobility of 0.11 cm²V⁻¹s⁻¹ was determined in the liquid crystalline phase and 0.21 cm²V⁻¹s⁻¹ in the crystalline phase. Similar values by the same technique were measured in crystals of PBI 2a with four chlorine substituents in the bay area. The crystal packing of this compound is different from the one-dimensional columns that are formed by the unsubstituted analogues. Furthermore, two-dimensional contacts between the twisted perylene planes are present.[143] Malenfant et al. incorporated PBI 3 into thin film transistors by means of vacuum deposition and measured electron mobilities up to 0.6 cm²V⁻¹s⁻¹.[144] In later work by Chesterfield et al. mobilities of 1.7 cm²V⁻¹s⁻¹ were reported for films of 3.[145]
The electron mobilities found stimulated researchers to design well ordered perylene structures. Gregg and coworkers studied films of PBIs 4–7 prepared by different preparation techniques (vacuum evaporation, spin coating, and Langmuir Blodgett technique). The three liquid crystalline compounds 4–6 were found to form highly ordered thin films with structures that were similar to that of the crystal structure of 7. The PBI stacks were found to orientate parallel to the surface, independent of the preparation method or the used substrate. This orientation is imposed by the offset π–π stacking of the perylenes in combination with the side chain conformation, which is forced out of the plane of the perylene core. Conductivity can be
expected to be optimal along the stack direction. It was therefore concluded that the obtained film structure might not be very favorable for solar cell applications for which conductivity perpendicular to the substrate is required, but it might be interesting as an active layer in FETs. Gregg et al. further studied the possibility of n-type doping of thin films of 4 with dopant 4'.\textsuperscript{[147-151]} The dopant was designed in such a way that the cation of dopant 4' is coupled to the molecule itself and therefore no free ions were present in the crystal lattice of films of 4/4' making the chance of recombination of charge carrier and cation much smaller. An exponential increase in the conductivity with an increase in doping density was found, but the number of free carriers per added dopant was found to be much lower than one. This effect was ascribed to coulombic forces between electrons and cations, which prevent most of the negative charge carriers to be truly mobile. At higher dopant concentrations, the polarizability of the film increases causing an increase in the fraction of free carriers. It appeared that 4 and 4' form very stable mixed stacks since large aggregates were formed in THF at concentrations where no aggregation of the two individual species was observed. The authors proposed that the driving force for aggregation is the delocalization of the dopant electron over a large number of stacked molecules.

\textbf{Figure 2:} Absorption (A, B) and fluorescence (C, D) spectra of molecular dissolved and aggregated 2b (A, C) and 8 (B, D) in different solvents. The molecular dissolved spectrum is recorded in chloroform for 2b and methanol for 8.

In contrast to what Gregg et al. reported for compounds 4–7, Balakrishnan et al. discovered a different stacking conformation for the differently substituted PBIs 2b and 8.\textsuperscript{[152]} The absorption and fluorescence spectra showed different packing of the perylene aggregates in both poor solvents and thin films (Figure 2). Compared to the molecular dissolved perylene, the absorption spectrum of aggregated 2b in poor solvents revealed a new band at higher wavelength ($\lambda=$565
Perylene bisimides and their (photo)physical properties

Relative to the 0-0 transition, enhanced transition strengths for the transitions from ground level to the higher level electronic states (0-1, 0-2 and 0-3) were observed (Figure 2A). The fluorescence signal in solution was completely quenched (Figure 2C), but in the more concentrated film a red shifted emission at 635 nm was observed. For 8, relatively enhanced absorption strengths were also visible at shorter wavelengths, but no distinct signal, only an absorption tail at higher wavelength, was observed (Figure 2B). The fluorescence spectrum of 8, in both solution and film, revealed an emission at ~607 nm (Figure 2D). The emission quantum yield of the film of 2b was three times lower than that of 8. From these absorption and fluorescence data, together with data from differential scanning calorimetry and X-ray diffraction studies, the authors concluded that molecules of 2b are strongly π-π stacked in a co-facial configuration leading to the distinct red shifted absorption and the strongly red shifted and largely quenched emission. For perylene 8, because of the “swallow tail”, the co-facial arrangement is distorted and this leads to a less pronounced red shifted absorption band and a smaller red shifted emission band with a higher fluorescence quantum yield.

Würthner et al. were the first to report on liquid crystalline (LC) perylenes 9b–e with substituents in the bay area. Spectroscopic investigations on the aggregation behavior of 9a–d in methylcyclohexane revealed that the larger the bay area substituent of the perylene was, the weaker the aggregation and the larger the longitudinal shift between the stacked perylenes. For 9a no fluorescence was seen and for 9b only little fluorescence was detected, which was attributed to intramolecular charge transfer between the trialkoxy phenyl subunits and the PBI core. For 9c–e, the four electron donating phenoxy groups connected to the perylene were found to change the energy levels and no quenching of the fluorescence was observed. From X-ray diffraction studies on the LC-mesophases it was concluded that 9a,c formed disordered and 9,b,d ordered hexagonal columnar mesophases. For 9e different results were obtained; the phenoxy substituted PBI revealed the weakest aggregation behavior and a highly disordered crystalline layered structure was found in the LC-mesophase. This observation was explained by the possibility of π-π interactions between interdigitated phenoxy groups in the LC phase of 9e.
For all the PBIs 9a–e it was concluded from absorption and fluorescence spectroscopic studies that J-aggregates were formed. This was confirmed by molecular modeling studies. The angles $\alpha$ between the molecular plane and the aggregation direction for 9b–e were determined to be 35–45° (Figure 3). Theoretically above an angle of 54.7° the molecules form H-aggregates, whereas below 54.7° they form J-aggregates.

In a later report, the charge carrier mobility of 9a was determined and compared to that of the chlorinated counterpart 9e.[153] PR-TRMC measurements revealed that charge carrier mobilities of 9a and 9e in their LC phases were in the same order of magnitude (0.01 and 0.02 cm$^2$V$^{-1}$s$^{-1}$, respectively). The charge carrier lifetime of 9e, however, appeared to be 100 times longer than that of 9a. Possible explanations are (i) a better packing of 9e that results in an ordered columnar phase and (ii) a higher electron affinity of 9e leading to stable radical anions.

Recently the group of Würthner reported PBI 10. By replacement of the trialkoxyaryl substituents in 9a for trialkylaryl substituents, no photoinduced electron transfer is possible between the substituents and the perylene core and both the monomer and the aggregates become highly fluorescent. In contrast to 9a, 10 forms H-type aggregates. The fact that stacks of 10 are still highly fluorescent was attributed to a rotational stacking of the perylene cores, thereby allowing optical transitions between the ground state and the lower excitonic energy state.[154]

An et al. investigated the electron mobility in aggregates of PBIs 9a, and 11, which both exhibit disordered columnar hexagonal mesophases in the temperature ranges of −10 °C to 360 °C and −10 °C to 226 °C, respectively.[155] The relatively low clearing point of 11 allows for easy processing of films from the melt. The charge carrier mobility in the liquid crystal phases was determined by the steady-state space-charge limited current (SCLC) technique, giving mobility values of 0.2 cm$^2$V$^{-1}$s$^{-1}$ and 1.3 cm$^2$V$^{-1}$s$^{-1}$ for 9a and 11, respectively. Much lower mobilities were determined for pressed pellets of the same materials by the PR-TRMC method.

Shinkai and coworkers functionalized PBI with two cholesterol units to create perylenes with gel forming properties.[156] Perylene 12 formed stable transparent gels in mixtures of aromatic and alcoholic solvents when present in concentrations of 50 mol%. Analogues of 12 with substituents in the bay area of the perylene were not able to gelate the mixed solvents, however, when these analogues were mixed into the gel, efficient energy transfer between 12 and these species was
observed. Würthner et al. also showed that PBIs with phenoxy substituents in the bay area are able to gelate. PBI 13, functionalized with urea groups, formed gels in apolar solvents such as toluene and CCl₄. Spectral changes in the absorption and fluorescence spectra indicated π-π stacking of the PBIs, whereas infrared spectroscopy revealed hydrogen bonding networks between the PBIs. Atomic force microscopy of the material on a graphite surface showed the presence of fiber-like structures, which displayed high fluorescence as measured by confocal laser scanning microscopy.

![Figure 4: Schematic representation of the stacked arrangement of PBIs 14 (dark rectangle) within aggregates of melamine derivatives (light features with tails).](image)

Besides covalent functionalization to introduce solubility and gelating properties to the PBIs, non-covalent interactions have been utilized to functionalize the PBIs in a supramolecular fashion and to create well defined systems.

Thalacker and Würthner reported on co-aggregates of PBI 14 and melamine derivatives functionalized with alkyl tails (Figure 4).[158] Perylene 14 was mixed into aggregates of the amphiphilic melamines up to 1:1 stoichiometry. Even at low perylene concentrations, UV-Vis and fluorescence spectroscopy indicated that the perylenes formed aggregated stacks within the melamine assemblies. Chirality in the perylene stacks could be introduced by using chiral tails attached to the melamines.

Faul et al. were able to organize PBI with ionic side groups into well defined stacks by complexing oppositely charged (chiral) surfactants.[159-161] Some examples of the systems studied by this group are depicted in Scheme 2. Complex 15a forms a two-dimensional columnar thermotropic LC phase with the perylenes stacked in a H-aggregate. In DMSO the complex formed a lyotropic phase with weakly aggregated perylenes, which could be transformed into an aligned film by non-uniform evaporation of the DMSO.[160] Complexes 15b formed aggregates in solution with the perylenes stacked face-to-face (H-aggregate) in a left handed helical arrangement. The surfactants were able to induce chirality in the perylenes, both in solution and in films. In the solid state, both systems are highly ordered and form lamellar morphologies.
More complex structures consisting of multiple linked PBIs have also been described. Perylene trimer 16 was found to aggregate in solution and to form fibers with diameters of 4 to 150 nm and an aspect ratio around 500 when evaporated on glass slides.\cite{162} The fibers were studied by polarizing scanning confocal microscopy from which it was concluded that the trimer planes are perpendicular to the fiber axis. Single-fiber fluorescence images and spectra were collected and revealed a strong red-shifted fluorescence indicative of a high degree of electronic delocalization within the fibers. It was possible to break up this delocalization by photobleaching the chromophores and this leads to a blue shift in the observed fluorescence. Similar systems have been extensively studied in the group of Wasielewski.\cite{163-165} Trimer 17 and pentamer 18 were reported to dimerize in solution with the perylenes aggregating in a cofacial arrangement comparable to that of covalent dimer 19. Electron-nuclear double resonance (ENDOR) spectroscopy revealed rapid electron hopping, instead of band-like transport, between the aggregated perylenes in 17, comparable to the observations in 19. Pentamer 18 forms 130 nm long rod-like nanostructures on hydrophobic surfaces as was revealed by atomic force microscopy. Spectroscopic studies on 18 in solution revealed excimer-like species with a lifetime of 20 ns upon photoexcitation. Singlet-singlet annihilation of the excimer-like state occurred with exciton hopping times of 5 ns.
3.3 Oligomers and polymers

Besides aggregation of monomeric PBI units, several examples are known in which phase-to-phase aggregation of perylenes is promoted by an oligomeric or polymeric architecture.
Janssen et al. reported on polymers 20, which contain several PBIs connected by flexible polytetrahydrofuran spacer units (m \( \leq 3, 14, 33 \)).\(^{[166, 167]}\) From absorption and fluorescence spectroscopy it was concluded that the PBIs form H-like aggregates in \( \alpha\)-dichlorobenzene, as depicted in Figure 5a, with increased aggregation for the polymers with the shorter polytetrahydrofuran segments. The photoluminescence spectra revealed monomer-like and excimer-type fluorescence. The monomeric perylene fluorescence most likely originates from dangling perylenes (Figure 5c) whereas the excimer-type emission is believed to come from well-defined aggregated stacks (Figure 5a). Time-resolved fluorescence spectroscopy revealed characteristic lifetimes for these species (3 and 17 ns, respectively), but also an additional short lived luminescence component, which was ascribed to the deactivation of monomer-like fluorescence by excimer formation or energy transfer (Figure 5b).

![Figure 5: Proposed states of self-organization of the alternating copolymers of PBI. PBI chromophores are represented by the rectangles; polyTHF by the solid lines. In b the possibility of energy transfer from a single dangling perylene to an aggregate is illustrated.](image)

Li and coworkers reported a series of oligomers of alternating PBI and ethyleneglycol spacers incorporating up to 6 PBI units (oligomer 21 incorporating 3 PBI units is shown in Scheme 4).\(^{[168, 169]}\) The authors concluded from NMR and UV-Vis spectroscopic data that the oligomers fold to allow \( \pi\)-\( \pi \) stacking of the PBIs as depicted in Scheme 4, after which aggregation of the folded oligomers occurs yielding larger aggregates. Recently, it was shown that the folding and unfolding of the oligomers can be followed by single molecule spectroscopy.\(^{[170]}\) The same group reported on alternating DNA-PBI copolymers in which the DNA is connected to the PBI through a tetraethyleneglycol spacer (Figure 6a).\(^{[171]}\) Aggregation and thus folding of the polymers was monitored by recording the absorption ratio of the \( 0 \rightarrow 0 \) and \( 0 \rightarrow 1 \) transitions; the ratio \( A^{0-0}/A^{0-1} \) is 1.6 for the non-aggregated state and goes to lower numbers upon aggregation. At room temperature a value of \( A^{0-0}/A^{0-1} = 1.10-1.15 \) was found for polymers containing 1–5 PBI units indicating weak interactions between the perylenes. Upon heating the polymer up to 90 °C the ratio decreased to 0.77–0.87 revealing increased ordering of the polymer structure as monitored by the PBI aggregation. At higher temperatures hydrophobic interactions started to play a more pronounced role leading to a folding of the polymer. A hairpin structure incorporating five perylene bisimides and six base-pair hairpin stems revealed even stronger aggregation of the perylenes due to cooperativity between DNA folding and PBI aggregation (Figure 6b). This structure could be disrupted after binding of complementary DNA strands.
The rigid calixarene based oligomeric structure 22 was synthesized in the group of Würthner. From the absorption spectrum of 22 it was concluded that no strong exciton coupling was present between the chromophores. Upon excitation of the inner PBI (highest bandgap), almost exclusive emission of the outer PBI (lowest bandgap) units was observed, indicating efficient energy transfer, most likely of the Förster-type. From their measurements a Förster distance of 62.7 Å between the chromophores was calculated.

### 3.4 Acceptor-Donor systems and applications in photovoltaics

The high electron affinity of PBIs makes them suitable as electron acceptor materials in applications such as photovoltaic devices. It is of interest, therefore, to combine architectures with well-defined perylene morphologies, which facilitate energy and electron transport, with donor materials capable of electron and hole transport. The literature offers many examples of PBI-donor architectures varying from orthogonally aggregated, to hydrogen-bonded, and further to covalently bonded structures.

To date, one of the best photovoltaic devices incorporating PBIs in its active layer is based on a blend of discotic hexabenzocoronene HBC1 and PBI 23. The active layer was prepared by spin coating a 1:1 mixture of the two materials in chloroform onto indium tin oxide (ITO). From atomic force microscopy (AFM), scanning electron microscopy (SEM), and absorption spectroscopy on the films it was concluded that a vertically segregated structure, with large interfacial areas between the electron-accepting perylene crystallites and electron donating liquid crystalline HBC1 domains, was formed. This close to ideal bulk heterojunction morphology of the film led to a photovoltaic device with maximum external quantum efficiencies (EQE) of over 34% and a maximum power efficiency of ~2% at λ=490 nm (see Appendix 1 for a definition of these terms). Recently, a similar blend, with room temperature crystalline HBC2 and 23 was investigated. Upon annealing the active layer, while in contact with an elastomeric stamp, the photovoltaic response in the cell was improved due to the formation of larger vertically segregated crystalline domains of the two components. More investigations have been performed on these structures to get more insight in the film morphology and the photogeneration of charges. In contrast to what was found for previous structures, blends of PBI 24 and HBC3 resulted in stacks with an alternating conformation of the donor and acceptor.
systems in which perylene and hexabenzocoronene units are covalently connected have been studied by fluorescence spectroscopy\textsuperscript{[180]} and scanning tunneling microscopy.\textsuperscript{[181]}

\begin{equation}
    R = \text{C}_2\text{H}_5 \quad \text{R} = \text{C}_6\text{H}_{13}
\end{equation}

\begin{equation}
    \text{HBC1:} \quad R' = \text{C}_12\text{H}_{25} \\
    \text{HBC2:} \quad R' = \text{C}_12\text{H}_{25} \\
    \text{HBC3:} \quad R' = \text{CH}_2\text{CH(C}_6\text{H}_{13})(\text{C}_8\text{H}_{17})
\end{equation}

\textbf{Scheme 5}

Poly- or oligo phenylene vinylene can also act as donor materials in devices with PBI acceptors. Herrikhuizen et al. reported on nanometer-sized fiber-like networks of PBI 11 when this compound was drop-casted from methylecyleohexane (MCH) on a gold surface. When 11 was mixed with fiber forming oligo (p-phenylene vinylene) (OPV) derivatives in MCH the two compounds were found to form separate aggregates. In films prepared from this solution, charge separation was observed between the n-type perylene stacks and the p-type OPV fibers, however, bulk heterojunction solar cells prepared from these films showed poor performance, probably due to a lateral alignment of the stacks.

A similar mixed system from water-soluble PBI 25 and a water-soluble OPV resulted in stacks of alternating acceptor and donor units.\textsuperscript{[182]}

In triad molecule 26, the OPV and PBI units are covalently connected. Upon photoexcitation, charge separation between the two units was observed both in films and in solution. The lifetime of the charge-separated state was found to be significantly longer in ordered thin films than in solution. This observation was explained by the possibility that charges migrate to neighboring molecules thereby preventing direct recombination. Nevertheless, no successful solar cell could be prepared from these films.\textsuperscript{[183]}
Perylene bisimides and their (photo)physical properties

Scheme 6

In the related molecule 27, charge separation between the donor and acceptor site was also observed upon photoexcitation. In apolar solvents, 27 was found to form hydrogen bonded aggregates, most likely dimers, according to NMR, UV-Vis, and CD spectroscopy.\textsuperscript{[184]}

The supramolecular triad donor-acceptor-donor complex 28 was reported by Schenning and Würthner. It consists of two diaminotriazine functionalized OPVs (DOPVs), which are hydrogen bonded to a PBI, as depicted in Scheme 6. The complexes were found to self assemble into J-type chiral stacks with strong exciton coupling between the perylenes as evidenced by a pronounced red shift of the perylene $S_0\rightarrow S_1$ electronic transition and the shape of the observed CD signal. A complete quenching of the fluorescence of DOPV and the PBI in the aggregate was observed, from which it was concluded that photoinduced electron transfer takes place between the donor and acceptor units. This observation was supported by transient absorption spectroscopy studies. Spin-coated samples from methycyclohexane on a PEDOT:PSS\textsuperscript{i/glass} slide revealed micrometer-long supercoiled fibers of the well defined co-aggregates. So far no efficient photovoltaic devices were built from this complex, again probably due to an alignment of the fibers parallel to the surface\textsuperscript{[185, 186]}

More recently the same groups have shown that the self assembly of complex 29 can lead to networks enabling electron and hole transport in thin films, as was measured in a FET prepared from a film of 29.\textsuperscript{[187]} Hole and electron mobilities of $\sim 10^{-7}$ cm$^2$V$^{-1}$s$^{-1}$ were measured. Mixtures of PBI and DOPV analogues that cannot form hydrogen bonded structures led to sandwiched structures incapable of charge transport.

\textsuperscript{i}Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)
The group of Janssen reported on oligomer 30, which is an OPV with dangling PBIs in the side-arms.\textsuperscript{[188]} Both in solution and as a film, efficient photoinduced charge transfer takes place in these oligomers. UV-Vis and CD spectroscopic measurements revealed exciton coupling between the OPV and the PBI with a preferred helical orientation. Besides fast charge separation also fast charge recombination was detected, which is most likely unfavorable for application in photovoltaics.

Wasielewski and coworkers reported on donor-acceptor system 31, which is comprised of four PBIs attached to a central zinc porphyrin core.\textsuperscript{[189]} The molecule self-assembled into ordered nanoparticles with a diameter of up to 150 nm in both solution (toluene) and the solid state. The absorption spectrum evidenced the existence of strong exciton coupling between parallel stacked PBI units, whereas no strong coupling between the porphyrin units could be observed. The self-assembly was found to be mainly driven by interactions between the PBI units; the zinc-porphyrins were still able to bind pyridine without disrupting the aggregate. A structure as depicted in Figure 7 was proposed for the nanoparticles.

Photoexcitation of the nanoparticles resulted in electron transfer from the zinc porphyrin to the PBI in 3.2 ps, after which time the electron migrated away from the zinc porphyrin cation over an average distance of 21 Å (5 layers). Charge separation appeared to be faster, whereas charge recombination was a bit slower when compared to model compounds that consisted of only one PBI connected to one porphyrin.

![Figure 7: Schematic drawing of the organization of 31 in nanoparticles with PBIs in dark-grey and porphyrins in light-grey.](image)

More recently the same group reported on trimer 32 consisting of three donor-acceptor pairs (diethyl aniline-PBI) connected to a central core that, like 17, was found to dimerize in solution.\textsuperscript{[190]} Charge separation and recombination were studied with transient absorption spectroscopy and compared to monomeric equivalents of the trimer that do not dimerize. Although dimerization revealed many photophysical changes, the electron transfer rates in the aggregated trimer appeared to be the same as in the non-aggregated monomeric species.

Oligomer 33 and similar oligomers that consist of a porphyrin main chain with perylene monoimide sidearms have been reported by Lindsey et al.\textsuperscript{[191-193]} Absorption spectra gave evidence of weak coupling between the chromophores in the oligomers. Fluorescence studies revealed efficient energy transfer from the perylene monoimides to the porphyrin upon photexcitation of the perylene monoimide at 490 nm.
Oligothiophene-perylene monoimide architectures 34–36 have been described by Cremer et al.\textsuperscript{194-198} By varying the length of the thiophene oligomers, the absorption range could be varied with the longer polythiophenes covering a broader range of the visible spectrum. Fluorescence quenching in these systems was attributed to photoinduced electron transfer from the oligothiophene to the perylene monoimide. Solar cells of these compounds in combination with a fullerene derivative were prepared, giving a power conversion efficiency up to 0.48% for 34 (n=4). Detailed transient absorption spectroscopy studies on 36 (n=2, 4) revealed a very fast charge separation process (2 ps) and a relatively slow charge recombination (50 ps).\textsuperscript{197} No information on the aggregation behavior of the perylene and thiophene units in solution or in the film was given, although some kind of ordering would be expected to be present given the molecular structure and the performance of the solar cells.
In a different approach Bäuerle et al. reported polymer 37, which consists of a PEDOT backbone with PBI sidearms. The PEDOT and the PBI form a donor-acceptor pair of which the redox properties were investigated with the help of electrochemistry.\cite{199, 200} The application of this material in solar cells has not yet been reported.

Functional solar cells of regioregular polythiophene (P3HT) and PBIs 24 have been reported by the group of Friend. Photovoltaic cells with an active layer of perylene crystals and P3HT in a weight ratio of 8:2 reached a EQE of 11% after annealing.\cite{201} By annealing, the efficiency was improved due to an increase in the crystallinity of P3HT and the formation of larger crystals of 24, which enhanced hole and electron mobility respectively.

By replacing P3HT with poly (2,7-carbazole), Müllen and coworkers could improve the EQE to 16% with a power efficiency of 0.6% under illumination with solar light.\cite{202}

![Scheme 9](image)

**Scheme 9**

Recently Shin et al. have published a comparative study on photovoltaic cells that consist of an active layer of P3HT and the PBI derivatives 38–41.\cite{203} Under similar conditions, the best solar cell performance was obtained for 40, probably due to its broad absorption band and improved stacking ability. It was found, however, that annealing of devices that contained 38 in the active layer drastically improved the power efficiency, whereas this was not the case for the other perylene bisimide devices because of their higher glass transition temperatures. The highest power conversion efficiency (0.182%) was reached for an active layer of P3HT and 38 in a 1:4 weight ratio after annealing at 80 °C. The electron donating substituents of 39 had a positive influence on the open circuit voltage (V_{oc}) because of the higher LUMO level, but were unfavorable for the short-circuit current (J_{sc}), most likely because of hampered stacking of the molecules due to the presence of the pyrrolidinyl groups.

![Scheme 10](image)

**Scheme 10**
For an easy overview, the characteristic values of the aforementioned bulk heterojunction solar cells are collected in Table 1. For comparison, other types of cells are also listed. The highest power conversion efficiency for perylene-based solar cells (2.5%) was reported for a device based on a multiple bilayer architecture of copper phthalocyanine (CuPc) and perylene bisbenzimidazole 42 with Ag interlayers,\textsuperscript{[204]} a perfection of the single bilayer device as reported by Tang et al. with a power conversion efficiency of 1\%\textsuperscript{[205]} The active layer in these devices, however, was not prepared by simple spin-coating as in the case of the previous examples but by thermal vacuum evaporation yielding crystalline films. A bilayer device comprising thermally evaporated 42 and spin-coated poly(p-phenylene vinylene) M3EH-PPV provided a power conversion energy of 0.71\%.\textsuperscript{[206]} The highest power conversion efficiency for bulk heterojunction solar cells is based on an active layer of the fullerene derivative [6,6]-phenyl-C61-butyric acid methylester (PCBM) and P3HT, yielding power conversion energies approaching 5\%.\textsuperscript{[207-209]}

\begin{table}[h]
\centering
\begin{tabular}{|l|l|l|l|l|l|l|}
\hline
Acceptor & Donor & Ratio pery:donor (wt\%) & EQE (%) & Monochromatic power efficiency (%) & Power efficiency AM 1.5,\%a & Reference \\
\hline
24 & HBC & 60:40 & 34 (490 nm) & 1.95 (490 nm) & - & 38 \\
24 & P3HT & 80:20 & 7 (495 nm) & 0.45 (540 nm) & - & 68 \\
36 & Poly(2,7-carbazole) & 80:20 & 16 (490) & 3.2 (490 nm) & 0.63 & 67 \\
38 & P3HT & 80:20 & - & - & 0.139 & 68 \\
39 & Poly(2,7-carbazole) & 50:50 & 19 (490 nm) & - & 0.182 b & 68 \\
40 & P3HT & 50:50 & 2 (500 nm) & - & 0.061 & 68 \\
41 & P3HT & 50:50 & - & - & 0.004 & 68 \\
42 & CuPc & 2 bilayers & - & - & 2.5 & 69 \\
42 & M3EH-PPV & bilayer & 18 & - & 0.71 c & 71 \\
PCBM & P3HT & ~50:50 & - & - & 5 & 72–74 \\
\hline
\end{tabular}
\caption{Solar cell efficiencies for some of the best PBI-containing photovoltaic cells; for comparison the performance of one of the best organic solar cells, a PCBM-P3HT cell, is shown as well.}
\end{table}

\footnotesize
\textsuperscript{a} simulated solar light with 100 mW cm\textsuperscript{-2} illumination \\
\textsuperscript{b} annealed samples \\
\textsuperscript{c} 80 mW cm\textsuperscript{-2} white light

Previous research from our group has involved the use polyisocyanides to order chromophores such as thiophenes, porphyrins, and perylene bisimides (see Chapter 2). These ordered structures are of great interest for application in, for example, organic solar cells and FETs, since the well ordered array of chromophores might facilitate efficient energy and electron transport. De Witte et al. have reported the PBI functionalized polyisocyanides 43 (Scheme 11).\textsuperscript{[132, 133]} UV-Vis and CD spectroscopy revealed that the chromophores were excitonically coupled in a helical fashion. Fluorescence spectroscopy showed a broad structureless red shifted emission at 620nm, with a fluorescence lifetime of 19.9 ns. The fluorescence observations, together with the fact that not such a large shift was present in the absorption spectrum when compared to the monomer spectrum, pointed to the generation of an intramolecular excimer-like species. Infrared spectroscopy revealed the presence of hydrogen bonding interactions between every first and fifth monomer unit, as in poly(isocyanoo-L-alanayl-D-alanine methyl ester) (L,D-PIAA) (see
Chapter 3

The polymer strands could be visualized with AFM. By combining AFM and confocal fluorescence microscopy, two different species were recognized: (i) species not visible by AFM that gave a monomer-like fluorescence. These were ascribed to oligomers lacking a tight packing of the chromophores; and (ii) polymer fibers, as visualized by AFM, displaying an excimer-like emission due to the tight face-to-face packing of the chromophores.

These polymers were thought to be interesting candidates as n-type material in photovoltaic cells, however, the solubility of the material was too low to apply them as such. Furthermore, the high organization of the perylenes would also make it of interest to study the material as a FET on the single molecule level or in the bulk. Chapter 4 describes the synthesis of two variations of 43, which both have increased solubility namely, polymer 44 with longer alkyl tails on the periphery and polymer 45 with phenoxy substituents in the bay area of the perylene (Scheme 11). The bulkiness of the non-planar PBIs in the latter polymer was expected to decrease the excimer formation, which might be of interest since excimer formation may be unfavorable for exciton transport if the excimer-like species is formed as a separated dimer within the PBI array. In this case, the excimer site might act as an energy trap where energy is lost in the form of fluorescence. The PBI in 45 is a less efficient acceptor compared to that in 44 due to the electron donating phenoxy groups. It is of interest to study this effect in connection with the performance of 44 and 45 as materials in photovoltaic cells (see Appendix 2).

\[ \text{Scheme 11} \]
Chapter 4

Synthesis and characterization of PBI-functionalized polyisocyanides

This chapter describes the synthesis and characterization of perylene tetracarboxylic acid bisimide (perylene bisimide, PBI) functionalized polyisocyanides, in particular polymers 2 and 3 (Scheme 1). As explained in Chapter 3, previous work on polymer 1 showed that these type of polymers have interesting photophysical properties and are possibly interesting for optoelectronic applications, such as photovoltaics (see also Chapter 5 and 6).

Scheme 1

4.1 Synthesis

4.1.1 Synthesis of polymer 2

Perylene bisimide functionalized polymer 2 was synthesized following the strategy previously described for the synthesis of polymer 1\[^{133, 210}\] with some minor modifications (Scheme 2). Hexyl-heptyl amine was reacted with perylene di-anhydride 4 to give the symmetrically substituted perylene diimide 5, which, after partial hydrolysis with potassium hydroxide in tert-butanol, yielded perylene mono-anhydride 6. Compound 6 was subsequently functionalized with a tert-butyloxy carbonyl (Boc)-protected amine by reaction with mono-Boc 1,3-diaminopropane. The protected amine 7a was converted into the free amine 8 by removal of the Boc-group with an excess of trifluoroacetic acid (TFA).

Alternatively, 7a could be prepared directly from 4 by the reaction of dianhydride with a 1:1 mixture of 1-hexylheptyl amine and N-Boc-1,3-diaminopropane in a mixture of DMF and imidazole at 95 °C. Imidazole increases the solubility of the dianhydride 4 and hence the rate of the reaction. Using this procedure compound 7a was obtained as a statistical mixture with the two symmetrically substituted perylenes 7b and 7c (Scheme 3A). This mixture was then treated with a solution of TFA in dichloromethane to remove the Boc groups. After deprotection the products were easily separated by column chromatography to give 8 in an overall yield of 4.3% with respect to starting material 4. The yield of the reaction is low, however, during work-up, it was evident that starting material was still present. Therefore the reaction can probably be
optimized by an increase in the reaction time and temperature. This strategy then might provide a quick route for the synthesis of 8 from 4 with reasonable yield.

In the next step, amine 8 was coupled to Boc-L-alanine with the use of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) and hydroxybenzotriazole (HOBT) as coupling reagents to give 9. After removal of the Boc-protective group, amine 10 was formylated using 4-nitrophenyl formate. Dehydration of the resulting formamide 11 with diphosgene and N-methylmorpholine (NMM) resulted in the formation of isocyanide 12.

By using different ratios of either nickel (II) perchlorate or the nickel initiator complex 13 (Scheme 3B) isocyanide 12 was polymerized (for ratios see Table 1). The nickel complex (13) was synthesized by the addition of azidopropylamine to Ni(C=N-tBu)4(ClO4)2 in dichloromethane. Upon addition the reaction mixture changed from yellow to red and after five minutes faded back to yellow. After work-up, compound 13 was obtained in quantitative yield. Similar to what has previously been reported for other nickel complexes, 1H NMR spectroscopy revealed that 13 was present in three different conformations with two in greater quantity (see Section 4.6.2). Infrared spectroscopy revealed the carbene like structure of the species (N-C=N stretching vibration at v=1585 and 1542 cm⁻¹), while the C=N stretching frequency at v=2254 cm⁻¹ for Ni(C=N-tBu)4(ClO4)2 had moved to v=2227 cm⁻¹ with a tail to higher wavenumber due to the asymmetry of the complex.[26, 211-213]

The polymerization reaction of the isocyanide with nickel (II) perchlorate most likely is initiated by water or ethanol (R₁=-OH or -OEt),[16, 213] which are the two nucleophiles present under the reaction conditions. Termination most likely happens upon addition of a free proton from the solvent to the growing polymer chain.
Synthesis and characterization of PBI functionalized polyisocyanides

Scheme 2: Synthesis of PBI functionalized polyisocyanide 2. (a) 1-hexylheptyl amine, DMF / imidazole, 110 °C; (b) KOH, tert-butanol; (c) 1-hexylheptyl amine and mono-Boc-1,3-diaminopropane (1:1), DMF / imidazole, 95 °C; (d) mono Boc-1,3 diaminopropane, DMF, 90 °C; (e) TFA, CH$_2$Cl$_2$; (f) Boc-1-alamine, EDC, HOBt, DIPEA, CH$_2$Cl$_2$; (g) TFA, CH$_2$Cl$_2$; (h) 4-nitrophenyl formate, CH$_2$Cl$_2$; (i) diphosgene, NMM, CH$_2$Cl$_2$, -30 °C; (j) Ni(ClO$_4$)$_2$ in EtOH-CH$_2$Cl$_2$ (2:98 v:v) or 13 in CH$_2$Cl$_2$.

In the case of nickel complex 13, initiation of a tert-butyl isocyanide monomer by 3-azidopropylamine has already taken place. Propagation occurs by the feeding of the complex with isocyanide 12; no incorporation of the other tert-butylisocyanides attached to the nickel occurs because the rate of polymerization of this monomer is slower as a result of the bulky tert-butyl group.\cite{26, 212}

By using 3-azidopropylamine as initiator, the polymer will become end-functionalized with an azide-group (R$_1$=-C(N-tBu)-NH-(CH$_2$)$_3$-N$_3$). It was impossible to conclusively prove that the azide group was connected to the polymer, although there are strong indications that this indeed is the case (see Appendix 3). This azide offers a reaction site for modification of the polymer terminus with a functionality such as a second polyisocyanide block or other functional groups. A possible reaction utilizing the azide is the copper catalyzed Huisgen [3 + 2] cycloaddition with an acetylene, also known as the “click-reaction”.

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Upon polymerization of isocyanide 12 the reaction mixture turned slightly darker. Diluted samples at concentrations for absorption experiments (~10^-6 M) taken during the course of the polymerization reaction turned from yellow to red (see cover). This color change is indicative of PBIs aggregating and, in this particular case confirms the intermolecular stacking of the PBIs on polymerization. Polymerizations with 1/500 and 1/1000 equivalents of catalyst took circa 60 minutes. At the same monomer concentration, the polymerization with 1/10,000 equivalents of catalyst took 2–3 days. The polymers were purified by repetitive precipitation, first with methanol / water and then with methanol, until no monomer fluorescence was visible (see Section 4.6.2). In contrast to the poor solubility of 1, polymers of 2 obtained from the reaction with catalyst ratios of 1/500 and 1/1000 were well soluble (at least 10 mg·mL^-1) in chlorinated solvents (CH₂Cl₂, CHCl₃, dichloroethane, and tetrachloroethane) and solvents such as benzene, toluene, and THF. The polymers from the reaction with catalyst ratios of 1/10,000 were well soluble in the reaction mixture when formed, but it was impossible to completely redissolve them after workup. Analysis by gel permeation chromatography (GPC, Figure 1) gave an indication of the relative sizes of the polymers formed under the different polymerization conditions; the lengths of the shorter polymers were also determined by AFM (see Section 4.4.1 for more details). The polymerizations prepared by the lower catalyst ratios showed shorter elution times demonstrating that indeed longer polymers had been formed. The GPC traces of these longer polymers, however, revealed a bimodal molecular weight distribution. This might indicate that two different polymerization mechanisms are active, possibly involving two different catalytic species (e.g., Ni(I) and Ni(II); Chapter 2). For the polymerization carried out by 1/500 equivalents of Ni(ClO₄)₂ a shoulder at shorter elution times was visible. The polymerization reaction with 1/1000 equivalent of catalyst 13 was the only sample in which a clear unimodal distribution was observed. According to GPC and AFM, the polymers formed from the reaction with Ni(ClO₄)₂ (1/500) were of higher molecular weight than those formed by catalyst 13 (1/1000). It has been previously observed that initiation through initiated nickel complexes, such as 13, is more efficient than in the case where Ni(ClO₄)₂ is used. The efficient initiation results in lower molecular weights and narrower weight distributions. In addition, the polymerization with Ni(ClO₄)₂ as the catalyst is less well-defined as the exact identity of the initiating species is not known. (e.g., H₂O, EtOH, vide infra) and more polymerization routes are therefore possible. This is possibly the reason for the observed bimodal distribution.
Table 1: Catalyst ratios, GPC maxima, and molecular weight data obtained by length analysis using atomic force microscopy (AFM).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>equivalents catalyst</th>
<th>GPC maxima</th>
<th>AFM average length</th>
</tr>
</thead>
<tbody>
<tr>
<td>a Ni(ClO₄)₂</td>
<td>1/500</td>
<td>6m15s; tail 5m46s</td>
<td>261 nm</td>
</tr>
<tr>
<td>b Ni(ClO₄)₃</td>
<td>1/10.000</td>
<td>6m7s; 5m20s</td>
<td>(up to 2 μm)</td>
</tr>
<tr>
<td>c 13</td>
<td>1/1000</td>
<td>6m19s</td>
<td>180 nm</td>
</tr>
<tr>
<td>d 13</td>
<td>1/10.000</td>
<td>5m58s; 5m30s</td>
<td>(up to 2 μm)</td>
</tr>
</tbody>
</table>

Figure 1: GPC traces of polymer 2 prepared using Ni(ClO₄)₂ / monomer ratios of a) 1/500 and b) 1/10.000 Ni(ClO₄)₂; idem using 13 / monomer ratios of c) 1/1000 and d) 1/10.000 catalyst 13 (bottom).

Attempts to polymerize 12 with TFA as the initiator, as performed for L-alanyl-D-alanine derived isocyanides, were unsuccessful.[¹,²]

4.1.2 Attempted synthesis of PBI functionalized polyisocyanides with longer peptide side chains.

Polyisocyanides with longer peptide sequences can be expected to have stronger hydrogen bonding networks in their side chains, which in turn will increase the stability of the polymer backbones. It may also allow polymerization with acid (TFA) instead of nickel, for example when an L-alanyl-D-alanine fragment is used as part of the peptide side chain.[²] Polymerization by acid is of great interest since it may give polymers of micrometer length.

In peptide synthesis the peptide chain is usually built up by the coupling of amino acids to the amino side of the growing peptide chain and not to the acid side. Coupling to the acid side will lead to racemization of the amino acid unit on the acid terminus, when activated by a coupling reagent (Scheme 4).[²¹⁵,²¹⁶] In the synthesis of polyisocyanides with a functional group (F) on the outside, this means that the synthesis has to start with group F, to which amino acids can be coupled step by step (Scheme 4, route(1)).
Chapter 4

Scheme 4: The two routes to build up a peptide chain containing functional group F. In route (1), F is first attached to an amino acid, which subsequently reacts with a second amino-protected amino acid. In this way the chiral centers will not undergo racemization. In route (2), two amino acids are first coupled together and F is subsequently attached. This route will lead to racemization of the carbon to which R2 is attached since the acid in the reaction is an N-acyl amino acid. (Note: in route 1 the Boc-protected amino acid is not N-acylated but forming a carbamate).

In many cases, however, it would be much more favorable to first build up the peptide part and in the last step attach the functional group F (Scheme 4, route (2)). With the latter approach the functional group is not involved in every step of the synthesis, which is favorable with respect to the overall reaction yield concerning functional group F. In addition, the synthesis is more versatile since it can be applied to many different functional groups.

Scheme 5: Synthesis of Boc-D-alanyl-L-alanyl-glycine. (a) EDC, HOBut, DIPEA, DMF / EtOAc; (b) HCl / EtOAc; (c) Boc-D-alanine, EDC, HOBut, DIPEA, DMF / EtOAc; (d) 4 M NaOH, MeOH, 1,4-dioxane (1:5:14 v:v:v).

The problem of racemization in route 2 can be circumvented by using the achiral amino acid glycine as the molecular building block to which F is attached. Following the above rational, the peptide chain Boc-D-alanyl-L-alanyl-glycine was synthesized (Scheme 5). Glycine methyl ester was coupled to Boc-L-alanine using EDC as the coupling reagent. After removal of the Boc group, Boc-D-alanine was coupled to the dipeptide to give Boc-D-alanyl-L-alanyl-glycine methyl ester as the product. Hydrolysis of this compound with sodium hydroxide in methanol / dioxane yielded Boc-D-alanyl-L-alanyl-glycine. This tripeptide was subsequently coupled to amine 8 to yield compound 14 (Scheme 6). Analogous to the synthesis of 2, the amine of 14 was deprotected with TFA and subsequently formylated with 4-nitrophenyl formate to yield 15. Reaction of 15 with diphosgene and NMM in CH₂Cl₂, CHCl₃, or
Synthesis and characterization of PBI functionalized polyisocyanides

Acetonitrile at different temperatures varying between –30 °C and 30 °C did not result in the formation of isocyanide 16 but in complete recovery of the starting material.

\[
\text{Scheme 6: Attempted synthesis of 16. (a) Boc-D-alanine-L-alanine-glycine, DIPEA, HOBt, EDC; (b) TFA, CH}_2\text{Cl}_2; (c) 4-nitrophenyl formate, CH}_2\text{Cl}_2; (d1) diphosgene, N-methylmorpholine, various conditions; (d2) Burgess reagent, various conditions.}
\]

The failure of this reaction was attributed to the low solubility of 15 in the mentioned solvents. An alternative method to the formation of isocyanides is the reaction with methyl N-(triethylammoniumsulphonyl)-carbamate, also known as the Burgess reagent. This reagent is a known dehydration reagent for formamides and the mechanism of reaction is depicted in Scheme 7.[217, 218] The advantage of this reagent is that it is reactive in solvents such as DMF and at higher temperatures. Unfortunately, the reaction of 15 with the Burgess reagent in either refluxing CH}_2\text{Cl}_2 or in DMF at 70 °C did not give any conversion of the starting material, although under the applied reaction conditions 15 was completely soluble.

\[
\text{Scheme 7: Mechanism of the action of the Burgess reagent in the dehydration of a formamide.}
\]

The low solubility of 15 in aforementioned solvents is most likely due to the presence of the strong intermolecular interactions caused by hydrogen bonding between the four amide units present in formamide 15 combined with the \( \pi-\pi \) stacking ability of the large aromatic perylene plane. Evidence for this was found in the infrared spectrum of solid 15, which revealed an N-H vibration at \( v=3284 \text{ cm}^{-1} \), which is typical for strong hydrogen bonded amides. This is in contrast to the N-H vibration present at \( v=3351 \text{ cm}^{-1} \) in formamide 11. It is likely that the reaction of 15 to 16 cannot take place due to the presence of intramolecular hydrogen bonds between the amide
groups, which prevent the formamide to perform a nucleophilic attack on the diphosgene. It was therefore concluded that although incorporation of more amino acids into the side chain of the polyisocyanide might look favorable for the stability of the polymer chain, it also makes the synthesis very difficult or even impossible for solubility reasons.

4.1.3 Synthesis of polymer 3

Analogous to the synthetic route from amine 8 to polymer 2, polymer 3 was prepared from amine 17 (Scheme 8). Amine 17 was coupled to Boc-L-alanine to give 18. After deprotection and subsequent formylation 19 was subjected to dehydration by diphosgene to give 20. Polymerization was performed with 1/1000 equivalents of catalyst 13, as this gave the best result for the polymerization of PBI 12 according to GPC. In contrast to the 20 minutes needed to polymerize 12, it took seven days before monomer 17 was completely consumed. This slow polymerization can be ascribed to the bulkiness of the PBI and is in line with to the slow polymerization reported for tert-butyl isocyanide. During the polymerization of 20 the reaction mixture turned slightly darker (from purple to deep purple), but the color change was not as clear as in the preparation of 2. Besides the polymer, a small amount of side products was formed. Because of the small scale of the reaction, the side products were not characterized, but according to TLC one of them was most likely formamide 19.

Scheme 8: Synthesis of PBI functionalized polyisocyanide 3. (a) Boc-L-alanine, EDC, HOBT, DIPEA, CH$_2$Cl$_2$; (b) TFA, CH$_2$Cl$_2$; (c) 4-nitrophenyl formate, CH$_2$Cl$_2$; (d) diphosgene, NMM, CH$_2$Cl$_2$; 30 °C; (e) Ni(ClO$_4$)$_2$ in EtOH / CH$_2$Cl$_2$ (2:98 v:v) or 13 in CH$_2$Cl$_2$. 

Polymer 3 was separated from monomeric starting material and catalyst by size exclusion chromatography (BioBeads). A fraction was collected that gave two spots on TLC (silica); a small baseline spot and a stretched band with an $r_f$ value of 0.4. Since both compounds eluted as one fraction from the size exclusion column, both seemed to be of high molecular weight. To determine whether the two fractions had a different degree of polymerization (i.e., consisted of
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(oligomers and polymers), a small amount of the band from rf of 0.4 was isolated by preparative thin layer chromatography and analyzed by AFM. This technique, however, showed no discrimination between the isolated fraction and the unfractionated sample (vide infra). Some of the material probably remained on the baseline due to partial physisorption as is more often observed for polymers. Figure 2 shows the GPC trace of polymer 3 (black) together with that of polymer 2, polymerized with 1/1000 of catalyst 13, and formamide 19 for comparison. A multimodal distribution for polymer 3 is visible with a low molecular weight fraction at an elution time of ~10 minutes and a high molecular weight fraction at an elution time of ~6 minutes, even earlier than the elution of polymer 2. From the analysis of AFM images of 3 (see Section 4.4.1), an average molecular weight of 1.1 million Dalton (length 110 nm) was determined, whereas for polymer 2 the molecular weight was determined to be 1.2 million Dalton (length 180 nm). The elution times for polymers 2 and 3 therefore seem not to be comparable; the elution behavior of a rod-like polymer in a gel is not very straightforward (see Chapter 7), and the different chemical composition might also have an influence on the elution time. Polymer 3 appeared to be well soluble in chlorinated solvents and in solvents such as toluene and THF. Its solubility was even better than the solubility of 2, which might be attributed to the different PBI substituents, but also to the shorter polymer length (vide infra).

![Figure 2: GPC traces of polymer 3(—), polymer 2 (—), and PBI 19 (—).](image)

### 4.2 Spectroscopic Characterization

#### 4.2.1 NMR spectroscopy

Compared to monomer 12, the $^1$H NMR spectrum of polymer 2 revealed broadened peaks for all protons (Figure 3A and B) as is characteristic for polymers. The aromatic perylene signals were extremely broadened and hardly visible except for a signal at $\delta=8.70$ ppm, which is shifted downfield by circa 0.1 ppm compared to the monomer. This shift can be expected when these protons are in the deshielding zone of a neighbouring perylene core.

In the $^1$H NMR spectrum of polymer 3 (Figure 3C and D) broadened peaks were also visible. The broadened aromatic protons signals were clearly shifted upfield by circa 0.2 ppm compared

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$^{ii}$ Molecular weights were calculated from the average polymer length, assuming an increase of 4.2 Å in length per four monomer units (Chapter 2).
to monomer 20 as a result of the above mentioned shielding effect. A similar upfield shift was observed for the aliphatic protons between δ=1.8 and 0.8 ppm.

For both polymers it can be concluded that the PBIs in the polymer are in close vicinity to the protons in the polymer repeat units. Since the effect in polymer 3 is different from that in 2, a somewhat different organization of the PBIs in the two polymers is likely.

4.2.2 Infrared spectroscopy
In order to obtain more structural information on polymer 2, the polymerization of 12 (c = 14 mM) by catalyst 13 (ratio 1/740) was followed in time by IR spectroscopy. This experiment confirmed that the reaction proceeds very fast compared to the polymerization of, for example, isocyanopeptides.[221] The low nickel concentration was needed in order to be able to follow the reaction at all. The graphs in the upper panels of Figures 4a and 4b show the spectra of the reaction mixture after 0, 75, 525, and 1005 seconds. In the lower panels the difference spectra between the reaction after 1005 seconds (polymer) and 75 seconds (monomer) are shown. Positive peaks in the lower graphs represent resonances that disappeared or decreased upon polymerization, whereas negative peaks correspond to resonances that appeared or are amplified in the polymer. Most characteristic for the polymerization reaction is the disappearance of the isocyanide peak at ν=2140 cm⁻¹ and from this signal it was concluded that the reaction was completely finished after 1005 seconds. Between ν=1700 and 1550 cm⁻¹ the vibrations of the polyisocyanoolanine backbone are present, which are partly masked by the perylene C=O stretch absorptions (ν=1695 and 1654 cm⁻¹) and the C=C ring stretch absorptions (ν=1596 and 1581 cm⁻¹).
Figure 4: Changes in infrared absorption signals during polymerization of PBI 12 in CH₂Cl₂ (from light grey to black curves): a) between ν=3500 and 1300 cm⁻¹ and b) between ν=880 and 600 cm⁻¹. The top panels in a) and b) show the changes during the polymerization reaction, the bottom panels the difference spectra between 1005 and 75 seconds.

In the difference spectrum a small increase at circa ν=1625 cm⁻¹ is observed, which might be assigned to the increasing number of imine functions in the polyisocyanide backbone. In the region ν=3500–3100 cm⁻¹, three peaks can be distinguished for monomer 12. The two vibrations at ν=3438 and 3391 cm⁻¹ correspond to the trans and cis amide N-H stretch vibrations, respectively. The low intensity vibration at ν=3307 cm⁻¹ most likely stems from stacked amides in the trans configuration. Upon polymerization the absorptions at ν=3438 and 3391 cm⁻¹ shift to ν=3294 cm⁻¹ indicative of hydrogen bond formation of the amides exclusively in the trans configuration. For the other amide absorptions changes are also observed during the polymerization reaction. An intensity decrease at ν=1686 cm⁻¹ and an intensity increase at
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The polymerization of polymer 3 was too slow to be followed by IR spectroscopy in a controlled manner. The IR spectrum of polymer 3, compared to that of PBI 19 in the solid state, however, revealed changes characteristic of hydrogen bonding between the amides. Most apparent was the change in absorption from $\nu=3376 \text{ cm}^{-1}$ for PBI 19 to $\nu=3308 \text{ cm}^{-1}$ for polymer 3 (Figure 5).

4.2.3 UV-Vis and CD spectroscopy

The UV-Vis spectroscopic features of polymer 2 were found to be similar to those observed for polymer 1. The absorption spectrum of 2 in chloroform, between $\lambda=400$ and 600 nm exhibited the vibronic bands of the PBI $S_0-S_1$ oscillation (Figure 6A, top). Compared with the spectrum of monomer 11, the absorption spectrum of polymer 2 revealed a blue shifted maximum due to a relatively increased oscillation strength of the 0-1 and 0-2 vibrational transitions compared to the 0-0 transition; this can be quantified by the ratio of the absorptions $A_0^{1,0} / A_0^{0,1}$, which was 1.66 for the monomer and 0.66 for the polymer.
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Figure 6: A) Absorption (top) and CD spectrum (bottom) and B) fluorescence spectrum (c=10^-7 M) of polymer 2 (intensity fluorescence ×5, black) and PBI 11 (grey).

In addition, the maxima of all vibronic bands are red shifted by 2–6 nm and a broad absorption tail develops at an energy lower than that of the 0-0 transition of monomer 11. These spectral changes upon polymerization are reminiscent for weak exciton coupling (strong exciton-phonon coupling) between the PBIs in H-type aggregates. Polyisocyanides are known to adopt a 41 helical structure in which dipole-dipole interactions between the nth and the (n+4)th units (e.g., C1-5), dominate (Figure 7). In such weakly coupled aggregates, excited states are grouped into vibronic bands that correspond to the single molecule vibronic lines (0-0, 0-1, etc) in the case of vanishingly small electronic interactions. Of particular interest is the relative intensity of the A°/°° band; the intensity of this band diminishes with increasing exciton bandwidth and is thus a useful measure of the electronic coupling.

The formation of exciton states that result from intermolecular interactions leads to broader spectral features in polymer 2 compared to monomer 11. The loss of oscillator strength in the A°/°° band (and simultaneous increase in higher energy bands) is primarily due to the interband coupling between the zero-order vibronic excitons in the A°/°° band with the zero-order vibronic excitons in the higher energy bands (A°/°1, A°/°2, etc.), mediated by excitonic interactions. Such interactions lead to a decrease in the A°/°° / A°/°1 ratio as well as a slightly increased spectral separation between the 0-0 and 0-1 absorption peaks. The demise of the A°/°° / A°/°1 ratio is a precursor to the more conventional blue-shifted, main absorption peak characteristic of H-aggregates with much stronger excitonic coupling (see Appendix 4 for a worked out dimer case). The rigid red shift of the whole spectrum upon going from monomer 11 to polymer 2 is likely due to a gastocrystal shift induced by aggregation (though it is possible that the weak C1-2 (Figure 7) interactions also contribute to a small red shift).

A detailed analysis of the absorption spectrum of polymer 2 is provided in the modeling section of Chapter 5.
The CD spectrum of 2 reveals strong positive and weaker negative signals for the exciton coupled S₀-S₁ vibronic transitions between λ=420 and 600 nm, whereas no CD signal is detected for the monomer. This signal is indicative of a chiral orientation of the PBIs, induced by the L-alanyl unit in the polymer backbone, similar to what has been observed for the same polymer backbone with other chromophores. The CD effect is unlike any other signals observed for chiral perylene bisimides stacks. This can be rationalized by considering the multiple chiral interactions in which every perylene bisimide unit is involved, that is, every unit has chiral interactions with neighboring units within the same stack (C₁-5) and with units in neighboring stacks (C₁-2). Both interactions contribute to the observed CD signal as was already shown before for porphyrin functionalized polyisocyanides.

The signal that arises from interactions between the PBIs at positions n and n+1 (e.g., C₁-2) can be expected to be located at a higher wavelength and reflects the helicity of the polymer backbone, whereas the signal for the interaction between PBIs at positions n and n+4 (e.g., C₁-5) originates from the helicity of the S₀-S₁ transitions within the PBI stacks. The positive signal at higher wavelength, most likely originating from a positive bisignate signal, would correspond to a right handed polymer helix. This is in agreement with the smaller positive Cotton effect at λ=317 nm that originates from the helicity in the polyimine backbone. The latter signal is similar to that observed for right handed helices in poly(isocyano-L-alanyl-D-alanine methyl ester)s (L,D-PIAAs) and reflects the robustness of the isocyano L-alanyl backbone as it is uninfluenced by the outer PBI substituents. In addition, the negative CD signal at low wavelengths is likely to originate from a positive bisignate signal, also suggesting a right-handed helicity within the PBI stacks (e.g., C₁-5). This conclusion implicates that the polymer helix contains a little less than 4 units per helical turn.

Compared to monomer 11, the fluorescence spectrum of polymer 2 showed a broad structureless and red-shifted emission at λ=608 nm (Figure 6B) characterized by a fluorescence quantum yield of 3.7% (in air, excitation at the absorption maximum, λ=492 nm). The fluorescence lifetime was determined to be 24.5 ns, whereas that of monomeric perylene species is in the order of 3–4 ns (see chapter 5). The long fluorescence lifetime and the low quantum yield of the emission indicate a parallel orientation of the PBI transition dipoles, in agreement with the conclusions from the absorption spectra.

The featureless red-shifted emission of more than 70 nm in the polymer, together with the fact that the shift in the emission spectrum is much larger than the shift in the absorption spectrum,
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are indicative of the formation of an intramolecular excimer-like species. An excimer is a complex of identical molecules in which the interaction is repulsive in the ground state, but attractive in the excited state. Excimer species are formed only after excitation of monomeric species and therefore the emission, but not the absorption, is red-shifted. The chromophores in an excimer are typically 0.3–0.4 nm apart\textsuperscript{[235]} and can involve more than two chromophoric units in molecular aggregates.\textsuperscript{[132, 133, 236, 237]} Ground state cofacial stacking is known to promote excimer formation due to the greatly enhanced interaction of the initially localized excited state with the ground state of a nearby molecule.\textsuperscript{[190, 238]} The formation of excimers of aromatic hydrocarbons is restricted to a parallel cofacial configuration and confirms the conclusion that the PBIs stack in an H-aggregated fashion.\textsuperscript{[235]}

In the absorption spectra of 3 and 19, in addition to the S\textsubscript{0}-S\textsubscript{1} transition, also the S\textsubscript{0}-S\textsubscript{2} transition was visible at \( \lambda = 448 \) nm (Figure 8). Similar to the observations for 2 the S\textsubscript{0}-S\textsubscript{1} transitions of 3, compared to monomer 19, revealed relatively increased intensities for the 0-1 and 0-2 oscillations with respect to the 0-0 oscillation; \( A^{0-0}/A^{0-1} \) equaled 1.48 for the monomer and 1.07 for the polymer suggesting (weak) electronic interactions between the chromophores.\textsuperscript{[166, 169, 171]} A blue shift of 4 nm of the absorption maxima was also detected and, in contrast to 2, no red-shifted component was observed for the S\textsubscript{0}-S\textsubscript{1} transitions. For the S\textsubscript{0}-S\textsubscript{2} transition a minute red shift of 2 nm was found.

For 3 the relatively enhanced oscillation strength for the S\textsubscript{0}-S\textsubscript{1} transition in the blue part of the spectrum is similar to observations for PBI dimers\textsuperscript{[189]} and might be indicative of H-aggregation of the PBIs. The absence of a red shifted component, however, is atypical and has not been observed in dimer model systems.\textsuperscript{[189]} Besides excitation coupling, changes in the spectrum might also be caused by conformational changes (see the CD spectrum below) induced by the steric interactions between the bulky PBIs, which makes the interpretation of the absorption spectra more complex.

![Figure 8: A) Absorption (top) and CD spectrum (bottom) and B) fluorescence spectrum (c=10^{-7} M) of polymer 3 (black) and PBI 19 (grey) in CHCl\textsubscript{3}](image)

The CD spectrum of 3 revealed CD signals for the perylene groups that are 30 times smaller in intensity than the CD signal observed for 2. This suggests that the PBIs in the C\textsubscript{1-4} geometry have either a very small twist angle with respect to each other or that this angle fluctuates.
between positive and negative values along the stack. The weak CD effect actually might not originate from exciton coupling, but from induced chirality in the perylene plane; for the phenoxy substituted PBIs an excess of an M or P twist is likely to be induced by the incorporation of the PBIs in the helical polymer backbone (Figure 9). Such an effect has previously been noted for aggregates of similar PBIs for which similar CD effect were observed.\textsuperscript{11581}

A relatively strong signal was found in the CD spectrum of 3 at $\lambda=284$ nm preceded by a broad signal around $\lambda=338$ nm. The signal located at $\lambda=284$ nm was most likely caused by a chiral interaction of the phenoxy substituents, however, the imine backbone signal is also expected in this region. It is therefore difficult to conclude anything on the helical conformation from the CD spectrum in this region.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig9.png}
\caption{Illustration of the P and M chiral conformations of the PBI planes in 3. For clarity the functional groups on the PBI plane are replaced by hydrogens.}
\end{figure}

The fluorescence spectrum of polymer 3 revealed a slightly red-shifted emission at $\lambda=607$ nm compared to $\lambda=605$ nm for the monomer, a value comparable to the shifts in the absorption spectrum. The fluorescence quantum yield of 3 amounted to 3.0\% with respect to the monomer. This low quantum yield is in line with H-aggregated PBIs, however, it can also be attributed to electron transfer between the PBI and neighboring phenoxy substituents. The emission spectra provided no evidence for the excimer formation that was observed for 2, therefore allowing the conclusion that the steric bulk of the phenoxy groups of the PBIs in 3 indeed seem to be able to prevent this formation.

4.3 Stability measurements

4.3.1 Thermal stability of polymer 2

The thermal stability of polymer 2 was investigated by temperature dependent CD spectroscopy and differential scanning calorimetry (DSC) measurements. The CD signal in tetrachloroethane gradually decreased when the temperature was increased from $-10$ °C to 110 °C. This is probably due to increased thermal motion of the perylene bisimide. Reducing the temperature back to $-10$ °C resulted in the initial signal being completely restored, even after five cycles (Figure 10a). The DSC measurement on the solid polymer revealed an endothermic peak at 85 °C in the heating trace with a corresponding exothermic peak at 58 °C in the cooling trace (Figure 10b). Such a transition was not detected in solution with either CD spectroscopy or with DSC and was therefore ascribed to the melting and crystallization, respectively, of the alkyl tails in the periphery of the polymer. No other transitions, except decomposition at 285 °C, could be detected. The polymer seems to be very stable and after one week in tetrachloroethane solution
no changes in the CD spectrum were observed. The fluorescence spectrum, however, revealed a small monomer-like signal (<1.5% monomer), which slowly increased over time. The monomer-like emission might be the result of the unwinding of the helix at its terminal ends or it could be caused by the slow decomposition of the polymers, starting at its terminal, because of reaction of the polyimide backbone with carbene- or radical-like species in solution (especially chloroform, see Chapter 7.4). In the solid state, the polymer is very stable over periods of over two years.

Figure 10: Thermal behavior of polymer 2 measured by a) CD spectroscopy (at 504 nm) and b) DSC. In a) and b) both heating (black) and cooling (gray) curves are depicted.

4.3.2 Conformation of polymer 3 in different solvents

Absorption and CD spectra in dichloromethane-methanol (99:1 v:v), dichloromethane, tetrachloroethane (TCE), and toluene revealed that polymer 3 adopts different conformations in these solvents (Figure 11). The differences in conformation are most clearly visible in the CD spectra. Whereas the spectra in CH$_2$Cl$_2$ and CH$_2$Cl$_2$ / MeOH showed a positive signal around $\lambda$=520 nm, a negative signal, which is red shifted by circa 20 nm, was observed in TCE and toluene. The absorption and fluorescence emission spectra (not shown) remained roughly the same, except for the spectra in TCE, which were red-shifted by circa 8 nm. These observations indicate that the (chiral) conformation of the PBIs is dynamic and most likely involves a change in the twist of the PBI plane. In TCE the interactions between the PBIs seem to be different given the red-shifted absorption and emission spectra. Upon heating the solution in TCE from 20 to 110 °C all absorption, emission, and CD signals decreased and were not restored upon cooling. The signal also slowly decreased in time without any heating, whereas this was not observed for the solution in CH$_2$Cl$_2$. This indicates that the conformation in TCE is thermodynamically unstable. Additional studies are needed to obtain more insight into the exact nature of the dynamic processes involving PBI groups. Polarity of the solvent possibly plays a role and, for the used solvents, increases in the following order: toluene < TCE < CH$_2$Cl$_2$ < CH$_2$Cl$_2$ / MeOH.$^{[239]}$
4.4 Morphological investigations

4.4.1 Atomic Force microscopy

Solutions of 2 in CHCl₃ were spin-coated onto mica and investigated by AFM. For the differently prepared polymers (different catalyst / monomer ratios of Ni(ClO₄)₂ and 13) fiber-like structures were observed with heights of 1.5 ± 0.5 nm (vide infra). The fibers tended to aggregate or cross each other (Figure 12C, black arrows) and in these cases an increased height was observed. Upon dilution, the fiber-like structures kept the same height and it is therefore assumed that these structures are single polymer fibers. As can be seen in Figure 12B and D, lower catalyst ratios lead to longer polymers. In these cases sometimes exceptionally long polymer fibers, over 2 μm, were observed for samples taken from the reaction mixture. It was impossible to redissolve these very long polymers after precipitation. For the smaller fibers, (1/500 and 1/1000 equivalents of catalyst), in addition to the heights, also the lengths were analyzed (see also Section 4.1.1).
Figure 12: AFM images of polymer 2 spin-coated from chloroform onto mica. The polymers were prepared using catalyst / monomer ratios of A) 1/500 Ni(ClO$_4$)$_2$ (4×4 μm), B) 1/10,000 Ni(ClO$_4$)$_2$ (4×4 μm), C) 1/1000 catalyst 13 (6×6 μm), and D) 1/10,000 catalyst 13 (4×4 μm). In image C black arrows indicate aggregated fiber and the white arrows single fibers.

The length and height distributions, determined from the AFM images (Figure 12C), of polymer 2, prepared using a catalyst 13 / monomer ratio of 1/1000, are shown in Figure 13. An average length of 180 ±130 nm and a height of 1.5 ± 0.5 nm were measured. In this evaluation, only single fibers were included (e.g., white arrows in Figure 12C), that is, fibers that showed no steps in height along their contours. Since the polymer fibers of 2 tended to aggregate, only relatively few fibers per image (a total of ca. 100) could be included for the length analysis. The lengths measured by AFM are probably underestimated since longer fibers have a higher probability to aggregate and therefore were not counted. By an analogous method samples of polymer 2, prepared by using a Ni(ClO$_4$)$_2$ / monomer of 1/500, where found to have an average length of 261 nm. Assuming that 2 forms a 4$_1$ helix with a helical pitch similar to that of other isocyanopeptides (4.2 Å),$^{[1]}$ the average lengths of 180 nm and 261 nm correspond to molecular weights of 1.2×10$^6$ and 1.8×10$^6$ Dalton, respectively. The height measured by AFM is usual slightly underestimated for several reasons, which include a strong surface-molecule interaction flattening the polymers on the surface and the indentation of the macromolecules by the AFM tip.$^{[90]}$
In some cases the fibers were found to be aligned in the same direction (Figure 12B and 14, left image), which is attributed to hydrodynamic flow in combination with a low humidity during sample preparation.\textsuperscript{[94]} When the fibers on the surface were exposed to CHCl$_3$ vapor an increase in the aggregation of the polymer molecules was found to occur (Figure 14).

Polymer 2 could also be visualized on highly ordered pyrolytic graphite (HOPG) and glass substrates (Figure 15). On HOPG polymer 2 showed stronger aggregation than on mica and many loops formed by the fibers were observed. Although the glass surface is much rougher than mica or HOPG, it was also possible to visualize the polymer on this substrate. This opens possibilities to study fluorescence and topography at the same time using a combined AFM and confocal microscopy setup.\textsuperscript{[132]}
Figure 15: Polymer 2 spin-coated onto A) HOPG (3×3 µm), B) HOPG (1.4×1.4 µm), and C) glass (1.6×1.6 µm). The polymer was prepared using a catalyst 13/monomer ratio of 1:1000.

AFM images of polymer 3 on mica and HOPG revealed short fibers together with small blobs (Figure 16). On HOPG almost all polymers were found close to a graphite step. Heights and lengths of the fibers were analyzed from the images of 3 on mica (the blobs were excluded from this analysis). The resulting distributions are shown in Figure 17 and give an average length of 109 ± 63 nm and a height of 2.9 ± 0.5 nm for the fibers.

Figure 16: Polymer 3 spin coated onto A) mica (1.7×1.7 µm) and B) HOPG (2.4×2.4 µm)

It should be noted that, in particular for polymer 3, lower height values were measured for a series of AFM measurements on different days, which can be attributed to the influence of humidity.\textsuperscript{[90]} Under ambient conditions the substrate mica is covered by a layer of water molecules of which the thickness is dependent on the humidity. When the mica substrate is more hydrophilic than the absorbed molecules, the latter will appear lower in the AFM images because of a thicker layer of water on the mica than on the adsorbates.
Figure 17: Distributions of analyzed lengths (A) and heights (B) of single polymer fibers of 3 on mica as observed by AFM.

The blobs that are observed in the AFM images of 3 are possibly oligomers and this finding corresponds well with the low molecular weight fraction observed by GPC. The observed height of polymer 3 is almost double the height of 2. A higher height can be expected for 3 because of the presence of the butyl spacer in 3 instead of a propyl spacer in 2 and because of the more rigid terminal 2,6-diisopropylphenyl group in 3 compared with the 1-hexyl-heptyl group in 2. This, however, cannot account for the observed difference of 1.5 nm. Another explanation may be found in the different orientation of the PBI groups in the side arms. Whereas the PBIs in 2 are likely to make an angle smaller than 90 degree with the polymer backbone (pine tree-like, see chapter 6), the PBIs in 3 can be expected to be more perpendicular to the polymer axis because of their steric bulk. The latter orientation will result in a higher diameter of the polymer. Differences in hydrophilicity of the two polymers might also play a role in the height as observed by AFM. The relatively short average length of the polymer of 3 (especially when the blobs would be included in the length determination) compared with 2 can be attributed to the slower polymer reaction in the former case, which leaves more room for termination reactions.

4.4.2 Light scattering

Lengths and diameters of polymer 2, prepared using a catalyst 13 / monomer ratio of 1/1000, were also determined in solution by a combination of elastic and quasi-elastic light scattering measurements.[240, 241]

The quasi elastic light scattering data (Figure 18) were fitted to the theoretical model of Maeda and Fujime, which allows the calculation of the polymer length and the rotational diffusion coefficient from the polarized correlation function in cases where these parameters cannot be measured directly from the depolarized correlation function.[240] The model assumes that the first cumulant of the polarized correlation function for a rod can be expressed by the following equation:

\[
\frac{\Gamma_v}{Q^2} = D - \frac{1}{3} \cdot (D_\parallel - D_\perp) + \frac{L^2}{12} \cdot \Theta \cdot f_1(QL) + (D_\parallel - D_\perp) \cdot f_2(QL)
\]

iii The described measurements were performed by Maria Angela Castriciano at Istituto per lo Studio dei Materiali Nanostruttrati ISMN-CNR, Messina, Italy.
where \( D = \frac{1}{3} \cdot (D_\parallel + 2D_\perp) \) (\( D_\parallel \) is the component of the diffusion coefficient in the direction parallel to the long axis of the rod and \( D_\perp \) the orthogonal component), \( L \) is the length of the rod, \( \Theta \) the rotational diffusion coefficient, and \( f_1(QL) \) and \( f_2(QL) \) are two tabulated functions.

**Figure 18:** Quasi-elastic light scattering data fitted using the Maeda and Fujime model.

The values for \( L \), \( \rho \) (ratio between the cross-section and the length of the rod), and related parameters have been derived accordingly. By using these values, a good agreement between the elastic light scattering experimental data and the model (line in Figure 19) was obtained. The data are in agreement with a rod-like model and give a (weight) average length of 400 nm ± 50 nm and a value of \( \rho = 0.008 \), which corresponds to a diameter of 2.0 nm ± 0.5 nm.

**Figure 19:** Elastic light scattering data (circles) and the fit to a rod-like model (line).

The heights obtained by AFM and the elastic light scattering measurements are in good agreement, with a slightly lower value obtained by AFM as can be expected (see Section 4.4.1). The length obtained by light scattering should be compared to the weight average length obtained from the AFM data, which amounts to 276 nm (with a statistical error \( \sigma \) larger than the value itself). In the case of the length the value obtained by AFM is also smaller than the value obtained by light scattering. This is probably a result of the underestimation of the length by AFM (see Section 4.4.1). Partial aggregation of the polymer fibers in solution could also overestimate the value obtained by light scattering, however, the obtained diameter of 2 nm is
very reasonable and indicates that aggregates do not contribute much to the measured value of the length.

### 4.5 Conclusion

Polyisocyanides 2 and 3, derived from L-alanine with different perylene bisimide (PBI) side groups have been prepared. In both polymers the backbone is stabilized by hydrogen bonding between the amide functions of every \( n^{\text{th}} \) and \((n+4)^{\text{th}}\) monomer unit, as was revealed by infrared spectroscopy. Absorption, CD, and fluorescence spectroscopies conducted on polymer 2 revealed that the PBIs are weakly excitonically coupled (strong exciton-phonon coupling) in a chiral fashion, with the \( n^{\text{th}} \) and \((n+4)^{\text{th}}\) PBIs stacked in an H-aggregated fashion. For polymer 3 interpretation of the photophysical data was more difficult. Absorption and fluorescence spectroscopy also indicated weak exciton coupling between the PBIs, probably in an H-aggregated fashion. The CD signal does not seem to originate from excitonically coupled PBIs, but is more likely the result of a helical shape induced in the prochiral PBI planes of 3. Moreover, the CD signal of 3 varies in different solvents and the signal in tetrachloroethane is lost when the solution is heated to high temperatures. The conformation of polymer 2, in contrast, seems to be very stable when going to higher temperatures. Atomic force microscopy studies on the two polymers adsorbed on surfaces revealed fiber-like structures. Polymer molecules of 3 are relatively short compared to those of 2, which was attributed to the slow polymerization of the bulky monomeric precursor of 3. Light scattering data on 2 could be fitted to a rod-like model and revealed similar dimensions for the polymer as those determined by AFM.

### 4.6 Experimental

#### 4.6.1 General methods and materials

The following solvents were distilled prior to use under atmospheric pressure and under a nitrogen atmosphere. CH\(_2\)Cl\(_2\) and CHCl\(_3\) were distilled from CaH\(_2\) and CaCl\(_2\) respectively, MeOH from Na, and DMF from BaO. \(N\)-methylmorpholine was distilled under reduced pressure. All other chemicals were commercial products and used as obtained, unless stated otherwise. Silica gel (0.035–0.070 mm, pore diameter 6 mm) from Acros was used for column chromatography and silica 60 F\(_{254}\) coated glass plates (Merck) were used for thin layer chromatography. Gel permeation chromatography was performed on a Shimadzu size exclusion chromatographer equipped with a guard column and a styragel®HT-6E (7.8×300 mm, Waters) column with differential refractive index and UV detection using chloroform as an eluent (1 mL-min\(^{-1}\) at 30 °C). \(^1\)H NMR and \(^{13}\)C NMR spectra were recorded on a Bruker DMX-200 MHz, a Bruker AC-300 MHz, or an Inova 400 MHz instrument at room temperature. Chemical shifts (\(\delta\)) are reported in ppm relative to tetramethylsilane (\(\delta = 0.00\) ppm). The following measurements were recorded at room temperature unless stated otherwise: FT-infrared spectra on a ThermoMattson IR300 spectrometer equipped with a Harrick ATR unit (the compounds were measured as a solid), UV-Vis spectra on a Varian Cary 50 spectrometer, fluorescence spectra on a Perkin Elmer Luminescence spectrometer LS50B, and CD spectra on a Jasco J600 CD spectrometer equipped with a Peltier temperature control unit. The infrared spectra on
solutions were measured on a Bruker Tensor 27 in a fluid cell of NaBr. Differential Scanning Calorimetry (DSC) measurements were performed on a Perkin Elmer Pyris Diamond DSC at a scanning rate of 5 °C min⁻¹. An empty high purity aluminum pan was used in the reference furnace in all DSC measurements and the base line correction curve determined with empty furnaces was subtracted from all thermograms. FAB mass spectra were recorded on a VG-7070E mass spectrometer with 3-nitrobenzyl alcohol as matrix. MALDI-TOF spectra were measured on a Bruker Biflex III spectrometer, with dithranol as matrix. High resolution ESI mass spectra (HR-MS) were recorded on a JEOL AccuTOF spectrometer with polyethylene glycol as an internal reference. The sprayed solutions for the HR-MS spectra of the perylene bisimide compounds were prepared by dissolving ~1 mg PBI in 50-100 µl CH₂Cl₂ and subsequently diluting this solution to 1 mL MeOH.

\[N,N'-\text{Bis}(1\text{-hexylheptyl})-3,4:9,10\text{-perylenedicarboximide (5)}, \text{[242]}\]
\[N-(1\text{-hexylheptyl})\text{perylene-3,4:9,10-tetracaboxylic-3,4-anhydride-9,10-imide (6),[243]}\text{ and } N\text{-Boc-1,3-diaminopropane[244]}\text{ were synthesized according to literature procedures.}\]

For assignment of the chemical shifts in the NMR spectra, the protons in the PBI compounds are numbered as shown in Scheme 8.

**Scheme 8:** Numbering of proton and carbons as used for the assignment of chemical shifts in the NMR data.

### 4.6.2 Synthesis

**1-Hexylheptylamine**

This compound\textsuperscript{[245]} was synthesized according to a literature procedure for an analogous compound\textsuperscript{[246].} To methanol (200 mL) under argon was added dihexyl ketone (12.7 g, 0.064 mol), ammonium acetate (50.1 g, 0.650 mol), NaCNBH₃ (20.0 g, 0.318 mol), and crushed dry 4 Å molecular sieves (1 spoon). After refluxing the mixture for 48 h, the mixture was filtered over Hyflo and the residue was washed with demi-water (200 mL). From the combined filtrates, 1-hexylheptylamine was extracted with diethyl ether (3 x 50 mL). The organic layer was washed with aqueous 1M KOH (2 x 50 mL) and brine (50 mL), and after drying over MgSO₄ evaporated in vacuo to dryness. The resulting oil was subjected to column chromatography (hexane : EtOAc : MeOH, 3:1:1 v/v) to give 1-hexylheptylamine in 93% yield (11.942 g, 0.0600 mol).
HNMR: (δ ppm, CDCl₃, 400 MHz): 3.33 (br, 2H, NH₂), 2.78 (qn, 1H, NH₂CH, 3 JHH = 4.9 Hz), 1.65–1.40 (br, 4H, NH₂CHCH₂), 1.40–1.20 (br, 16H, alkyl), 0.89 (t, 6H, CH₃, 3 JHH = 6.6 Hz).

PBI 7
Under a N₂ atmosphere PBI 6 (760 mg, 1.33 mmol), N-Boc-1,3-diaminopropane (3.8 g, 22 mmol), and zinc acetate (ZnAc₂·2H₂O, ~10 mg) were dissolved in DMF (130 mL) and heated at 90 °C for 18 h. After evaporation of the solvent in vacuo, the product was dissolved in CHCl₃ (100 mL) and washed with an aqueous 10% (w/w) citric acid solution (2×100 mL), followed by brine (100 mL). The organic layer was dried (Na₂SO₄) and evaporated in vacuo to dryness. The resulting red solid was subjected to column chromatography (0.5–1% MeOH in CHCl₃) resulting in the asymmetric perylene bisimide 7, which was slightly contaminated with N,N'-di-Boc-1,3-propyldiamine (present in low quantities in the starting material N-Boc-1,3-diaminopropane). PBI 7 was used in the preparation of PBI 8 without further purification.

1 H NMR (δ ppm, CDCl₃, 400 MHz): 8.53 (br, 2H, 8), 8.43 (d, 2H, 8, 3 JHH = 8.2 Hz), 8.36 (d, 2H, 9, 3 JHH = 8.2 Hz), 8.30 (d, 2H, 9, 3 JHH = 8.2 Hz), 5.24 (br, 1H, NH), 5.17 (m, 1H, 7), 4.25 (t, 2H, 10, 3 JHH = 6.4Hz), 3.18 (m, 2H, 12), 2.24 (m, 2H, 6), 1.96 (qn, 2H, 11, 3 JHH = 6.2 Hz), 1.85 (m, 2H, 6), 1.46 (s, 9H, (CCH₃)₃), 1.40–1.20 (br, 16H, 2–5), 0.82 (t, 6H, 1, 3 JHH = 6.8 Hz).

di-Boc-1,3-propyldiamine: 4.89 (br, 2H, NH), 3.15 (m, 4H, CH₂N), 1.60 (m, 2H, CH₂CH₂CH₂), 1.43 (s, 18H, C(CH₃)₃)

PBI 8
To a solution of 7 (708 mg) in CH₂Cl₂ (200 mL), trifluoroacetic acid (TFA, 6 mL) was added and the mixture was stirred for 4 hrs. After evaporation of the solvent in vacuo, the product was dissolved in CH₂Cl₂ (200 mL) and subsequently washed with an aqueous 10% (w/w) sodium bicarbonate solution (2 × 100 mL) and brine (100 mL). The organic layer was dried (Na₂SO₄) and finally evaporated in vacuo to give 8 (558 mg as a red solid in an overall yield of 67% starting from 6).

1 H NMR (δ ppm, CDCl₃, 400 MHz): 8.58 (br, 2H, 8), 8.50 (d, 2H, 8, 3 JHH = 7.6 Hz), 8.44 (d, 2H, 9, 3 JHH = 7.6 Hz), 8.39 (d, 2H, 9, 3 JHH = 7.6 Hz) 5.18 (m, 1H, 7), 4.28 (br, 2H, 10), 2.81 (br, 2H, 12), 2.25 (br, 2H, 6), 1.92 (br, 4H, 11, 6), 1.77 (br, 2H, NH2), 1.40–1.20 (br, 16H, 2–5), 0.82 (t, 6H, 1, 3 JHH = 6.8 Hz).

MALDI-TOF: m/z 630.5 (M+H)⁺.

Alternative route to PBI 8
Perylenetetracarboxylicdianhydride 4 (3.46 g, 8.83 mmol) was suspended in a solution of imidazole (10 g) in DMF (10 mL). Subsequently, N-Boc-1,3-diaminopropane (1.76 g, 8.83 mmol, 1.0 equiv.) and 1-hexylheptylamine (1.57 g, 9.01 mmol, 1.2 equiv.) were added and the mixture was heated at 95 °C for 14 h. The reaction mixture was cooled to room temperature and a solution of EtOH / H₂O / Citric acid (100 mL, 1:1:0.1 w/w) was added before the mixture was stirred for 20 min. The precipitate was filtered off and washed extensively with a 5% MeOH/CHCl₃ solution. After evaporating the filtrate to dryness, the solid was dissolved in CH₂Cl₂ (30 mL) and an excess of TFA (5 mL) was added. The mixture was stirred for 4 h, evaporated to dryness, and redissolved in CH₂Cl₂ (100 mL). The solution was washed with a saturated solution of NaHCO₃ (2 × 100 mL) and water (100 mL) and evaporated in vacuo.
Synthesis and characterization of PBI functionalized polyisocyanides

Purification by column chromatography (0.5–15% MeOH / CH₂Cl₂) yielded 0.24 g (4.3%) of compound 8. The compound had the same physical properties as shown above.

PBI 9
A solution of 8 (448 mg, 0.71 mmol) in CH₂Cl₂ (500 mL) was subjected to the subsequent addition of Boc-L-alanine (151.4 mg, 1.1equiv.), hydroxybenzotriazole (HOBt, 124.7 mg, 1.1equiv.), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC, 159.2 mg, 1.1equiv.) and N,N'-diisopropyl ethylamine (DIPEA, 0.13 mL, 1.1eq). The mixture was stirred for 15 h and washed with an aqueous 10% (w/w) citric acid solution (2 × 400 mL), brine (100 mL) and an aqueous 10% (w/w) sodium carbonate solution (2 × 500 mL). The organic layer was concentrated and subjected to column chromatography (1–5% MeOH in CH₂Cl₂) to give 9 (450 mg, 79%) as a red solid.

1H NMR (δ ppm, CDCl₃, 400 MHz): 8.61 (br, 2H, 8, 3JHH = 8.0 Hz), 8.57 (d, 2H, 8, 3JHH = 8.0 Hz), 8.50 (d, 2H, 9, 3JHH = 8.0 Hz), 8.39 (d, 2H, 9, 3JHH = 8.0 Hz), 6.97 (t, 1H, NH-CH₂, 3JHH = 6.0 Hz), 5.19 (m, 3H, 7 and NH-Boc), 4.27 (m, 3H, 10 and CH-ala), 3.34 (m, 2H, 12), 2.25 (m, 2H, 6), 2.00 (qn, 2H, 11, 3JHH = 6.4 Hz), 1.90 (m, 2H, 6), 1.48 (s, 9H, C(CH₃)₃), 1.44 (d, 3H, CH₃-ala, 3JHH = 6.8 Hz), 1.40–1.20 (br, 16H, 2-5), 0.83 (t, 6H, 1, 3JHH = 7.2 Hz).

13C NMR (δ ppm, CDCl₃, 75 MHz): 172.5 (C=O), 163.5 (C=O perylene), 155.0 (C=O), 134.8, 133.9, 131.5, 129.3, 129.2, 126.3, 126.1, 123.1, 122.8, 122.7 (aromatic perylene), 79.9 (C(CH₃)₃), 55.1 (7), 50.1 (CH₃-ala) 38.0 (10), 36.5 (12), 32.7 (6), 32.1, 29.5 27.3, 22.9 (2–5), 28.7 (C(CH₃)₃), 28.3 (11), 19.3 (CH₃-ala), 14.1 (1).

MALDI-TOF: m/z 701.0 (M-Boc+2H)+.
HR-MS (ESI) m/z: calculated for C₄₈H₅₆N₄O₇Na: 823.40467, found: 823.40365.

PBI 11
To a solution of 9 (518 mg, 0.65 mmol) in CH₂Cl₂ (60 mL), trifluoro acetic acid (14 mL) was added and the mixture was stirred for 4 h. After evaporation of the solvent in vacuo, the product was redissolved in CH₂Cl₂ (100 mL) and subsequently washed with an aqueous 10% (w/w) sodium bicarbonate solution (2 × 100 mL) and brine (100 mL). The organic layer was dried (Na₂SO₄) and concentrated to circa 100 mL after which an excess of 4-nitrophenyl formate (540 mg, 3.2 mmol) was added. After stirring the mixture for 14 h the solution was washed with a saturated aqueous solution of sodium bicarbonate (2 × 100 mL) and brine (100 mL). The solvent was evaporated in vacuo and the solid was subjected to column chromatography (1–2% MeOH in CH₂Cl₂) to give 11 (436 mg, 92%) as a red solid.

1H NMR (δ ppm, CDCl₃, 400 MHz): 8.67 (d, 4H, 8, 3JHH = 8.0 Hz), 8.61 (d, 2H, 9, 3JHH = 8.2 Hz), 8.60 (d, 2H, 9, 3JHH = 8.2 Hz), 8.26 (s, 1H, HC(O)N), 6.94 (t, 1H, NHCH₂, 3JHH = 5.5 Hz), 6.46 (d, 1H, HC(O)NH, 3JHH = 7.4 Hz), 5.18 (m, 1H, 7), 4.67 (m, 1H, CH-ala), 4.28 (t, 2H, 10, 3JHH = 6.3 Hz), 3.33 (m, 2H, 12), 2.24 (m, 2H, 6), 2.00 (qn, 2H, 11, 3JHH = 6.3Hz), 1.88 (m, 2H, 6), 1.51 (d, 3H, CH₃-ala, 3JHH = 7.0 Hz), 1.40-1.20 (br, 16H, 2–5), 0.83 (t, 6H, 1, 3JHH = 6.7 Hz).

13C NMR (δ ppm, CDCl₃, 75 MHz): 171.6 (C=O), 163.5 (C=O perylene), 160.6 (HC=O), 134.7, 133.8, 131.4, 129.3, 129.2, 126.2, 126.0, 123.1, 122.8, 122.5 (aromatic perylene), 55.1 (7), 48.1
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(CH-ala), 38.0 (10), 36.8 (12), 32.7 (6), 32.1, 29.6, 27.3, 22.9 (2–5), 28.2 (11), 19.3 (CH₃-ala), 14.4 (1).

FT-IR (cm⁻¹, ATR): 3351 (NH-stretch), 2954, 2920, 2855 (C-H stretch), 1696, 1653 (O=CN and amide), 1592 (C=C aromatic), 1342 (C-N stretch) 811, 746 (CH aromatic).

UV-Vis (CHCl₃): λ_{max} (ε) = 373 (3910), 433 (5110), 460 (17780), 491 (48760), 528 nm (81140 mol⁻¹ L cm⁻¹).

Fluorescence (CHCl₃, λ_{exc} = 492 nm): λ_{max} = 535, 577 nm.

MALDI-TOF: m/z 728.9 (M+H)+.

HRMS (ESI) m/z: calculated for C₄₄H₄₈Na₄O₆ (M + Na⁺) 751.3472; found: 751.3463.

Polymer 2 (from catalyst Ni(ClO₄)₂)

To a stirred solution of 12 (15 mg, 0.0212 mmol) in CHCl₃ (3 mL) was added 1/500 equiv. of Ni²⁺ catalyst (0.15 mL of a solution of Ni(ClO₄)₂·6H₂O (10 mg, 0.027 mmol) in 98 mL CHCl₃ and 2 mL ethanol). After 2.5 h, according to TLC, the isocyanide was completely consumed. The
polymer was concentrated to a smaller volume (~10 mL) and precipitated in of MeOH / H2O (100 mL, 1:1 v/v) under vigorous stirring. The solid was collected by centrifugation and subsequent decantation of the solvent. Subsequently, the polymer was redissolved in chloroform (5 mL) and precipitated in methanol (~60 mL) after which the solid was collected. The latter step was repeated several times until no monomer emission (λmax = 535 nm) was observed for the solid dissolved in chloroform. Drying in \textit{vacuo} gave the polymer as a red solid in 98% yield (135 mg).

**1 H NMR (δ ppm, CDCl₃, 400 MHz):** 8.68 (br, 8H, 8, 9), 5.18 (br, 1H, 7), 4.28 (br, 3H, 10, CH-alan), 3.34 (br, 2H, 12), 2.6–0.4 (br, 31H, 6, 11, CH₃-alan, 2–5, 1).

**FT-IR (cm⁻¹, ATR):** 3291 (NH), 2946, 2924, 2855 (C-H stretch), 1695, 1654 (O=CN, amide), 1593, 1578 (C=C aromatic), 1342 (C-N stretch), 810, 747 (CH aromatic).

**UV-Vis (CHCl₃):** λmax = 372 (3500), 468 (17740), 492 (26180), 534 nm (17540 mol⁻¹ L cm⁻¹).

**Fluorescence (CHCl₃, λc = 492 nm):** λmax = 608 nm.

**Initiator complex 13**

To a well-stirred suspension of Ni(iBuCN)₄(ClO₄)₂ (52 mg, 0.088 mmol) in CH₂Cl₂ (10 mL) under argon, was added 3-azidopropan-1-amine (8.8 mg, 0.088 mmol, 1 equiv.). The initially yellow solution changed rapidly to red and over 3 min faded back to yellow. After stirring for 30 min the solvent was evaporated to obtain a yellow solid in quantitative yield. Thee conformations of the product were present in solution.

**1 H NMR (δ ppm, CDCl₃, 400 MHz):** 8.13, 7.52, 7.01 (br, 1H, NH-CH₂), 8.01, 7.78, 7.11 (br, 1H, NH=C(CH₃)₂), 3JHH = 8.0 Hz, 4.20, 3.52 (m, 2H, NH-CH₂), 3.60, 3.52 (m, 2H, N₃-CH₂), 2.12, 1.98 (m, 2H, CH₂-CH₂-CH₂₂), 1.75, 1.73, 1.45 (s, 9H, NH-C(CH₃)₂), 1.60, 1.57 (s, 27, C=N-C(CH₃)₃).

**13C NMR (δ ppm, CDCl₃, 75 MHz):** 178.2, 176.1 (N=C-N), 123.9 (C=N), 60.5 (C=N-C(CH₃)₃), 57.7, 56.4 (NH-C(CH₃)₂), 49.5 (NH-CH₂), 49.1 (CH₂-N₃), 48.2, 41.4 (NH-CH₂ and CH₂-N₃), 31.0, 28.6 (C=N-C(CH₃)₂), 29.6 (C=N-C(CH₃)₂), 29.2, 27.5 (CH₂CH₂CH₂).

**FT-IR (cm⁻¹, ATR):** 3294 (N-H), 2983, 2941 (C-H), 2227 (C=N), 2096 (N₃), 1585, 1542 (N=C=N), 1095 (ClO₄⁻).

**UV-Vis (CHCl₃):** λmax (ε) = 253 (11600), 286 nm (5800 mol⁻¹ L cm⁻¹).

**MS (FAB) m/z:** 589.3 (M−ClO₄⁻).
and an aqueous 10% (w/w) sodium carbonate solution (2 × 50 mL). The organic layer was dried (Na₂SO₄), concentrated, and subjected to column chromatography (5% MeOH in CHCl₃), yielding 1.96 g (86%) of Boc-L-alanyl-glycine methyl ester as a white solid.

1H NMR (δ ppm, CDCl₃, 200 MHz): 7.73 (t, 1H, NH, 3JHH = 5.7 Hz), 6.11 (d, 1H, NH, 3JHH = 7.3 Hz), 4.32 (br, 1H, CH-ala), 4.03 (m, 2H, CH₂-gly), 3.72 (s, 3H, OCH₃), 1.44 (s, 9H, C(CH₃)₃), 1.38 (d, 3H, CH₃-ala, 3JHH = 7.0 Hz).

13C NMR (δ ppm, CDCl₃, 50 MHz): 173.7, 169.8, 155.1 (C=O), 79.0 (C(CH₃)₃), 51.5 (CH-ala), 49.6 (OCH₃), 40.5 (CH₂-gly), 27.8 (C(CH₃)₃), 18.0 (CH₃-ala).

Boc-D-alanyl-L-alanyl-glycine methyl ester

Boc-L-alanyl-glycine methyl ester (7.01 g, 27.3 mmol) was dissolved in HCl-saturated ethyl acetate. The mixture was stirred for 1 h after which the reaction mixture was concentrated to a small volume and i-BuOH was added twice and evaporated under reduced pressure to remove the excess of HCl. The resulting L-alanine-glycine methyl ester HCl salt (5.1 g, 25.9 mmol, 95%) was dissolved in EtOAc / DMF (150 mL, 1:1 v/v). To this solution Boc-L-alanine (4.9 g, 25.9 mmol, 1.0 equiv.), DIPEA (12 mL, 68.7 mmol, 2.7 equiv.), HOBt (4.34 g, 28.4 mmol, 1.1 equiv.), and finally EDC (5.4 g, 27.9 mmol, 1.1 equiv.) were added. After stirring for 22 h the solvent was evaporated in vacuo and the product was dissolved in EtOAc (50 mL). This solution was washed with an aqueous 10% (w/w) citric acid solution (2 × 50 mL) followed by brine (20 mL), and finally an aqueous 10% (w/w) sodium carbonate solution (2 × 50 mL). The organic layer was dried (Na₂SO₄) and evaporated to dryness, yielding Boc-D-alanyl-L-alanyl-glycine methyl ester as a viscous yellow oil (6.1 g, yield 61%).

1H NMR (δ ppm, CDCl₃, 300 MHz): 7.68 (br, 1H, NH), 7.5 (d, 1H, NH, 3JHH = 6.0 Hz), 5.75 (d, 1H, NH, 3JHH = 6.3 Hz), 4.64 (qn, 1H, CH-ala, 3JHH = 6.9 Hz), 4.20 (br, 1H, CH-ala), 4.01 (m, 2H, CH₂-gly), 3.73 (s, 3H, OCH₃), 1.44 (s, 9H, C(CH₃)₃), 1.42 (d, 3H, CH₃-ala, 3JHH = 6.9 Hz), 1.37 (d, 3H, CH₃-ala, 3JHH = 6.9 Hz).

13C NMR (δ ppm, CDCl₃, 75 MHz): 172.7, 172.3, 169.7 155.1 (C=O), 79.7 (C(CH₃)₃), 52.1, 50.3 (CH-ala), 48.6 (OCH₃), 40.9 (CH₂-gly), 28.2 (C(CH₃)₃), 18.3, 18.0 (CH₃-ala).

FT-IR (cm⁻¹, ATR): 3308 (NH), 3297 (NH), 1746 (C=O ester), 1662 (amide I), 1519 (amide II).

Boc-D-alanyl-L-alanyl-glycine

Boc-D-alanyl-L-alanyl-glycine methyl ester (0.577 g, 1.74 mmol) was dissolved in a mixture of a aqueous 3M NaOH (1 mL, 3mmol, 1.8 equiv.), dioxane (14 mL) and MeOH (5 mL). After stirring the solution for 12 h, 10% (w/w) NaHSO₄ solution (200 mL) was added and the water solution was extracted with EtOAc (5 × 200 mL). The combined EtOAc solutions were evaporated to dryness, yielding Boc-D-alanyl-L-alanyl-glycine (0.345 g, 62%)
was stirred for 15 h and washed with an aqueous 10% (w/w) citric acid solution (2 × 50 mL), brine (20 mL), and an aqueous 10% (w/w) sodium carbonate solution (2 × 50 mL). The organic layer was dried (Na$_2$SO$_4$), concentrated, and subjected to column chromatography (0–5% MeOH in CH$_2$Cl$_2$). The product was dissolved in CH$_2$Cl$_2$ (3 mL) and precipitated in diisopropyl ether (20 mL). The precipitate was filtered off, washed with diisopropyl ether, and dried to give 3 (107 mg, 55%) as a red solid.

$^1$H NMR (δ ppm, CDCl$_3$, 400 MHz): 8.61 (d, 4H, 3$^3_{J_{HH}}$ = 8.0 Hz), 8.57 (m, 4H, 3J$_{HH}$ = 7.4 Hz), 4.36 (m, 1H, CH$_2$-gly), 4.25 (m, 1H, CH$_2$-gly), 4.13 (m, 1H, 10), 4.05 (m, 1H, CH-D-ala), 3.85 (m, 1H, 10), 3.56 (m, 1H, 12), 3.26 (m, 1H, 12), 2.26 (m, 2H, 6), 2.01 (m, 2H, 11), 1.89 (m, 2H, 6), 1.56 (m, 2H, 6), 1.42 (m, 2H, 6), 1.39 (m, 2H, 11), 1.38 (m, 2H, 11), 1.37 (m, 2H, 11), 1.35 (m, 2H, 11), 1.33 (m, 2H, 11), 0.83 (t, 6H, 1, 3J$_{HH}$ = 6.4 Hz).

$^{13}$C NMR (δ ppm, CDCl$_3$, 75 MHz): 173.1, 172.1, 168.6, 156.0 (C=O), 163.5, (C=O perylene), 134.9, 133.7, 131.4, 129.2, 129.1, 126.0, 123.1, 122.8, 122.4 (aromatic perylene), 80.7 (C(CH$_3$)$_3$), 54.9 (7), 51.2 (CH-D-ala), 49.3 (CH-L-ala), 43.4 (10), 38.0 (CH$_2$-gly), 36.2 (12), 32.5 (6), 31.9, 29.4, 27.1, 22.8 (2–5), 28.5 (C(CH$_3$)$_3$), 27.8 (11), 17.6 (CH$_3$-D-ala, CH$_3$-L-ala), 14.3 (1).

FT-IR (cm$^{-1}$, ATR): 3316 (NH), 2946, 2925, 2855 (C-H stretch), 1692, 1649 (O=CN, amide), 1593, 1576 (C=C aromatic), 1339 (C-N stretch), 809, 745 (CH aromatic).

MALDI-TOF: m/z 828.9 (M-Boc + 2H)$^+$, 928.9 (M + H)$^+$, 950.9 (M + Na)$^+$.

HR-MS (ESI) m/z: calculated for C$_{53}$H$_{64}$N$_6$O$_9$Na: 951.46325; found: 951.45654; for C$_{53}$H$_{65}$N$_6$O$_9$: 929.48130; found: 929.47812.

**PBI 15**

Starting from PBI 14 (117 mg, 0.13 mmol) PBI 15 was prepared following the same procedure described for the preparation of 11, with the difference that reaction of the free amine of 14 with 4-nitrophenyl formate resulted in precipitation of PBI 15 in the reaction mixture. The formed precipitate was filtered off, washed with diisopropyl ether, and dried in vacuo to give 15 (67 mg, 55%) as a red solid.

$^1$H NMR (δ ppm, DMSO-d$_6$/CDCl$_3$ (9:1), 400 MHz): 8.50–8.05 (m, 11H, 8, 9, NH), 7.99 (s, 1H, HC(O)N), 7.66 (t, 1H, NH, 3J$_{HH}$ = 5.5 Hz), 7.50 (m, 1H, 7), 4.38 (m, 1H, CH-L-ala), 3J$_{HH}$ = 7.0 Hz), 4.27 (m, 1H, CH-D-ala), 3J$_{HH}$ = 7.0 Hz), 4.04 (m, 2H, 6), 3.71 (m, 2H, CH$_2$-gly), 3.22 (m, 2H, 12), 2.19 (m, 2H, 2–5), 1.84 (m, 4H, 11, 6), 1.40–1.20 (m, 22H, 2–5, CH$_3$-ala), 0.83 (t, 6H, 1, 3J$_{HH}$ = 6.2 Hz).

FT-IR (cm$^{-1}$, ATR): 3284 (NH), 2950, 2924, 2855 (C-H stretch), 1692, 1649 (O=CN, amide), 1593, 1576 (C=C aromatic), 1342 (C-N stretch), 810, 746 (CH aromatic).

MALDI-TOF: m/z 856.9 (M-Boc + 2H)$^+$, 928.9 (M + H)$^+$, 950.9 (M + Na)$^+$.

HR-MS (ESI) m/z: calculated for C$_{53}$H$_{65}$N$_6$O$_9$: 929.48130; found: 929.47812.

**PBI 18**

Amino-butyl-phenoxy perylene 17 was reacted with Boc-L-alanine following the same procedure as described for the preparation of 9 to give 18 in 92% yield as a red/purple solid.

$^1$H NMR (δ ppm, CDCl$_3$, 400MHz): 8.24 (s, 2H, 5), 8.20 (s, 2H, 5), 7.42 (t, 1H, 1, 3J$_{HH}$ = 7.8 Hz), 7.27 (m, 10H, 2, 7), 7.11 (m, 4H, 8), 6.95 (d, 8H, 6, 3J$_{HH}$ = 8.6 Hz), 6.22 (br, 1H, NH), 4.97 (br, 1H, NH), 4.14 (t, 2H, 9, 3J$_{HH}$ = 7.0 Hz), 4.08 (m, 1H, CH-ala), 3.29 (m, 2H, 12), 2.69 (sept, 2H, 3,
\[ J_{HH} = 6.8 \text{ Hz} \], 1.72 (qn, 2H, 10, \[ J_{HH} = 7.3 \text{ Hz} \]), 1.61 (qn, 2H, 11, \[ J_{HH} = 7.3 \text{ Hz} \]), 1.39 (s, 9H, C(CH\text{3})\text{3}), 1.30 (d, 3H, CH\text{3}-ala, \[ J_{HH} = 7.2 \text{ Hz} \]), 1.10 (d, 12H, 4, \[ J_{HH} = 6.8 \text{ Hz} \]).

**PBI 19**

Following the same procedure as described for the synthesis of PBI 11, PBI 19 was obtained from PBI 18 in 92% yield as a red solid.

\[ \text{1H NMR (6 ppm, CDCl}_3, 400 MHz): 8.25 (s, 2H, 5), 8.19 (s, 2H, 5), 8.09 (s, 1H, NC(O)H), 7.42 (t, 1H, 1, \[ J_{HH} = 8.0 \text{ Hz} \]), 7.27 (m, 10H, 2, 7), 7.11 (m, 4H, 8), 6.96 (d, 8H, 6, \[ J_{HH} = 8.0 \text{ Hz} \]), 6.51 (br, 1H, NH), 6.25 (br, 1H, NH), 4.49 (m, 1H, CH-ala), 4.13 (t, 2H, 9, \[ J_{HH} = 7.2 \text{ Hz} \]), 3.31 (m, 2H, 12), 2.69 (sept, 2H, 3, \[ J_{HH} = 6.8 \text{ Hz} \]), 1.75 (m, 2H, 10), 1.63 (m, 2H, 11), 1.61 (d, 3H, CH\text{3}-ala, \[ J_{HH} = 7.2 \text{ Hz} \]), 1.05 (d, 12H, 4, \[ J_{HH} = 6.9 \text{ Hz} \]).

\[ \text{13C NMR (6 ppm, CDCl}_3, 75 MHz): 171.3 (C=O), 162.9, 162.8 (C=O perylene), 160.6 (HC=O), 155.5, 155.4, 154.9, 154.8 (C-O), 145.3, 132.8, 132.7, 130.3 (aromatic perylene), 129.8, 129.7 (7), 129.2 (1), 124.4, 124.3 (8), 123.7 (2), 122.6, 122.3, 120.5, 120.4, 119.9, 119.4 (aromatic perylene), 120.1, 120.0 (5), 119.7, 119.6 (6), 47.6 (CH-ala), 40.0 (9), 39.1 (12), 29.6 (11), 25.4 (10), 24.1 (4), 18.8 (CH\text{3}-ala).

UV-Vis (CHCl\text{3}): \chi_{max} = 266 (32040), 284 (34070), 446 (15020), 542 (20830), 580 nm (32160 mol\text{-1} L \text{ cm}^{-1}).

Fluorescence (CHCl\text{3}, X_{exc} = 550 nm): \chi_{exc} = 605 nm.

MALDI-TOF: m/z 1088.8 (M + H)+.

HR-MS (ESI) m/z: calculated for C\text{68}H\text{54}N\text{10}O\text{Na}: 1111.38941, found: 1111.38832

**PBI 20**

PBI 20 was obtained in 93% from PBI 19 following the procedure described for the synthesis of PBI 12. For conversion to the isocyanide a total of 15 equiv. of NMM and 3.2 equiv. of diphosgene were used, which were added in 4 steps starting with 2.5 equiv. of NMM and 0.5 equiv. of diphosgene. The reaction was followed by TLC and when more NMM and diphosgene were required they were added taking care that NMM was present in excess with respect to diphosgene.

\[ \text{1H NMR (6 ppm, CDCl}_3, 400 MHz): 8.24 (s, 2H, 5), 8.21 (s, 2H, 5), 7.42 (t, 1H, 1, \[ J_{HH} = 8.0 \text{ Hz} \]), 7.27 (m, 10H, 2, 7), 7.11 (m, 4H, 8), 6.96 (d, 8H, 6, \[ J_{HH} = 8.0 \text{ Hz} \]), 6.51 (br, 1H, NH), 6.25 (br, 1H, NH), 4.49 (m, 1H, CH-ala), 4.13 (t, 2H, 9, \[ J_{HH} = 7.2 \text{ Hz} \]), 3.31 (m, 2H, 12), 2.69 (sept, 2H, 3, \[ J_{HH} = 6.8 \text{ Hz} \]), 1.75 (m, 2H, 10), 1.63 (m, 2H, 11), 1.61 (d, 3H, CH\text{3}-ala, \[ J_{HH} = 7.2 \text{ Hz} \]), 1.05 (d, 12H, 4, \[ J_{HH} = 6.9 \text{ Hz} \]).

\[ \text{13C NMR (6 ppm, CDCl}_3, 50 MHz): 166.0 (C=O), 163.3 (C=O perylene), 163.1 (CN), 155.8, 155.2 (C-O), 145.6, 133.0, 132.8, 130.5 (aromatic perylene), 130.0 (7), 129.4 (1) 124.7, 124.6 (8) 123.9 (2), 122.9, 122.5, 120.7, 120.6, 120.1, 119.6 (aromatic perylene), 120.3, (5), 119.9, 119.8 (6), 53.5 (CH-ala), 39.4 (9, 12), 29.1 (3), 26.6 (8), 25.2 (10), 24.0 (4), 19.7 (CH\text{3}-ala).

FT-IR (cm\text{-1}, ATR): 3376 (NH), 3064, 2963, 2928, 2867 (C-H stretch), 2137 (CN), 1699, 1659 (O=CN, amide), 1587 (C=C aromatic), 1487, 1410 (C-H bend), 1338 (C-N stretch), 1309, 1285, 1202 (ether), 879 + 745 (C-H aromatic).

UV-Vis (CHCl\text{3}): \chi_{max} = 266 (32040), 284 (34070), 446 (15020), 542 (20830), 580 nm (32160 mol\text{-1} L \text{ cm}^{-1}).

HR-MS (ESI) m/z: calculated for C\text{68}H\text{54}N\text{10}O\text{Na}: 1093.37885, found: 1093.38105
To a stirred solution of 20 (20 mg, 0.019 mmol) in CHCl\textsubscript{3} (2 mL) catalyst 13 was added (1 mL of a 0.019mM solution of 13 in CHCl\textsubscript{3}). According to TLC, the isocyanide was completely consumed after 7 days. The polymer was purified by size exclusion chromatography (Bio­Beads) using CH\textsubscript{2}Cl\textsubscript{2} as eluent and obtained as a red solid in 80% yield (16 mg).

\begin{align*}
{^1}\text{H NMR (8 ppm, CDCl}_3, 400 MHz):} & \ 8.40-7.60 \ (br, \ 4H, \ 5), \ 7.60-5.80 \ (br, \ 24H, \ 1, \ 2, \ 6, \ 7, \ 8, \ NH), \\
3.64 \ (br, \ 3H, \ CH-ala, \ 12), \ 2.55 \ (br, \ 2H, \ 3), \ 1.80-0.80 \ (br, \ 19H, \ 10, \ 11, \ CH\textsubscript{3}-ala, \ 4). \\
\text{FT-IR (cm}^{-1}, \ \text{ATR):} & \ 3308 \ (NH), \ 3061, \ 2958, \ 2921, \ 2868, \ 2850 \ (C-H \ \text{stretch}), \ 1701, \ 1659 \ (O=CN, \ amide), \ 1587 \ (C=C \ \text{aromatic}), \ 1487, \ 1410 \ (C-H \ \text{bend}), \ 1341 \ (C-N \ \text{stretch}), \ 1310, \ 1286, \ 1200 \ (ether), \ 877, \ 750 \ (C-H \ \text{aromatic}). \\
\text{UV-Vis (CHCl}_3): \lambda_{\text{max}} (\varepsilon) & = 266 \ (29410), \ 285 \ (30263), \ 448 \ (12381), \ 533 \ (19932), \ 572 \ \text{nm (21373 mol}^{-1} \ \text{L cm}^{-1}). \\
\text{Fluorescence (CHCl}_3, \ \lambda_{\text{exc}} = 550 \ \text{nm):} \lambda_{\text{max}} = 606 \ \text{nm}. \\
\end{align*}

4.6.3 Fluorescence quantum yield

Quantum yields were determined following a procedure described on the internet.[247] The quantum yield of polymer 2 was determined relative to PBI 11. UV-Vis and fluorescence spectra of polymer 2 were measured in a 1 cm cuvette using solutions in chloroform with an absorbance below 0.1. For polymer 2, measurements were performed on solutions in the concentration range (monomer units) $1.5 \times 10^{-7} - 2.7 \times 10^{-6}$ M; for PBI 11 the concentration range was $6.1 \times 10^{-8} - 6.1 \times 10^{-7}$ M. The fluorescence spectra were recorded (excitation at $\lambda = 492$ nm, slit = 2.5 nm) between $\lambda = 500-900$ nm (slit 2.5 nm). The integrated emission was plotted against the absorbance at $\lambda = 492$ nm for both polymer 2 and PBI 11 (see Figure 20A). The relative quantum yield is given by ratio of the gradients: grad(2)/grad(11)*100% and amounted to 3.7%.

The fluorescence quantum yield of 3 was determined relative to 19 in an analogous manner. Solutions of polymer 3 were measured in the concentration range (monomer units) $1.1 \times 10^{-7} - 5.8 \times 10^{-6}$ M and for PBI 19 in the range $1.4 \times 10^{-8} - 3.3 \times 10^{-6}$ M. The fluorescence spectra were recorded (excitation at 550 nm, slit =2.5 nm) between 560–900 nm (slit 2.5 nm). The quantum yield was determined from the plot in Figure 20B and amounted to 3.0%.

![Figure 20](insert figure path)

**Figure 20:** Plots of the fluorescence peak area as function of the absorbance intensity for polymer (black) and corresponding monomer (grey). A) Plot of polymer 2 and PBI 11. B) Plot of polymer 3 and PBI 19.
4.6.4 Atomic Force Microscopy

AFM measurements on the polymer fibers of 2 and 3 were performed with a commercial apparatus AFM (Nanoscope III instrument, Digital Instruments). A solution of the polymers (~10^{-6} M in CHCl_{3}) was spun (1600 rmp) onto freshly cleaved graphite or Muscovite Mica. All images were recorded with the AFM operating in the tapping mode in air at room temperature with a resolution of 512 x 512 pixels, using moderate scan rates (1–2 lines sec^{-1}). Commercial tapping-mode tips (NT-MDT, NSG10) were used with resonance frequencies of 190–325 kHz. Lengths and heights were evaluated using image recognition software “Scanning Adventure” developed by Jaques Barbet.[248] For all values derived from AFM data presented, the error is given as the standard deviation of the measurements from many different sessions.

4.6.5 Light scattering

Elastic and quasi-elastic light scattering measurements were made with a home-built goniometer apparatus.[3] The exciting light source was a 15 mW polarized He:Ne laser (633 nm). The investigated scattering angle range was 20–150° and correspond to exchanged wave vector Q values of 4.6–25.6 μm^{-1} (the exchanged wave vector Q equals [(4\pi n)/\lambda]sin(\theta/2), where n is the refractive index of the sample and \lambda the wavelength of light in vacuum). To collect the polarized and depolarized contributions of the light scattered from the sample, a Glan-Taylor polarizer was placed in the incident laser path and a Glan-Thomson analyzer in the scattered beam. Artifacts due to fluorescence were eliminated by an interference filter on the observation path during the measurements. The samples (concentration 100 μM in chloroform) were placed in an optical cylindrical cell of 8 mm path length and were thermostated by a homemade water circulating bath. The temperature controller provided a constant temperature of (298 ± 0.01) K.
Chapter 5

Photophysical and electronic properties of PBI functionalized polyisocyanides: Modeling and photophysical studies

To get more insight in the structural and optoelectronic properties, PBI functionalized polyisocyanides 1 and 2 have been studied by molecular dynamics modeling. In addition, photophysical studies have been carried out on polymer 2, to give experimental information on the optoelectronic properties. This work in this chapter forms a publication in Chemistry, A European Journal.

\[ \text{Figure 1: PBI functionalized polyisocyanide } 1 (R=C_2H_5), 2(R=C_6H_{13}). \]

5.1 Modeling: Morphology

As a first step in the modeling study of polyisocyanides with pendant perylene bisimides (Figure 1), a complete morphological investigation was performed. The conformation of the polyisocyanide template in the absence of chromophores was first explored using the Dreiding force-field as it is particularly suited to reproduce hydrogen bonds, which play a crucial role in the stability of the polyisocyanide backbone. The torsion potential around the polymer backbone, however, is not properly accounted for by the original Dreiding force field and has been corrected against \textit{ab initio} MP2 6-31G** quantum-chemical calculations. The polymer helices were built according to a "step-by-step" approach where oligomers of increasing size were grown. At each step, the lowest energy structures were retained for the generation of the larger size oligomers. From this conformational study, the most stable conformer was identified as a right-handed helix (for an L-alanine amino acid) with an average angle of 21.3° between two successive units along the helix axis, 3.76 units per turn, and a pitch length of 67.8 Å. Such a conformation was very robust against long molecular dynamics simulations at room temperature.

\[ \text{iv The modeling study was performed at the Université de Mons-Hainaut in the group of David Beljonne.} \]

\[ \text{v The photophysical study was carried out at the University of Cambridge in the group of Richard Friend.} \]
Table 1. Comparison of the calculated (Dreiding force field) structural parameters of unsubstituted polyisocyanides with the corresponding values extracted from optical studies of polyisocyanides bearing porphyrin derivatives.\cite{251}

<table>
<thead>
<tr>
<th></th>
<th>Angle between units n and n+4</th>
<th>Distance between units n and n+4</th>
<th>Units per turn</th>
<th>Pitch length</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dreiding</td>
<td>21.3°</td>
<td>4.34 Å</td>
<td>3.76</td>
<td>67.8 Å</td>
</tr>
<tr>
<td>Experimental</td>
<td>22°</td>
<td>4.2 Å</td>
<td>3.75</td>
<td>68.7 Å</td>
</tr>
</tbody>
</table>

The predicted geometric parameters are in excellent agreement with the corresponding data extracted from a detailed spectroscopic study of polyisocyanides substituted with porphyrin derivatives (Table 1).\cite{251} Thus, the positioning in space of the chromophores in these helices is fixed to a large degree by the template effect enforced by the polyisocyanide core, which in turn arises mostly from the formation of an H-bonded network (Figure 2). In addition, dynamic modeling revealed that all the H-bonds point in the same direction explaining the extremely high dipole moment of these molecules (in the range 2.8–3.6 Debye per repeating unit).\cite{252} The next step of the modeling involved the grafting of PBI chromophores onto the helical polymer. The PBI molecules were linked to the backbone by a short saturated spacer that was submitted to a conformational search. Based on the local minima found for the relevant torsions all possible helical stacks were constructed, among which the most realistic conformations based on simple steric arguments were selected for further investigations. The values of the torsion angles defining the conformation of the spacer and their combination had a considerable impact on the relative arrangement of the chromophores in the resulting 3D structures. Geometric optimizations were performed on systems of increasing complexity and converged to the identification of three local minima on the potential energy surface. To avoid finite size effects along the polymer direction, periodic boxes out of these three structures were subjected to further structural refinements. These helices, hereafter referred to as h1, h2, and h3, differ by the relative orientation of the PBI chromophores with respect to the main axis of the polyisocyanide backbone (Figure 2). In h1, the PBIs are oriented with their long axis forming an angle of ~60° with the helical direction. This is an open structure that shows the lowest density among the three helical arrangements.
Modelling and photophysical studies

Figure 2. Most stable conformation of the unsubstituted polyisocyanide helix as obtained from Dreiding force field calculations (top). The H-bonds are indicated by dashed lines. Top view of h1, h2, and h3 (bottom).

The helix h3, in contrast to h2, presents a much more compact, pinetree-like structure where the PBI chromophores are lying almost flat on the helical core (the average angle between the PBI main axis and the helix direction is 26°). A similarly dense structure is achieved in h2, although in contrast to h3, the chromophores are maintained in an orthogonal orientation (average angle of 94°) with respect to the helical growth direction. The interactions between the PBIs are different for all three helices. In h1 the PBIs interact mostly by face-on interactions, whereas in h2 the chromophores are lying more in an edge-on organization. In h3 the PBI interactions also involve a cofacial arrangement, yet with translational displacement along the PBI long axes. In each of the three cases, the polymer self-organizes into a right-handed helix with 3.7–3.9 molecules per helical turn (resulting in an average rotation angle between two successive PBI units along the stacking direction of ~21° for h1, ~24° for h2, and ~11° for h3). With the exception of h3, the angles are close to the value measured for the porphyrin-substituted polyisocyanide (22°), thus confirming that grafting of the PBI units does not perturb the structural organization of the polyisocyanide template. From an energetic point of view, the potential energies calculated for these local minima indicate that h3 is the most stable (mainly due to attractive Van der Waals interactions), followed by h2 and h1.

The three local minima, identified from the geometric optimizations at 0 K were then subjected to molecular dynamics simulations at room temperature. The aim of this study was twofold: i) it allows gauging of the stability of the conformers with respect to thermal fluctuations and, in addition, ii) the snapshots extracted along the Molecular Dynamics (MD) run can subsequently be used to assess the influence of conformational motion on the electronic and optical properties of the polymer. A comparison between the morphologies of the various structures obtained along the MD trajectory revealed that these follow quite substantial structural changes as far as the
relative arrangement of the PBI units is concerned (while the stiff helical backbone remained largely unaffected). The spacers connecting the PBI units to the carbon backbone thus allow some flexibility in the spatial positioning of the chromophores that organize into ordered domains separated by defects. This is particularly pronounced in the case of the sparse helix h1, which collapses into a structure similar to h2 along the MD run.

The measured angles between the PBI main axis and the helix direction indeed switched from an average value of 60° at time zero to 74° after 300 ps. The denser structures h2 and h3 maintained their overall organization during the full MD simulations (the corresponding rotation angles vary from 94° to 88° for h2 and from 26° to 27° for h3). Thus, the morphological analysis has allowed pinpointing three structures that differ by the conformation of the arms connecting the PBI to the template and yield different relative spatial orientations of the chromophores. From the three modelled helical conformations, h2 and h3 appear to be the most stable conformers.

5.2 Modeling: Spectroscopic study

The geometric structures generated from the morphology studies described above were used as input for quantum-chemical calculations of the electronic excited states (performed at the INDO/CCSD level). The results of these calculations were in turn injected into a phenomenological Holstein model to predict the spectroscopic properties of the helical supramolecular structures, namely, the optical absorption and circular dichroism spectra. A single effective high-frequency (0.17 eV) vibrational mode was included for which exciton-phonon coupling (Huang-Rhys factor of 0.6) was fitted against the absorption spectrum of an isolated PBI chromophore in solution. The model and its applications to spectroscopy have been largely described in previous works.

![Figure 3: Theoretical absorption spectra of structures h1, h2, and h3 (before and after the MD run) overlayed to the experimental spectrum of polyisocyanide 2 measured in a chloroform solution. Note that the theoretical spectra have been rigidly shifted to reproduce the position of the measured absorption maxima.](image)

The calculations have been performed on the polymer in gas phase, hence the more collapsed conformation is also the most stable. Because solvent effects are not taken into account, stable structures were not ruled out on the basis of the sole energetic argument. Absorption and CD spectra have been calculated on a number of conformers and the comparison with experimental results allowed identifying the most likely conformations in solution.
The polyisocyanide helices possess less than four monomer units per turn and therefore the PBIs grafted onto the template yield four quasi-one-dimensional stacks. The absorption and CD spectra were simulated for 20-mer chains (i.e., chains formed by four 1D stacks of five molecules each); test calculations on longer oligomers yield very similar results.\textsuperscript{vii}

The comparison of the measured and simulated (from snapshots at the beginning and end of the MD run) absorption spectra for the three helical structures is shown in Figure 3. A reasonable agreement between theory and experiment is observed in all cases, with a slightly better match for helix \textbf{h1}. The spectra show the characteristic features of a weakly coupled aggregate (Chapter 4).\textsuperscript{viii}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{spectra.png}
\caption{Theoretical circular dichroism spectra (before and after the MD run) of structures \textbf{h1}, \textbf{h2} and \textbf{h3} overlayed to the experimental spectrum of P3 measured in a chloroform solution. The dashed lines correspond to the spectra simulated for individual 1D stack.}
\end{figure}

At this stage it was very difficult to rule out any structure from the comparison between measured and simulated absorption spectra since linear absorption is not very sensitive to long-range interactions.\textsuperscript{[228]}

As the nearest neighbour couplings are very similar from one conformer to another, the computed spectra are only weakly dependent on the helical conformation and on its structural fluctuations during the MD run. This is particularly striking for \textbf{h1}, which shows very similar absorption lineshapes before and after the MD simulation, despite pronounced structural reorganizations. In addition, it is also conceivable that the limiting structures considered here are, in fact, all present in solution and contribute to the overall optical properties of the polymer.

\textsuperscript{vii} For each chain, the ground-state geometries of the individual chromophores were extracted from the full helical structures and single point INDO/CCSD calculations were performed on the H-adjusted molecules. The obtained vertical excitation energies and excitonic couplings (computed within the transition density approach) were then used to solve the Holstein Hamiltonian within the two-particle approximation (see refs. 7 and 8).

\textsuperscript{viii} The low-energy shoulder corresponds to the purely electronic 0-0 transition of the individual molecule and its relative intensity in comparison to the higher-energy phonon sidebands, is sensitive to the magnitude of the excitonic couplings. The couplings are all in the range of 400–500 cm\textsuperscript{-1} for the nearest neighbor interactions and significantly smaller than the geometric relaxation energy (0.6×0.17 eV = 823 cm\textsuperscript{-1}).
Circular dichroism spectroscopy provides a more critical test for the spatial organization of the chromophores in the helical polymer as it is far more sensitive to long-range interactions than linear absorption. When two chromophores are electronically coupled in a chiral structure, the two electronic excited states resulting from the interactions feature rotational strengths with opposite signs. Therefore, the intermolecular interactions between conjugated segments in helical conformations usually result in a double-peak signal (bisignated Cotton effect) in the CD spectrum; a right-handed helix is characterized by a positive peak followed by a negative peak with increasing energy, whereas the reverse indicates a left-handed helix. All conformers generated by the force field calculations were right-handed, at least from the mere inspection of the twisting angles between closely spaced PBI units along the four individual stacks. The experimental CD spectrum is in agreement with simulated data and shows the ‘+ / −’ sequence expected for a right-handed helix.

The simulated CD spectra for the three conformers before and after the MD run are shown in Figure 4. Strikingly, h3 shows a CD signal that is inverted with respect to h2 and to experimental results. This is also the case for h1 at t = 0 ps, but the bisignated effect switches sign during the MD simulation. All individual stacks extracted from the three conformations are, however, right-handed as proven by calculations retaining only molecules \( n, n+4, n+8 \), and so on.

Calculation of the rotational strength for all possible PBI pairs within the full structures (not shown) revealed the presence of both positive and negative interactions. In fact, on top of the right handedness conferred by the relative positions of the chromophores within each stack, molecules belonging to different stacks also arrange according to helical structures with opposite (left) handedness. The balance between the ‘right’ and ‘left’ interactions depends upon the conformation of the polymer chains, with only h2 providing a qualitative match with experimental data. It is interesting to see that the evolution of h1 towards that of h2 along the MD trajectory is accompanied by a reversal of the CD spectrum. It can be concluded from the modeling studies that the most probable conformation for these helical arrays in both solution and the solid state is the architecture h2. This modelled architecture accounts not only for all the physical observations (UV-Vis and CD), but predicts that the polyisocyano-perylenes would be ideal polymers for exciton and electron migration (see also Finlayson et. al.[259]). To study this aspect the photophysical behaviour of polyisocyanide 2 was examined.

5.3 Photophysical studies

To investigate the photophysical properties and excited state dynamics of polymer 2, time-correlated single photon counting (TCSPC) and transient absorption spectroscopy were performed. The TCSPC technique (Figure 5a) revealed an extraordinarily long radiative lifetime of \( \sim 24 \) ns in a CHCl\textsubscript{3} solution, compared to the usual value of 3–4 ns in the perylene monomer,[260, 261] together with the low quantum yield fluorescence (Chapter 4) this is strongly indicative of excimer-like excited states in the polymer.[133, 167, 262] When the polymer was spun onto a film, the system decayed rapidly and multi-exponentially due to the three dimensional energy migration within the film.
The polarization-sensitive transient absorption measurements performed on polymer 2 (Figure 5b) showed that the anisotropy in photo-induced absorption decayed on timescales of the order of picoseconds; faster than in other known \( \pi \)-conjugated polymers, such as polythiophene.\(^{[263]}\)

We consider that the faster energy transfer and depolarization process that take place in 2 are due to its compact helical structure,\(^{[264]}\) which promotes rapid exciton migration along the chiral arrangement of perylene stacks. The depolarization process is especially fast in thin films, reflecting the higher dimensionality of migration, relative to solution measurements.

The transient absorption spectra (Figure 5c–d) show ground-state absorption bleaching around \( \lambda \) = 525 nm, as well as a broad photo-induced absorption (PA) band (from \( \lambda \) = 550 nm to at least \( \lambda \) = 750 nm); the latter being indicative of strong interactions between the chromophores.\(^{[265]}\) The spectra obtained from both solution and film showed these features, although the shapes of the PA bands were rather different; possibly due to charge generation in the film. Furthermore, the non-linear dependence of the PA intensity on pump-fluence (Figure 6) suggests that bimolecular annihilation processes take place in the system. Early time decay kinetics are much faster than the ns-decay rates for excitons.

High fractional changes in optical density (above \textit{ca.} 1% in solution) are observed at short times showing an extremely high excitation density on chains. This suggests that the polymers are promising compounds for light-harvesting applications, such as photovoltaics.\(^{[266]}\)
Figure 5: (a) Time-resolved photoluminescence decay dynamics measured at $\lambda = 625$ nm. (b) Photo-induced absorption anisotropy spectra of polymer 2 at $\lambda = 690$ nm, in film and chloroform solution. The excitation wavelength was at $\lambda = 500$ nm with a fluence of 424 $\mu$J cm$^{-2}$. Transient absorption (fractional change in optical density $[OD]$) measurements on polymer 2, excited at $\lambda = 500$ nm, are shown in (c) solution and (d) film. The fluences of the transient absorption measurements for the solution and film were 353 and 389 $\mu$J cm$^{-2}$, respectively. The spectral features of bleaching and photo-induced absorption (PA, as a function of delay time are indicated for clarity.)
5.4 Conclusion

PBI based polyisocyanopeptides 1 and 2 have been studied using various experimental and computational methodologies providing unambiguous evidence that these ultrastiff polymers are ideal scaffolds for precisely organizing chromophoric arrays into functional 2D wires. Extensive molecular modeling dynamics refined previous models and revealed a $4_1$ helix in which the chromophores overlap along the polymer backbone. The calculated and spectroscopically observed architectures predict that these unique polymers are highly favourable systems for electron transport. This was confirmed by transient absorption spectroscopy studies, which indicate extremely high exciton migration rates and charge densities. The application of these materials in photovoltaics is described in the Chapter 6.
5.5 Experimental

5.5.1 Modeling

Morphology study

The molecular mechanics and dynamics calculations were carried out using the Cerius\textsuperscript{267} molecular modeling system from Accelrys Software Inc. with the Dreiding force field.\textsuperscript{250} The geometric optimizations were performed by molecular mechanics simulations with a conjugate gradient algorithm until a convergence criterion of $10^{-3}$ kcal mol$^{-1}$\AA$^{-1}$ was reached. In non-periodic systems, the long-range interaction cutoff is defined by a spline switching method; the spline-on and spline-off distances are set to 11 \AA and 14 \AA, respectively. In periodic systems, the long-range interactions are accounted for by using the Ewald summation method,\textsuperscript{268} which was parameterized to yield an accuracy of 0.001 kcal mol$^{-1}$ atom$^{-1}$ for interaction terms. The electrostatic interactions are taken into account by determining the charges on the atoms by means of the procedure developed by Gasteiger.\textsuperscript{269}

The molecular dynamics simulations were performed at room temperature in the NVT ensemble (i.e., particle number, volume and temperature are kept constant). The Nose-Hoover thermal bath coupling scheme\textsuperscript{270} was used with a relaxation time describing the coupling fixed at 0.01 ps. The Verlet velocity algorithm\textsuperscript{271} was used to integrate the equations of motion with a 1 fs time step. The long-range interactions are treated in the same way as for the molecular mechanics calculations.

The choice of the Dreiding force field was guided by the fact that it takes into account explicitly the formation of hydrogen bonds. As mentioned in Section 5.1, the torsion potential around the polymer backbone is not properly accounted for by the original Dreiding force field, as used in the Cerius package, and has been corrected against ab initio MP2 6-31G** quantum-chemical calculations. To achieve this, the force field parameters related to the torsion around the central carbon-based backbone were adjusted to reproduce the ab initio potential energy surface. The corrected torsion profile yields two minima for torsion angles of 60° and 110° and a rather shallow potential around these conformations (Figure 7). Note also that this modification of the torsion potential does not infer on the description of the rest of the polymer helical structure, as there are no crossing terms in the Dreiding force field, and the sequence of atoms involved in the backbone torsion is not found elsewhere in the system.

The conformation of polysisocyanides with pendant PBIs has been studied following a ‘step-by-step’ approach. After the validation (and adjustment, see above) of the force field, we performed a complete conformational search on the isocyanide monomer to build all possible conformations of oligomers, among which the lowest energy structures were selected for the generation of the larger size oligomers. The stability of unsubstituted polymer chains was then tested by running molecular dynamics simulations at room temperature. In a subsequent step, the PBI chromophores were grafted onto the helical template. To do this, we first performed a conformational search on the torsion angles along the short saturated spacer that ensures the junction between the polymer and the chromophores. Based on the local minima found for the relevant torsions, 27 helical stacks were constructed, among which the most realistic conformations based on simple steric arguments were selected and used as input for further molecular mechanics calculations. This step allowed refining the most realistic conformations that were then used as the starting point for the construction of structures obeying periodic
boundary conditions (in order to get rid of possible artefacts related to finite size effects). The construction of orthorombic periodic boxes out of these structures was also made by steadily increasing the amount of substitution of the polyisocyanide template with PBI units. The structural parameters of the unit cell were adjusted in the following way: the parameter $c$ along the polymer direction was adjusted to match to the helical pitch length, that is approximately 70 Å and the parameters $a$ and $b$ have been deliberately chosen, much larger than the size of the molecule in the $ab$ plane, so as to avoid interchain interactions. These periodic structures have then been optimized by molecular mechanics calculations with the parameters $a$ and $b$ fixed while allowing the parameter $c$ to vary. The resulting structures were found to be in very good agreement with the experimental data and were finally subjected to long molecular dynamics simulations at room temperature.

![Figure 7. Potential energy curve for the torsion around the carbon-based backbone of the polyisocyanide chain as calculated by the original and modified force-field methods together with the ab initio results.](image)

**Spectroscopic study**

Snapshots extracted along the MD runs described above were used as input for excited-state calculations performed at the Intermediate Neglect of Differential Overlap (INDO)/Coupled Cluster Single and Double (CCSD) level.[253, 254] The active space in the CCSD calculations was increased until convergence of the PBI excitation energy and transition dipole moment. Transition charge densities were calculated for each PBI chromophore $m$ and $n$ and the interaction $J_{mn}$ evaluated by a Coulombic sum.[272] In addition to electronic coupling there is significant electron-vibrational (EV) coupling within each helical stack. A single effective high-frequency ($\omega_0 = 0.17$eV) vibrational mode was included whose exciton-phonon coupling (Huang-Rhys factor, $\lambda^2 = 0.6$) was fitted against the absorption spectrum of an isolated PBI chromophore in solution. These parameters were injected into a Holstein-type aggregate Hamiltonian, which in a representation of one-excitons reads:

$$
H = \omega_0 \sum_n b_n^\dagger b_n + \omega_0 \lambda \sum_n (b_n^\dagger + b_n) | n < n | + \\
+ \sum_m \sum_n (J_{mn} + \Delta_m \delta_{mn}) | m > n | + D + \omega_0 - 0 + \lambda^2 \omega_0
$$

(1)
where $\hbar = 1$ is taken. The first terms represents the vibrational energy due to the high frequency mode (of frequency $\omega_0$), whereas the second term represents the linear EV coupling involving the same mode. The parameter $b_n^\dagger b_n$ is the creation (destruction) operator for vibrational quanta within the harmonic ground state nuclear potential of molecule $n$. The pure electronic state $|n\rangle$ indicates that the molecule at $n$ is electronically excited to the first optically allowed state, whereas all other molecules remain in their electronic ground states. The Huang-Rhys (HR) factor $\lambda_n^2$ measures the shift in the equilibrium positions of the ground and excited state nuclear potentials. The excitonic coupling is mediated by $J_{mn}$ contained in the double summation term in Equation 1. This term also contains the configuration-dependent transition frequency offset for the $n$th molecule, $\Delta_n$, relative to $\omega_{0,0} + D$, where $\omega_{0,0}$ is the gas-phase 0-0 transition frequency and $D$ is the gas-to-crystal shift induced by aggregation. Finally, in all that follows open boundary conditions were utilized.

The Holstein Hamiltonian above was solved by expanding the eigenstates of the system in the two-particle approximation. The absorption, $A(\omega)$, and absorption dissymmetry, $g_{abs}(\omega)$, were then evaluated as follows:

\[
A(\omega) = \langle \sum_\alpha d^{\alpha}(C)\delta(\omega - \omega_{\alpha(C)}) \rangle_C \tag{2}
\]

\[
g_{abs}(\omega) = \frac{1}{A(\omega)} \langle \sum_\alpha R_{abs}^{\alpha}(C)\delta(\omega - \omega_{\alpha(C)}) \rangle_C \tag{3}
\]

The (dimensionless) line and rotational strengths are represented by Equation 4 and 5, respectively

\[
d^{\alpha}(C) = \mu^{-2} \langle G | \hat{M} | \psi^{(\alpha)} > \rangle^2 \tag{4}
\]

\[
R_{abs}^{\alpha}(C) = \frac{4i}{c\mu^2} \langle G | \hat{\mathbf{m}} | \psi^{(\alpha)} > < \psi^{(\alpha)} | \hat{\mathbf{M}} | G > \tag{5}
\]

Here, $|G>$ is the aggregate’s electronic and vibrational ground state and $\prod_n | g_n; v_n >$ denotes a vibrationally excited state with a total of $\nu_t = \sum_n v_n$ quanta. Variables $\mathbf{m}$ and $\hat{\mathbf{M}}$ are the magnetic and electric dipole moment operators, respectively, with $\mu$ being the magnitude of the molecular transition dipole moment. In practice, the delta functions in Equations 2–3 were represented by Gaussian line shapes, with 1/e full widths of 0.16 eV.

### 5.5.2 Photophysical Characterization

Solutions were prepared by dissolving polymer 2 in chloroform. The solution used in the transient absorption measurement had an OD value of 0.4 and the solution used for the photoluminescence-decay-kinetics measurements had a concentration of 0.2 mg mL$^{-1}$. Films were spun from the polymer 2 in chloroform solution at a concentration of 10 mg mL$^{-1}$, with spin parameters of 2000 rpm and 60 s spinning time, in a nitrogen-filled glove box.

Transient absorption experiments were performed with the excitation at $\lambda = 500$ nm, using pulses of 150 fs duration, at a repetition rate of 1 kHz. A white-light continuum covering the spectral region from $\lambda = 530$ to 750 nm was generated in a 5 mm sapphire window from a part of the amplified Ti: sapphire fundamental at 800 nm pulses to probe the excited area of the sample. The
photoinduced transient absorption spectra were recorded using a diode array. The time delay between pump and probe pulses was compensated for chirp when measuring transient spectra. The excitation light was polarised at the magic angle (54.7°) relative to the probe light, except when anisotropy measurements were undertaken. The anisotropy data were obtained by measuring the transient absorption signals recorded at parallel ($\Delta I_{\parallel}$) and perpendicular ($\Delta I_{\perp}$) polarisations of the excitation and probe light. All measurements were taken at room temperature and films were measured inside a continuous gas flow environment.

The technique of time-correlated single photon counting (TCSPC) have been described in detail by Lakowicz.\textsuperscript{[274]} and by Silva et al.\textsuperscript{[267]} All measurements were taken at room temperature and films were measured inside a continuous gas flow environment.
Chapter 6

Photovoltaic behavior of perylene bisimide functionalized polyisocyanides

As explained in Chapter 3 perylene bisimides (PBI)s and especially well-organized PBI systems are of interest for application as n-type materials (acceptor) in photovoltaic systems. In this chapter we describe the investigation of photovoltaic systems incorporating polymers 2 and 3, which have well-defined PBI-arrays (Scheme 1). Monomeric PBIs 1a and b have been used for comparison in the studies described below.

![Scheme 1: PBI monomers 1 and PBI functionalized polyisocyanides 2 and 3 (see Chapter 4).](image)

The ordering of PBIs for the application in solar cells is important for several reasons: 1) it facilitates energy transport (ET) from an excited PBI site to a donor site where charge separation can occur; 2) it stabilizes charge separation (CS) through delocalization of the charges thereby minimizing the chance of charge recombination; 3) it allows fast charge transport (CT) to the electrode. Figure 1A illustrates these processes with a schematic representation of polymer 2 or 3 between two electrodes.

Ideally, the active layer of organic solar cells would consist of a blend of donor and acceptor molecules in which donor and acceptor are always in close contact for efficient charge separation (within 5–6 nm, which is the mean exciton diffusion length \[^{[275]}\]). Donor and acceptor molecules should also form continuous pathways to the corresponding electrodes for efficient charge harvesting. A schematic representation of such a heterojunction solar cell is shown in Figure 1B. Bulk heterojunction (BHJ) solar cells \[^{[276, 277]}\] are mainly prepared by casting a mixture of the donor and the acceptor, often followed by an annealing step, with the purpose to get phase

\[^{[x]}\] See appendix 1 and 2 for a short introduction on (organic) solar cells.
separation on the nanometer scale. In these cells, charge separation is often enhanced due to the close contact between the acceptor and the donor. Charge transport to the electrodes, however, might be hampered when donor or acceptor aggregates are isolated from the right electrode (Figure 1C).

Formation of these isolated aggregates might be circumvented by the use of extended aggregated structures such as the PBI arrays in polymer 2 and 3. PBIs in polymers 2 and 3 are pre-organized into long stiff arrays and can therefore form extended networks through the active layer, possibly connecting the majority of PBIs to the corresponding electrode (i.e., aluminum) (Figure 1D). The application of the two polymers in organic solar cells is discussed in this chapter.

![Figure 1: Schematic representations of organic solar cells with electron donor (D) and Acceptor (A) between Aluminum and ITO electrodes: A) illustration how the PBI arrays in polymers 2 or 3 can act in an organic solar cell. Upon excitation (hv) the PBI array facilitates the energy transfer (ET) to the donor site (D) where charge separation (CS) can occur, the negative charge can migrate to the electrode through the PBI array (CT); B) representation of an ideal solar cell morphology where excitons only need to travel a few nm to give charge separation and charges have a free pathway to migrate to their corresponding electrodes; C) representation of a phase separated morphology of the active layer; D) Representation of a network structure of an extended polymeric acceptor and a donor in the active layer.](image)

The preparation and performance of the photovoltaic systems incorporating either polymer 2 or 3 is described in Section 6.1 and the Kelvin probe Force Microscopy (KFM) study of photovoltaic cells of 2 is described in Section 6.2.
6.1 Photovoltaics

Photovoltaic devices were prepared with the active layer between front electrodes of indium tin oxide (ITO) / PEDOT:PSS and vacuum deposited back electrodes of lithium fluoride (1 nm) and aluminum (100 nm) (Figure 2). The active layer consisted of either polymer 2 or 3 as the n-type material and regioregular polythiophene (P3HT) as the p-type material.

Blends with weight ratios of the PBI polymer (either 2 or 3) and P3HT varying between 1:0 and 4:1 were spin cast at different rotation speeds (1500, 2500, and 4000 rpm) from CHCl₃, giving varying layer thicknesses; thin ( ~30 µm), medium (~60 µm), and thick (~120 µm). The current-voltage (J-V) characteristics of the cells were measured in the dark and under illumination with a tungsten halogen lamp at 75 mW cm⁻².

Figure 2: Preparation of the photovoltaic cells with active layers consisting of either 2 and P3HT or 3 and P3HT in different ratios. Top right: a photograph of a 2-P3HT cell, with the contact points to the LiF/Al and the ITO electrodes (ClIF/Al and CITO) indicated. The ITO contact point is created by scratching away a part of the active layer.
The results for the photovoltaic cells with an active layer consisting of polymer 2 and P3HT are shown in Figure 3. The power outputs for the different cells with different ratios of 2 and P3HT are depicted in Figure 3A. The best performances were obtained for the cells with the two polymers in a 1:1 weight ratio, which gave a maximum power output of 0.14 mW cm\(^{-2}\) for the thin cell. The performance of the cells is modest, however, under the same circumstances the power output of a cell with an active layer of monomeric di(hexylheptyl) perylenebismide (1a) and P3HT was revealed to be at least a 20-fold lower (Figure 3A). The external quantum efficiency (EQE) of the thin 1:1 P3HT:2 cell was found to be 8.2\% at 500 nm (Figure 3B). Measurement of the current-voltage (J-V) characteristics (Figure 3C and D) revealed an open circuit voltage \(V_{oc}\) of 0.62 V, a short circuit current density \(J_{sc}\) of 0.54 mA cm\(^{-2}\), and a fill factor (FF) of 0.338.

Annealing of the thick 1:1 P3HT:2 cell at 75 °C for 5 minutes did improve the power output by 40 \%. An increase in the \(V_{oc}\) and \(J_{sc}\) values, but a decrease in the FF value was observed. Annealing at higher temperature lowered the power output, with lower \(J_{sc}\) and FF values observed. The decrease in the FF value suggests that the annealing process does not improve the structure of the active layer in favor of charge transport to the electrode.
Figure 4: Performance of photovoltaic cells constructed from various blends of polythiophene P3HT and 3: A) power outputs of cells with different ratio’s of P3HT:3 spin cast with different layer thicknesses; B) spectral response for the medium 1:1 P3HT:3 cell; C) linear Current-Voltage (J-V) plots in dark (grey line) and under illumination (black line) for the medium 1:1 P3HT:3 cell; D) semilogarithmic J-V plot for the data in D.

The results for the photovoltaic cells with an active layer consisting of polymer 3 and P3HT are depicted in Figure 4. Again, the best performance in a series was obtained for the two polymers in a 1:1 weight ratio (Figure 4A). A power output of 0.10 mW cm\(^{-2}\) for the medium cell was obtained, which is comparable to the medium 1:1 cell incorporating polymer 2 (Figure 3A). The external quantum efficiency (EQE) of the thin 1:1 P3HT:3 cell was found to be 4.0\% at 560 nm (Figure 4B). Measurement of the current-voltage (J-V) characteristics (Figure 4C and D) revealed an open circuit voltage \(V_{oc}\) of 0.66 V, a short circuit current density \(J_{sc}\) of 0.42 mA cm\(^{-2}\) and a fill factor FF of 0.336.

The efficiencies of the solar cells incorporating polymers 2 and 3 in the active layer are modest compared to the state of art organic solar cells. Without optimizing the system, however, the energy efficiency does level with some of the better BHJ solar cells incorporating monomeric PBI compounds\(^{[203]}\) using a lower PBI content (see also Chapter 3). The slightly higher \(V_{oc}\) for the solar cells that incorporate 3 can be attributed to the fact that the LUMO (and HOMO) level of the PBIs in 3 are at a higher energy level than those of 2 due to the electron donating phenoxy groups in the bay area of the PBI\(^{[278]}\). The \(V_{oc}\) of a cell is determined by the energy gap between the HOMO of the donor (P3HT) and the LUMO of the acceptor (see Appendix 2).

The higher efficiency of polymer 2 compared with monomer 1a might be attributed to the improved percolation pathways facilitated by the PBI arrays in the polymer. To get more insight
into the structure–function relationship of the solar cells that incorporate polymer 2, Kelvin Probe Force microscopy (KPFM) measurements were carried out.

6.2 Kelvin Probe Force Microscopy investigations

Kelvin Probe Force Microscopy (KPFM) involves the use of a scanning probe to measure quantitatively, at high resolution, the potential of a surface with a lateral resolution of 10-100 nm and a potential resolution of a few mV. KPFM has been used to simultaneously characterize the morphology and surface potential of a wide variety of materials, such as organic acceptor-donor blends in transistors and in solar cells.

6.2.1 Surface potential of PV cells under illumination

AFM and KPFM measurements were performed on the photovoltaic blend of polymer 2 and P3HT of a solar cell (medium thickness) without an aluminum top electrode. The AFM image (Figure 5A) of this cell shows a surface that consists of intertwined bundles of fibers with cross-sections of circa 200 nm. Given the fact that both 2 and P3HT are known to self-organize into bundles of fibers upon spin-coating on a surface, and since all fibers have the same homogenous surface potential (SP) in the KPFM image (Figure 5B), it is impossible to distinguish polymer 2 and P3HT in the AFM or KPFM images. The polymers likely form a complex three-dimensional interpenetrated network of fiber-like structures.

When illuminated with white light, the blends show a significant photovoltaic activity, with the average surface potential getting more negative (darker, Fig. 5B, bottom). The average potential shift, calculated for different measurements performed with different tips, amounts to 90 ± 10 mV. This negative shift of the surface potential has been previously observed in KPFM on photoactive blends and is attributed to electrons being trapped in the blend under steady-state conditions while holes can move to the underlying anode. Also under light conditions, P3HT and polymer 2 cannot be distinguished.

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xiv The Kelvin Probe studies were performed at the Istituto per la Sintesi Organica e la Fotoreattività (ISOF) in Bologna.
Figure 5: AFM and KPFM studies on P3HT:2 films spin-coated on PEDOT:PSS: A) topographic image of a 60 nm thick film; B) corresponding KPFM image. Light was switched on during the measurement; C) measured SP variation when the sample is subjected to white light (60 mW cm$^{-2}$) illumination (white area) or not (grey area). Black lines show exponential fits of the charging and discharging process.

Figure 5C shows the response of the average surface potential (SP) going from the sample in the dark (grey area) to the sample under illumination (white area) and vice versa. The surface potential of $-23 \pm 2$ mV quickly decreases upon turning on the light and stabilizes at a value of $-113 \pm 4$ mV after several minutes. When the light is turned off, the SP value slowly returns to the value of $-23$ mV. Fitting of the measured SP trends to exponential curves (the first two curves are shown in black) gives time constants for charge separation and recombination of circa 45 and 1500 seconds, respectively. It appears that the surface remains charged for tens of minutes after turning off the light. The time constants are much longer than the photo induced charge generation ($\sim 10^{-12}$ s) or charge collection ($\sim 10^{-6}$ s) times and hence point to the dynamics of charge trapping and de-trapping. The charging–discharging dynamics on the second/minutes time scale suggest that the high, stable potential differences observed by KPFM are influenced by the presence of traps.

Light on-off cycles can be repeated several times without influencing the equilibrium surface potentials, suggesting that the observed variations are not influenced by photo-oxidation due to the presence of air.$^{xii}$

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$xii$ The KPFM measurements were performed under ambient conditions.
6.2.2 Surface potential of ultra-thin layers under illumination

With the purpose to be able to distinguish between P3HT and polymer 2 on the surface in order to get more insight into the process of charge separation between the two polymers, submonolayer-thick films of the two blended polymers were prepared on a flat surface of \( p \)-type Si(100) \((R \approx 10 \ \Omega \ \text{cm})\). Si(100) was used because it is very flat and steps or defects are absent in areas up to the micrometer scale. In addition and more generally it was used in view of its relevance in micro- and nano-electronics. The work function of Si is \( \approx 5.0 \ \text{eV} \),\[^{289}\] which is similar to the work function of the PEDOT:PSS substrate \( (5.0 \ \text{eV}) \)^{290} that was used for the preparation of the solar cells. The main difference with the PEDOT:PSS substrate is the presence of a thin layer \((1.5–2 \ \text{nm})\) of native oxide on the silicon surface. The deposited nanostructures can therefore be considered to be electronically insulated from the substrate, although partial charge transfer to the substrate can take place by electron tunneling, in view of the limited oxide thickness.\(^{291}\)

Figure 6A shows the AFM image of the P3HT:2 blend on Si(100). In Figure 6B and C the corresponding surface potential images, in dark and light respectively, as recorded by KPFM are displayed. Although the morphology is complex, two different kinds of structures can be observed namely, sparse, thick fibers (black arrow), which are surrounded by a more dense network of thinner fibers (white arrow). The thick fibers have an average width of \( 190 \pm 50 \ \text{nm} \) and a height of \( 17 \pm 3 \ \text{nm} \). The thin fibers exhibit an average width of \( 70 \pm 24 \ \text{nm} \) and a height of \( 3.5 \pm 1.0 \ \text{nm} \) (Figure 6B). Since all the observed fibers possess a cross-section that is much larger than the polymer diameters, they are composed of many bundled single polymer chains. The topography images do not offer information on the chemical composition of the observed features, however, the surface potential map obtained by KPFM reveals a clear contrast between the two architectures (Figure 6C). The surface potential of the thick fibers appears to be much more negative (darker in the KPFM image) than the silicon substrate, whereas the potential of the thin fibers is slightly more positive.
Figure 6: KPFM data on thin films of P3HT and P-PDI: A) AFM topography image of an ultra-thin blend of 2 and P3HT deposited on silicon; B) height profile of cross-section in a; C) surface potential image of the same area as in A), with no illumination and E) under white light (≈60 mW cm⁻²) illumination; D) and F) Measured (grey circles) and simulated (black lines) SP profiles obtained tracing an arbitrary line in the corresponding images C) and E). Z-ranges: A) 32 nm, C) 120 mV; and E) 120 mV

The potential difference observed between the two structures, which arises from a partial charge transfer between the two materials, indicates that the thick fibers are (mostly) composed of electron accepting polymer 2 and the thin ones of electron donating P3HT. The dimensions of the P3HT fibers are in good agreement with previous observations for fibers of P3HT.[292-294] The morphology of P3HT and polymer 2 in the blend (Figure 7C) is different from that observed for both polymers separately drop cast on a surface (Figure 7A and B). In the blend the P3HT strands adopt a stretched conformation bridging neighboring strands of 2. Polymer 2, on the other hand, forms large aggregated strands, probably due to the presence of P3HT (Figure 6A). Similar structures as in the blend, however, have been observed for samples of P3HT and 2 that were prepared in a different manner (Figure 7C insets and Figure caption).
Figure 7: AFM images of A) P3HT, B) polymer 2 and C) P3HT: 2 blend drop cast on SiOx. In C the insets show polymer 2 spin coated onto mica and P3HT onto SiOx. The aggregated form of 2 in the inset was obtained by exposing the sample to CHCl₃ vapor. Z ranges: (A) 20 nm, (B) 8 nm, and (C) 32 nm (inset: 2: 8 nm, P3HT: 6 nm). [294]

The KPFM images in Figure 6C and E, along with the corresponding potential profiles in Figure 6D and F (grey dots are cross-sections of lines in 6c and f), reveal that going from dark (6C and D) to light (6E and F) the overall surface potential becomes more negative. The clean areas that expose SiOx appear as positive patches with respect to the blend, due to charge transfer within the underlying substrate, as observed in thick layers as well. [285] In light, the KPFM resolution notably increases making it possible to resolve even the surface potential of single P3HT strands (white arrow in Figure 6E). More importantly, the surface potential difference between P3HT and 2 also changes.

To quantify this, it is important to realize that the surface potential differences between the nanoscale adsorbed architectures and the substrate, as measured by KPFM, are usually smaller than the actual difference, because the potential measured by the tip is governed by electrostatic interactions over a surface area much larger than the nanostructures. The effect of these long range interactions can be filtered out by using a recently developed procedure, in which the measured KPFM signal is deconvoluted from the transfer function of the microscope (see Experimental section). This procedure allows for the reconstruction of the surface potential image of the sample using a “charge image charge” model. From this model the true potential even of tiny nanometric structures can be obtained. [295, 296]

Figure 6D and F display the measured (grey dots) and simulated (black line) potential profiles measured in dark and under illumination, which are in good agreement. The deconvoluted
potential difference between polymer 2 and P3HT in the dark and in light are listed in the first row of Table 1.

**Table 1: Donor-acceptor potential differences**

<table>
<thead>
<tr>
<th>PBI</th>
<th>Donor-acceptor potential difference (P3HT-PBI)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Polymer 2</td>
</tr>
<tr>
<td>Dark</td>
<td>130</td>
</tr>
<tr>
<td>Light</td>
<td>210</td>
</tr>
<tr>
<td>Difference (light-dark)</td>
<td>80</td>
</tr>
</tbody>
</table>

The results can be compared with an analogous study by Liscio et al. on blends of P3HT and PBI 1b (Scheme 1). Figure 8 displays the topography and surface potential images of a film consisting of PBI 1b co-deposited with P3HT exposed to light. Large patches of amorphous P3HT (indicated by a 1 in Figure 8) are surrounded by smaller, more crystalline clusters of 1b (indicated by black and white arrows). The surface potential difference between 1b and P3HT, both in the dark and in light, are listed in Table 1. Different potentials were found for clusters of 1b that make contact with P3HT (black arrows, Figure 8) and for isolated clusters (white arrows). The summarized potential differences in Table 1 have been all corrected for broadening effects due to the finite KPFM tip size.

**Figure 8:** AFM and KPFM studies on 1b:P3HT blends. A) Topographic and B) corresponding KPFM images of a 1b:P3HT blend on native silicon oxide. The potential image is recorded under white light (60 mW cm\(^{-2}\)) illumination. Agglomerates of 1b are isolated (white arrows) or in contact (black arrows) with P3HT islands (marked with 1). C) and D) show the regions inside the boxes in A) and B) and reveal more detail on the morphology of the agglomerates of 1b, which are marked by a dot contour in the KPFM image. Z-ranges: A and C) 17 nm, B and D) 63 mV.
The numbers in Table 1 reveal that upon turning on the light, both in 2:P3HT and 1b:P3HT blends, the surface potential difference between acceptor and donor assemblies increases revealing a photovoltaic effect between the PBI and P3HT aggregates. The results between the two systems, however, differ.

Firstly, the potential difference observed between PBI 1b and P3HT, either with exposure to light or not, is much smaller than in the case of polymer 2 and P3HT. Secondly, the surface potential measured at different points on the thick fibers of 2 appears to be uniform within experimental error, which indicates a uniform level of charging of the material, whereas the charging of clusters of 1b in light varies greatly (Figure 8B and D). In particular, upon light irradiation the PDI clusters in contact with the P3HT island (black arrows) become much more negatively charged (they appear more dark in the KPFM image) than the clusters at a larger distance from any P3HT island (white arrows). Within individual aggregates (Figure 8D, marked by a dotted contour) it can also be seen that the part of the cluster in contact with P3HT has a higher negative charge, whereas the other part of the same cluster is less charged. This evidence indicates that the charges that are generated at the 1b:P3HT interface are strongly localized and do not diffuse very far from the acceptor-donor interface.

The AFM and KPFM results in Figure 6 indicate that, when deposited in ultrathin layers, polymer 2 and P3HT form architectures that are effectively phase-segregated yet interdigitated on the hundreds of nanometers scale. This structure thereby facilitates both a high contact area between the two materials and defined percolation paths for charges leading to effective and homogeneous charge separation. The uniform charging observed on thick and thin fibers shows that the photogenerated charges travel even tens of microns away from the visible 2:P3HT interfaces.

Although the acceptor-donor potential differences (Rows 1 and 2 in Table 1) observed for the blend that incorporates polyisocyanide 2 are much higher than those of the blend incorporating PBI 1b, the voltage build up upon illumination (light-dark difference, row 3 in Table 1) is the same and indicates that the electronic properties of polymer 2 are not significantly different from those of 1b.

Thin films of neat 2 or 1b adsorbed on native SiOx surfaces did not exhibit any change in potential upon light irradiation, whereas thin films of P3HT showed only a small and uniform (~70 mV) potential change, as can be expected due to the alignment of the P3HT HOMO level with the SP of the silicon substrate.[289, 290]

### 6.3 Conclusion

The PBI functionalized polyisocyanides 2 and 3, of which the syntheses have been described in Chapter 3, have been used for the preparation of photovoltaic cells. The photovoltaic cells do not match the state of the art power efficiencies of organic solar cells, but their performance is good when compared to photovoltaic systems of similar blends and much better when compared to cells incorporating a PBI monomer instead of a PBI functionalized polyisocyanide.

The improved performance of the polymer 2 in organic solar cells when compared to monomeric PBIs was further investigated by KPFM. KPFM measurements on the photovoltaic cells of polymer 2 and P3HT in dark and light revealed that a photovoltaic effect was taking place, but...
polyisocyanide 2 and P3HT could not be distinguished. On more diluted samples of polymer 2 and P3HT on silicon, the two polymer materials could be distinguished by their different surface potentials in the KPFM images. Upon turning on the light a photovoltaic effect between the two materials was observed. The increase in the surface potential difference between the two materials that was observed is comparable to that found in systems with P3HT and monomeric PBI, however, the charging of polyisocyanide 2 in the thin layer was much more homogenous than that of the monomer islands. This result shows that blends of polymer 2 and P3HT form well-interpenetrated networks with improved charge transport compared to blends incorporating monomeric PBI and is in line with the power outputs of the photovoltaic cells incorporating monomeric PBI and polymer 2.
6.4 Experimental

6.4.1 Solar cell preparation and current voltage measurements
Photovoltaic devices were prepared by spin-coating ~100 µL of a chloroform solution containing P3HT and polymer 2 or 3 in different ratios onto an ITO electrode covered with PEDOT:PSS. The mixtures were prepared by blending chloroform solutions of polymer 2 or 3 (10 mg mL⁻¹) in different weight ratios (see Figure 3A) with chloroform solutions of P3HT (10 mg mL⁻¹). The blends were spin-coated at different rotation speeds (1500, 2500 and 4000 rpm) giving films with different thicknesses (referred to as thin (~30 nm), medium (~60 nm), and thick (~120 nm)). The preparation of the solar cell was finished by depositing a top electrode of lithium fluoride (1 nm) and aluminium (100 nm) by vacuum deposition. The current-voltage (J-V) characteristics of the cells were measured in the dark and under illumination with a tungsten halogen lamp. UV and IR contributions were removed by a Schott GG380 and Schott KG1 filter, respectively. The final intensity of 75 mW cm⁻² generates a current density in these devices that was within ± 20% of the current density under solar illumination. This was confirmed by convolution of the spectral responses with an AM1.5 spectrum. For comparison, two cells in which polymer 2 is replaced by monomeric 1a were prepared.

6.4.2 Thin layer blends for KPFM measurements
The thin layers for the KPFM study were prepared by drop casting ~10 µL of a CHCl₃ solution containing both 2 (30 mg mL⁻¹) and P3HT (7.5 mg mL⁻¹) on silicon. Blended films of 1b:P3HT were prepared in a two step procedure starting from a concentrated solution of 1b (0.53 mg mL⁻¹) and a concentrated solution of P3HT (7.5 mg mL⁻¹) both in CHCl₃. First the 1b solution (10 µL) was drop cast onto SiOₓ. After 3 h, the P3HT solution (10 µL) was drop cast on top and the film was left to dry in air. The blend films have been prepared in an atmosphere saturated with vapors of CHCl₃ to slow down solvent evaporation and improve self assembling. The silicon substrate was cleaned prior to use with standard RCA procedure. In the ultra-thin layers used here very low concentrations of both materials were deposited at surfaces.

6.4.3 AFM / KPFM measurements
AFM combined with KPFM measurements were performed at room temperature in a sealed chamber filled with N₂ (RH < 10%) with a commercial apparatus (Multimode IIIA - Veeco equipped with Extender Electronics module). Antimony (n) doped Silicon tips were used. In order to obtain sufficiently large and detectable mechanical deflections, soft (k < 4 N m⁻¹) cantilevers with oscillating frequencies in the range 60 < ω < 100 KHz (SCM, Veeco) were employed. Both sides of the cantilever were coated with 20 nm of PtIr, with a buffer layer (3 nm) of Cr to improve the adhesion. To acquire “simultaneous” AFM and KPFM images, a topographic line scan was first obtained by AFM operating in Tapping Mode and then that same line is rescanned in Lift Mode with the tip raised to a lift height of about 20 nm. The basic principles of KPFM have been described in details elsewhere. In brief, KPFM provides a local measure of the Surface Potential (SP) differences between conductive tip and the sample.
Photovoltaic behavior of perylene bisimide functionalized polyisocyanides under investigation. SP is defined as: \((WF_{\text{tip}} - WF_{\text{sample}} - \Delta_{\text{pol}})/q\), where \(WF_{\text{tip}}\) and \(WF_{\text{sample}}\) are the work functions of the tip and the sample, \(\Delta_{\text{pol}}\) is the polarization induced by the tip, and \(q\) is the magnitude of the elementary charge. In the performed KPFM experiments, a bias voltage \((V_{\text{tip}} = V_{\text{DC}} + V_{\text{AC}} \sin \omega t)\) is applied directly to the tip holding the sample to the ground potential, \(\omega\) is the resonant frequency of the cantilever, \(V_{\text{DC}}\) and \(V_{\text{AC}}\) are a continuous and alternate bias, respectively. A feedback loop continually adjusts \(V_{\text{DC}}\) to nullify the force component at frequency \(\omega\) between the tip and the sample. \(V_{\text{DC}}\) is recorded as a function of the position yielding a map of the sample SP. The calibration and the optimization of the experimental parameters were achieved using the procedure proposed by Jacobs and co-workers.\(^{[300]}\)

Scanning Probe Microscopies are local probe techniques that reveal local features, which are not necessarily representative for the whole sample surface. Because of this, it is appropriate to record and process several images on different points of the sample surface. This makes it possible to minimize the influence of a particular sample area and to determine an average behavior. All the evaluations were carried out quantitatively and averaged over a large number of samples.

6.4.4 Deconvolution of the measured surface potential by KPFM.

The deconvolution of the surface potential (SP) of small nanostructures was performed by a method previously described by Liscio et al.\(^{[301]}\) The model is devised to remove the experimental artifact in the SP measurement due to the "effective area" of tip-sample interaction, and to calculate precisely the intrinsic SP of small nanostructures (i.e. asymptotic SP).

In brief, using the topography image we can distinguish the different regions corresponding to the three components: uncovered substrate, fibres of P3HT, and fibres of polymer 2. To each region, we assign the corresponding asymptotic SP value: \(SP_{\text{substrate}}\), \(SP_{\text{P3HT}}\), and \(SP_{\text{polymer 2}}\). The first two values can be directly obtained from the KPFM image because the corresponding regions are larger than the effective area. The "theoretical" distribution of surface potential obtained in this way corresponds to the ideal surface potential map measured by a KPFM with infinite resolution. This "theoretical" SP distribution is then convoluted with the effective area, which corresponds to the area of the surface that interacts electrostatically with the tip. This area depends on the tip radius and the tip-sample distance and is calculated with the method developed by Lyuksyutov.\(^{[302]}\) By convoluting theoretical SP distribution and effective area, the KPFM image can be calculated. The asymptotic value of the surface potential of fibers of polymer 2 \((SP_{\text{polymer 2}})\) is extrapolated by fitting the measured KPFM profiles to the calculated ones.
Chapter 7

Polyisocyanides in motion

7.1 Introduction

Polymerization of isocyanides derived from peptide units can yield long stiff polymers, such as 1 and 2, with lengths over 1 μm (Chapter 2). For polymer 1, single polymers with lengths even up to 14 μm have been observed by AFM when TFA was used as an initiator for the polymerization.[2]

![Polyisocyanides in motion](image)

The long stiff structures of polyisocyanides make it possible to easily map their topography by techniques, such as AFM, that have a nanometer resolution (Chapter 4 and 6). Polymers with a persistence length of 76 nm and lengths up to 14 micrometer, such as polymer 1, have an aspect ratio that fulfill the requirements to visualize its polymeric nature also by fluorescence microscopy, which has a resolution in the order of 300 nm. In contrast to AFM, fluorescence microscopy gives the possibility to record many images with short time intervals, thus making it possible to follow polymer movements in solution.

Obviously, the polymer needs to be fluorescent to be visualized by fluorescence microscopy. Polymer 2 fulfills this requirement due to the PBI side groups, even though the excimer–like fluorescence has a low quantum yield (Section 4.2 ). So far, however, no polymers of 2 were prepared with lengths close to 14 μm as was observed by AFM for polymer 1.

The study described in this chapter was preformed in collaboration with the Katholieke Universiteit Leuven (group of Prof. J. Hofkens).
This chapter describes the preparation of the random copolymer \( \mathbf{3} \), a polymer that combines the desired features of polymer \( \mathbf{1} \) and \( \mathbf{2} \) namely, micrometer lengths and a fluorescent functionality. The movements of these polymers in a polymer gel of \( \mathbf{1} \) have been studied by widefield fluorescence microscopy. The motions of the polymers are snakelike as described in the \textit{Reptation} theory by De Gennes\cite{303, 304}. Fluorescence microscopy movies are the first result in an attempt to relate actual visualized polymer movements to polymer physics’ theories such as De Gennes’ \textit{Reptation} theory. A short introduction on reptation theory is given below.

\textbf{7.1.1 Reptation theory}

The reptation theory, of De Gennes\cite{303, 304}, which was further developed by Doi and Edwards\cite{305, 306} and refined by others\cite{307, 308} is very successful in describing the dynamics of long polymer chains in a melt and in concentrated solution. The reptation theory is generally believed to be one of the most important mechanisms for polymer dynamics. It is important for understanding viscoelasticity and related mechanical properties that are important for applications in fields ranging from material science to biophysics.

In the reptation theory, the many-body problem of the motion of a chain entangled with many others is replaced by a model of a single chain in a “tube”, the tube representing the constraints from entanglement with other chains (Figure 1A). In this confined tube, movement of the polymer arises from the spontaneous formation and translation of defects (d, Figure 1B) along the polymer chain. At the end of the tube the polymer segments may retract into the existing tube (effectively shortening it) and subsequently diffuse into a new neighboring pore (stretching the tube) thus changing the tube contour at the end while the bulk of the tube does not change its shape. The result of these dynamics is a snakelike random motion, hence the name “reptation”.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Illustration of the reptation theory. (A) A single polymer chain in a tube with constraints from other chains. (B) Spontaneous formation and translation of defects along the polymer chain.}
\end{figure}
From reptation theory several relationships follow for single reptating polymers that can explain different macroscopic properties such as viscoelasticity.

The self diffusion coefficient of a single polymer \(D_{\text{rep}}\) scales with the polymer concentration \(c\) and the polymer mass \(M\) (or length) as:

\[
D_{\text{rep}} \sim c^{1.75} M^{-2}
\]

The viscosity \(\eta\) and the related reptation time \(T_r\), that is the time necessary for a polymer to diffuse a sufficient distance for all memory of the initial tube to be lost, was predicted to scale with \(M\) as:

\[
\eta \sim M^{3.4}
\]

However, in experiments \(\tau\) was found to scale with \(M^{3.4}\). These relationships and others have been investigated by several techniques such as Quasielastic light-scattering and Neutron scattering techniques. Direct observation of reptation has been achieved by fluorescence microscopy on actin filaments and DNA.

### 7.2 Synthesis and characterization

Polymerization of isocyanide 5 with TFA yielded very long polymers, as required for this study. The fluorescent isocyanide 4, however, does not polymerize under TFA conditions (Chapter 3). To obtain long polymers with fluorescent groups incorporated the copolymerization of isocyanides 4 and 5 (ratio 1:30) with TFA as initiator was attempted. After 36 hours of polymerization, the solution was gelated and a red baseline spot on TLC revealed the formation of a polymer incorporating monomer units of 4. Since isocyanide 4 alone does not polymerize with TFA, the incorporation of 4 into a polymer can only occur due to co-polymerization, and rules out the possibility of the formation of two separate homo polymers. Polymer 3 was prepared with differing molar ratios of monomers 4 and 5 from 1:500 to 1:30. For the
fluorescence microscopy measurements the 1:30 ratio, with the highest PBI content, gave the
best signal to noise ratio (*vide infra*).

**Scheme 2: (a) TFA / CH₂Cl₂**

The first attempt at the isolation of 3 involved the dropwise addition of the polymer solution to MeOH. Subsequently, the solid was collected either by filtration or centrifugation and decantation. The polymer lengths were checked by AFM before and after work-up. As can be seen in Figure 3A, before work-up polymers with length over 4 µm were visualized. After work-up, however, for the same sample only polymers with lengths shorter than 1 µm were found (Figure 3B). Apparently during work-up long polymers were lost. The same observation was made for polymers of 2 (Chapter 4) polymerized with 1/10.000 of Ni(II)-catalyst (see Figure 3C (before) and 3D (after)).

On one hand the presence of shorter polymers after work-up can be explained by the fact that not all material is able to be redissolved after precipitation. When specifically long polymers do not redissolve, fractionation takes place. Another explanation is that polymer strands are break during the work-up procedure. It is known that flows and turbulence in flows will break up polymers above a certain length. Filtration and centrifugation are probable causes of flows and turbulences.
To circumvent the loss of long polymers, a work-up procedure that keeps the polymer in solution was chosen. After reaction, the polymer gel was diluted and injected onto a GPC column and the polymer was collected in different fractions. Figure 3 shows the GPC trace of the reaction mixture and of two reinjected fractions. The traces of the two reinjected fractions show that fractionation was successful.

AFM images of the reaction mixture, the filtrered reaction mixture (treatment before injection on GPC), and of an early fraction collected from GPC, revealed that after GPC long polymers are still present (Figure 4A-C).
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Analogous to the synthesis of co-polymer 3, non-fluorescent polyisocyanide 1 was prepared with TFA as an initiator. During the polymerization process a transparent gel was formed and after three days, very little monomer remained. Without any work-up, the gel was used as the non-fluorescent matrix for fluorescence microscopy measurements. Samples were prepared by mixing fractionated polymer 3 (at low concentration) with the non-fluorescent polymer gel of 1.

7.3 Fluorescence microscopy imaging: Reptation

The mixed gel was placed between two glass covers and studied by fluorescence microscopy. Movies were recorded by taking images of the sample with a CCD camera every 50 milliseconds; the sample was illuminated at $\lambda=488$ nm. Figure 5A and B show a selection of images from two movies that were recorded. In the series of Figure 5A, a 5.3 $\mu$m long moving polymer is visible next to two fluorescent polymers that don’t move. The observed movement is reptation-like; the movement is along the contour of the polymer that is confined in a “tube” while the polymer ends are entering new “tubes” defined by the non-fluorescent polymer matrix.

---

Figure 3: GPC traces of polymer 3 and of two reinjected fractions that were collected.

Figure 4: AFM images of polymer 3 spin-coated on mica A) of reaction mixture; B) after filtration before GPC; C) after a GPC run.
Within about 380 seconds the polymer has lost its initial conformation. In Figure 5B reptation-like movements of a 3.5 μm long polymer in a different experiment are visible. In the upper series, dotted boxes are drawn to envisage parts of the “tube” that remain occupied by the polymer in many images, while the polymer ends are entering new “tubes”. The polymer in Figure 5B was seen to move at a much faster rate that in 5A; in circa 9 seconds the polymer had completely left its original “tube”.

The movies are the first result of fluorescence microscopy studies on polymer 3. Untill now the concentration of the polymer matrix was not controlled and during the measurement the solvent (CH$_2$Cl$_2$) was evaporating. At the moment it is therefore impossible to conclude whether the faster movement of the polymer in Figure 5B is due to the length of the polymer (smaller polymer and therefore faster) or due to a different concentration. As can be seen in Figure 5A, some polymers are not moving at all, which could be due to the fact that they also stick to the glass wall. The measurement conditions still need to be optimized to be able to do statistical measurements and correlate them to theory.

**Figure 5:** A) Selection of images from a fluorescence microscopy movie of a reptating polymer of 3 in a matrix of 1; B) images of another movie. The dotted boxes confine part of the “tube” made up by the polymer matrix that remains occupied by the fluorescent polymer during several images. No change in the shape can be observed on the polymer part within the dotted boxes. The numbers below the images give the time in seconds.
In addition to studying the reptation of these polymers, data can be extracted about the distribution of the end-to-end distance of a single polymer molecule. The end-to-end distance distribution for the polymer from the movie of Figure 5B is depicted in Figure 6. The end-to-end distance (R) versus the contour length (L) in principle gives information on the apparent stiffness of the polymer.\textsuperscript{317} Additional experiments in a controlled environment would allow deducing the persistence length (L\textsubscript{p}) of single polymer chains using the formula:

\[
R^2 = 4L_p^2 [L/L_p - 2(1 - e^{-L/(2L_p)})]
\]

according to the Kratky-Porod model.\textsuperscript{316, 322} Applying the formula on the data in Figure 6 results in an apparent persistence length of 196 nm for the observed chain.

\textit{Figure 6: Distribution of the end-to-end distance of the single polymer of Figure 5B during 75 seconds.}

\textbf{7.4 Fluorescence microscopy imaging: additional observations}

Several fractions from GPC, with detection times between 350 and 600 seconds after injection, were studied. In contrast to what would be expected, fractions that eluted later from the GPC column were found to contain the longest polymers; Figure 7 shows polymer molecules up to 7 \textmu m from one of the later fractions.

\textsuperscript{320} The factor 4 holds for chains confined in two dimensions.
At high illumination strength it was found that the polymers tend to split into two. Figure 8, displays several images of a movie that was recorded of a polymer molecule of 3 in an oligostyrene matrix that breaks two times during the recording. When the illumination intensity was decreased no polymer breaking was observed. Somehow the excitation energy seems to cause breakages in the polymer strands.

7.5 Conclusion and outlook

In this chapter the synthesis and isolation of micrometer long polyisocyanides of copolymer 3, which contains fluorescent PBI units, has been described. The isolation of long polymers was achieved by the fractionation of the reaction mixture on a GPC column. Preliminary results show that it is possible to follow the reptational movements of these polymers in a non-fluorescent matrix of polyisocyanide 1 by fluorescence microscopy. These observations make it possible to study polymer physics theories, such as the reptation theory by direct visualization of the motion of a single fluorescent polymer.
7.6 Experimental

7.6.1 General

CH$_2$Cl$_2$ was distilled from CaH$_2$ prior to use under atmospheric pressure and a nitrogen atmosphere. All other chemicals were commercial products and used as obtained, unless stated otherwise. Gel permeation chromatography was performed on a Shimadzu size exclusion chromatographer (SEC) equipped with guard column and a styragel®HT-6E (7.8 × 300 mm, Waters) column with differential refractive index and UV detection using chloroform as an eluent (1mL min$^{-1}$ at 30 °C). Fluorescence microscopy measurements were performed at the University of Leuven. Experimental details about the fluorescence microscope can be found elsewhere.$^{[323]}$

7.6.2 Synthesis of random copolymer 3

To a stirring solution of isocyano-L-alanyl-D-alanine methyl ester 5 (15.3 mg, 83 μmol) and isocyanide 4 (1.9 mg, 2.7μmol) in CH$_2$Cl$_2$ (3 mL) was added 0.1 M TFA (27 μL) in CH$_2$Cl$_2$. After 36 h the reaction mixture was gelated and on TLC (10% MeOH / CHCl$_3$) a red spot on the baseline was visible. The reaction mixture was diluted 2–3 times and filtered over a syringe filter (0.2 μm pore size). The solution (100 μl of 5–10 mg mL$^{-1}$) was injected onto GPC column and the fractionation was followed using UV detection at λ = 492nm. When, after ca. 350 sec, the first signal was detected, fractions of 0.5 mL were collected until the solution was colorless.

7.6.3 Synthesis of polyisocyanide 1 (D,L conformer)

Polyisocyanide 1 was synthesized according to a literature procedure.$^{[2]}$ For the polymerization of isocyano-D-alanyl-L-alanine methyl ester, 1/32 equivalents of TFA were used. The reaction mixture was not worked-up but directly used in the fluorescence microscopy study.

7.6.4 Sample preparation for fluorescence microscopy

Typically, to ca. 0.5 mL of a gel of 1 was added a drop (ca. 5 μL) of the fractionated solution of polymer 3 from GPC. A drop of ca. 10 μL was put between two glass cover plates that were cleaned with UV/O$_3$ before use.

7.6.5 Atomic Force Microscopy

AFM measurements of the polymer fibers of 3 were performed with a commercial apparatus AFM (Nanoscope III instrument, Digital Instruments.). A solution of the polymers (~ 10$^{-6}$ M in CHCl$_3$) was spun (1600 rmp) onto freshly cleaved Muscovite Mica. All images were recorded with the AFM operating in tapping mode in air at room temperature with a resolution of 512 × 512 pixels using moderate scan rates (1–2 lines sec$^{-1}$). Commercial tapping-mode tips (NT-MDT, NSG10) were used with resonance frequencies of 190–325 kHz.
Chapter 8

Nucleobase functionalized polyisocyanides

8.1 Introduction

This chapter describes the synthesis and characterization of (and towards) nucleobase functionalized polyisocyanides and block copolymers thereof.

Nucleobases are part of Nature's toolbox to create, through DNA and RNA, the molecular diversity that can be found in living organisms. The pathways of base pairing, DNA replication, and DNA / RNA transcription are intriguing and it is therefore understandable that a lot of research is focused on the mimicking of DNA and RNA.

Well-known is the DNA mimic PNA reported by Nielsen et al. [324] In PNA (peptide nucleic acid) the ribose-phosphate in the DNA backbone is replaced by 2-aminoethylglycine (Figure 1). Besides being self complementary, PNA also forms stable double helices with DNA and RNA[325-328] and can also be used as a template to transfer sequence information for RNA synthesis.[329, 330] The PNA backbone is not charged, hence the interactions between the polymers in PNA–DNA strands is stronger than in DNA–DNA strands because of the absence of charge repulsion. The duplexes between PNA and DNA or RNA are, in general, thermally more stable than the corresponding DNA–DNA or DNA–RNA duplexes,[331] the PNA–PNA duplex is the most stable one. These properties make PNA interesting for antisense and antigene applications; indeed the strong binding of PNA to messenger (m)RNA and high biological stability makes it possible to effectively inhibit translation of the target mRNA in the cell.[332]

![Scheme 1](image)

**Scheme 1**

Other DNA analogs with (i) high stability, (ii) high binding affinity toward complementary strands of DNA or RNA, and (iii) with potential applications as therapeutics using antisense strategies are morpholinos and locked nucleic acids (LNA) (Scheme 1).[332, 333] Morpholino is also a non-ionic DNA mimic with good blocker properties and has better solubility in water than PNA.[332, 334]
In contrast to PNA and morpholino, LNA is an ionic mimic with high affinity for ssDNA and ssRNA. Besides antisense applications, LNA also has been applied for the designing of probes and primer sequences.[335-338]

The above mentioned examples are designed as close mimics of DNA and are more (LNA) or less (PNA) structurally similar to DNA. Using polymerization methods, such as ATRP and ROMP, polymers functionalized with nucleobases that mimic DNA in a more conceptual way have been reported. These polymerization techniques can in principle give DNA mimics in high yields against lower costs. These polymers might be useful for all kinds of applications involving bio-recognition.[339]

Ilhan et al.[340] reported on thymine functionalized block copolymer 1 obtained via functionalization of a 1:1 random copolymer of styrene and 4-(chloromethyl)styrene in reaction with thymine-1-acetic acid. In a similar way a complimentary polymer functionalized with a diaminopyridine function was made. Unlike biopolymers such as DNA and RNA, these synthetic polymers are highly flexible and randomly substituted. By mixing the polymers in CHCl₃, 3.3 μm sized vesicle-like aggregates were obtained. By means of photoirradiation, the thymines could be partly cross-linked thereby stabilizing the vesicles and giving control of the size of the polymer. These systems were found to selectively incorporate CdSe particles functionalized with thymine groups.[341]

Lutz et al.[342] reported on an adenine functionalized copolymer of 9-(4-vinylbenzyl)-adenine and dodecyl methacrylate and its thymine functionalized counterpart (2), prepared via free radical polymerization. UV-Vis binding studies on mixtures of the two polymers revealed a melting behavior similar to that observed in DNA.

Marsh et al.[343] demonstrated that atom transfer polymerization (ATRP) can be used to synthesize well-defined homopolymers from silyl protected uridine (3) and also adenosine functionalized monomers. The nucleoside functionalized polymers were also polymerized from a solid support.[344]

Similarly, using ATRP, Spijker et al. synthesized block copolymers of polyethylene glycol (PEG) and either thymine or adenine functionalized polymethacrylate (PEG₄₅-PT₁₀ (4) and PEG₄₅-PA₁₀) in a controlled fashion.[345, 346] The two block copolymers form similar aggregates in water. In mixes of the two block copolymers, hydrogen bonding between adenine and thymine was observed and on average larger aggregates were seen. In a more recent paper, Spijker et al. showed that polymethacrylates functionalized with all four nucleobases can be prepared.[347]
Bazzi and Sleiman reported on the synthesis of adenine-containing block copolymer 5 using ring-opening metathesis polymerization of noncovalently protected monomers.\textsuperscript{348} Studies on the self-assembly of copolymer 5 revealed a cylindrical morphology, of which the shape was attributed to hydrogen-bond formation between the self-complementary adenine units in the micellar core.

The intention of attaching nucleobases to polyisocyanides is to create supramolecular scaffolds with well-organized arrays of nucleobases, thereby mimicking to some extend the nucleobase organization in single stranded DNA and RNA (ss-DNA and ss-RNA). Such a nucleobase functionalized polyisocyanide is interesting for a variety of reasons. On the one hand such a polymer can act as a template for any kind of polymerization of monomers that are functionalized with the complementary nucleobase\textsuperscript{347, 349} thereby mimicking the DNA transcription process (Figure 1, route a). On the other hand, mixing the synthetic polymer with (partly) complementary ss-DNA can lead to new biohybrid materials with biological activity.\textsuperscript{350, 351} Whereas ds-DNA has a helical pitch of 2.8–4.5 nm with 10.5 to 12 residues per turn, polyisocyanides have a helical pitch of 0.42 nm with \textit{ca.} 4 residues per turn. A biohybrid material of interacting ss-DNA and polyisocyanide might form structures as suggested in Figure 1 (route b) with the more flexible ss-DNA wrapped around the stiff polyisocyanide backbone.
8.2 Synthesis and characterization

8.2.1 Synthesis of adenine functionalized polyisocyanide 10

The synthesis route of adenine functionalized polymer 10 as shown in Scheme 3 was carried out to quickly test the possibility to synthesize nucleobase functionalized polyisocyanides and did not aim to obtain an optically pure polyisocyanide. Firstly, adenine was treated with 1 equivalent NaH and subsequently reacted with N-Boc 3-bromopropan-1-amine to obtain Boc-protected amine 6. After removal of the Boc-group by reaction of 7 with an excess of TFA in dichloromethane, amine 7 was coupled to N-formyl L-alanine using benzotriazol-1-yloxytris(dimethylamino)-phosphonium hexafluorophosphate (BOP) as a coupling reagent. BOP was used while it is known to prevent coupling of the amine to TFA. The latter reaction most likely leads to racemization of the alanine α-H as was explained before, (see chapter 3), which however was not further investigated. The thus formed formamide 8 was converted to isocyanide 9 by the action of diphosgene and NMM and in mixture of acetonitrile and THF (2:1) as a solvent.

Figure 1: proposed structure of nucleobase functionalized polyisocyanides and its possible function as template for other polymerizations (a) and for the creation of biohybrid materials with (partly) complementary DNA.
Scheme 3: Synthesis of polymer 10. (a) 1) Sodium hydride, DMF 2) N-Boc 3- bromoprop-1-amine; (b) TFA, CH₂Cl₂; (c) N-formyl-L-alanine, BOP, DIPEA, DMF; (d) Diphosgene, NMM, Acetonitrile / THF (1:2 v/v), -30°C; (e) Ni(II) in CD₂Cl₂, several conditions (see text).

The isocyanide was reacted with a Ni(II) initiator complex (complex 13 of Chapter 3) in CD₂Cl₂. Immediately an orange precipitate was formed while, according to ¹H-NMR, still most of the monomer was present. ¹H-NMR in DMSO-d₆ of the isolated precipitate revealed broad nmr-signals at roughly the same chemical shifts as for monomer 10 (Figure 2), confirming that polymer 10 had been formed, although in low yield. As for other polyisocyanopeptides (Chapter 2, 4 and refs [3, 130, 352]), the infrared spectrum of the polymer 10 revealed a red shift (from ν=1659 cm⁻¹ to ν=1643 cm⁻¹) in the amide-I region when compared to the spectrum of the monomer (Figure 3). At ν=2099 cm⁻¹ in the polymer spectrum, the azide vibration of the initiator is visible indicating that only short polymers are formed (compare with results in Appendix 3). Indeed no polymer structures could be visualized by AFM.

In an attempt to keep the polymer in solution during the reaction and to prevent termination due to precipitation, the reaction was carried out in DMSO-d₆. In this case no isocyanide was consumed according to ¹H NMR spectroscopy, not even after five days reaction time. The latter can be explained by the coordination of DMSO to the Ni(II) thereby preventing coordination of the isocyanide to the Ni(II) and thus polymerization.

In another attempt to keep the growing polymer in solution, succinimide was added to the polymerization in CD₂Cl₂ following the strategy described by Bazzi et al. [348] Upon hydrogen bond formation between adenine and succinimide the hydrophilic side of the adenine is shielded from the solvent, which improves the solubility of adenine in organic solvents. Under these polymerization conditions a precipitate was almost immediately formed. NMR and IR spectra of the worked-up precipitate were identical to those in Figures 2 and 3.
Chapter 8

8.2.2 Synthesis of adenine functionalized polyisocyanide 19

The results in Section 8.2.1 showed that it was possible to make adenine functionalized isocyanopeptides and polymers thereof although these were found to be short and only soluble in DMSO. This paragraph describes a more elegant route, to synthesize an optically pure isocyanide derived from two alanines. Instead of the direct coupling of N-formyl-L-alanine, the formamide was obtained by the Boc-protected intermediates to prevent epimerization. Instead of an amide linkage between the adenine and peptide parts, an ester linkage was chosen to limit the
number of amide bonds, with the intention to get a more soluble polymer in organic solvents.
The synthesis of polymer 19 is depicted in Scheme 4.

**Scheme 4:** Synthesis of polymer 19. (a) 1) Sodium hydride, DMF 2) 3-bromopropyl acetate; (b) K₂CO₃, MeOH; (c) DCC, DMAP, HOBt, Boc-l-alanine, DMF; (d) TFA / CH₂Cl₂; (e) BOP, DIPEA, Boc-d-alanine, DMF; (f) TFA / CH₂Cl₂; (g) sodium formate, ethylformate; (h) Diphosgene, NMM, THF, -30 °C; (i) Ni(ClO₄)₂ in CHCl₃/EtOH (94:6 v/v).

In the first reaction step, adenine was treated with 3-bromopropylacetate under basic conditions to yield the protected alcohol 11. Prior to this reaction 3-bromopropylacetate was synthesized by the esterification of 3-bromopropan-1-ol in a mixture of acetic anhydride and CH₂Cl₂. The refluxing of 11 in MeOH in the presence of a catalytic amount of K₂CO₃ yielded alcohol 12 quantitatively.

Compound 12 was coupled to Boc-L-alanine by using DCC as a coupling reagent in combination with DMAP and HOBt. After removing the Boc-group of 13 with TFA in CH₂Cl₂, Boc-D-alanine was coupled to amine 14 with BOP as the coupling reagent. The Boc-group of 15 was removed with TFA in CH₂Cl₂ and amine 16 was subsequently reacted in ethyl formate with sodium formate as a base to obtain formamide 17. Formamide 17 was converted into isocyanide 18 using NMM and diphosgene. Finally isocyanide 18 was polymerized by the catalytic action of
Ni(ClO₄)₂ (1/30 equiv.) with- and without the presence of an excess of succinimide. Both reactions were performed on small scale in a cuvette in order to be able to follow the reaction with CD spectroscopy. As was observed in the preparation of polymer 10, the addition of Ni(ClO₄)₂ to 18 in both reactions, resulted in a precipitate being formed and no CD effect could be observed.

The precipitate was not further characterized and the synthesis of a better soluble block copolymer of polystyrene and isocyanide 18 was pursued as described in Section 8.2.4.

8.2.3 Synthesis towards thymine functionalized polysisocyanides

Scheme 5 shows the synthesis towards the thymine functionalized isocyanide 25. Thymine propyl acetate 20 was synthesized following a procedure reported by Roy et al. Under microwave irradiation, thymine was doubly deprotonated using two equivalents of NaH and subsequently reacted with 3-bromopropylacacetate to yield 20.

COSY ¹H NMR spectroscopy confirmed that alkylation of the thymine had occurred at N-1 and not N-3 as described (see Section 8.5.1 for numbering); no COSY coupling between the NH and H-6 proton was observed. When less than two equivalents of NaH were used, the N-3 alkylated product (kinetic product) was the main one formed. The microwave reaction has a lower yield (43%) than some alternative procedures (e.g., first silylation of the thymine and subsequent selective N-1 alkylation, see Scheme 6 below), but it has the advantage of being only one step with a short reaction time and relatively good selectivity.

The acetate group of 20 was removed quantitatively to give alcohol 21 by treatment of 20 with a catalytic amount of base (K₂CO₃) in refluxing MeOH. Subsequently, 21 was coupled to Boc-L-alanine using HOBt, DMAP, and DCC to give 22. After Boc-deprotection of 22 with an excess of TFA, amine 23 was coupled to a second Boc-L-alanine using DIPEA and BOP to generate 24. Both coupling reactions (of 21 and 23) to Boc-L-alanine gave very low yields of the desired products (ca 16%). TLC and NMR spectroscopy of the crude reaction mixtures suggested...
complete consumption of the amine functionalized thymines (21 and 23), however, after purification only a small quantity of product, along with a lot of thymine and Boc-L-alanyl-L-alanine was found. The low yield, therefore, is thought to be caused by hydrolysis of the ester during column chromatography. It remains, however, unclear why hydrolysis is a problem in the synthesis towards thymine functionalized isocyanide 25, whereas in the synthesis of the adenine functionalized isocyanide 19 it is not. One possibility is the intramolecular involvement of the carbonyls of the thymine in the hydrolysis of 19.

To overcome the problem of hydrolysis, the amine functionalized thymine 29 was synthesized as a starting compound in the synthesis towards isocyanide 30. Thymine was converted to 26 using hexamethyldisilazane (HMDS) and trimethylchlorosilane (TMCS) according to a literature procedure. Silylated compound 26 was reacted with 1,3-dibromopropane to give 27. After converting 27 to 28 by reaction with NaN₃, 28 was converted to amine 29 by the Staudinger reaction using PMe₃ in THF / Water / NaOH. Amine 29 was isolated in the presence of sulfate salts. Synthesis towards isocyanide 30 will be the subject of further research.

Attempts to synthesize amine 29 from the alternative starting compound 32 by the reaction of the latter with either thymine or the silylated thymine 26 and N-Boc-3-bromopropan-1-amine were unsuccessful (Scheme 7). Reaction of thymine with N-Boc-3-bromopropan-1-amine gave, as concluded from NMR spectroscopy, bisalkylated thymine and unreacted thymine but no mono alkylated thymine 32. During the reaction of 26 with N-Boc-3-bromopropan-1-amine the Boc-group was lost (observed by ¹H NMR spectroscopy) and this resulted in the formation of multiple products.

**Scheme 6:** a) HMDS (3 equiv.), TMCS (0.5 equiv.), reflux, argon; b) 1,3-dibromopropane, DMF, 80 °C; c) NaN₃, DMF, 80 °C; d) PMe₃ / THF, THF / Water / 1 M NaOH (10:1:0.1, v/v).

**Scheme 7:** (a) 1) NaH, DMF 2) Boc-3-bromopropan-1-amine, 80 °C or 300 W microwave; b) N-Boc-3-bromopropan-1-amine, DMF 80 °C.
8.2.4 Synthesis of adenine functionalized isocyanide-styrene block copolymers

Polymerization experiments with isocyanide 18 showed that a solid precipitated from solution immediately upon addition of Ni(ClO₄)₂. As was shown for polymer 10, direct precipitation leads to short polymers that are only soluble in DMSO. For templating and hybridization experiments, longer polymers with a better solubility in other solvents (either organic or water) are desired.

In this paragraph the synthesis of block copolymer 33 is described (Scheme 8). The polystyrene block was introduced to increase solubility and therefore allows the formation of longer polyisocyanide blocks. The synthesis is analogous to the work described by Vriezema et al.[4, 130] and Cornelissen et al.[37] on other isocyanide-styrene block copolymers.

Isocyanide 18 was polymerized using 1/30 equivalents of nickel complex 34 to obtain block copolymer 33. Complex 34 (Scheme 8) was synthesized by the addition of polystyrene amine to Ni(C=N-iBu)₄(ClO₄)₂ in dichloromethane in a 1:1 molar ratio according to a literature procedure.[37] The polymerization reaction was performed both with (giving 33b) and without succinimide (giving 33a) present in the reaction mixture. Both reaction mixtures turned turbid during reaction time, but the reaction in the presence of succinimide remained clearer for a longer time. The reactions were followed by ¹H NMR spectroscopy. In time, the intensity of the isocyanide signals decreased and were replaced by broad, barely visible, signals in the baseline. From the measurements it was concluded that the polymerizations were finished after circa 40 hours, although not all monomer was consumed (40–50 % remained). The conversion of the reaction with succinimide present was higher than in the reaction without, which was confirmed by the intensity ratio of the adenine and styrene signals in the ¹H NMR spectra after work-up of the two polymers. It is, however, unclear whether this result is due to the presence of succinimide or due to slightly different reaction conditions (e.g., initiator-monomer ratio.). Block copolymers 33a and 33b were isolated from the reaction mixtures by precipitation from a chloroform / MeOH (99:1) solution in MeOH, followed by size exclusion chromatography, and again precipitation in MeOH.
Attempts to obtain a mass spectrum (Maldi, ES) of 33a and 33b were unsuccessful (see Section 8.5). From integration in 1H NMR spectrum it was estimated that circa 13 monomers of 18 had been incorporated in block copolymer 33b; this polymer was used in the aggregation experiments described in Section 8.3. In block copolymer 33a less monomers were incorporated.

8.3 Aggregation experiments with block copolymer 33

As has been shown by Vriezema and Cornelissen (Chapter 2)\[4, 37\] block copolymers of polyisocyanides and polystyrene have an amphiphilic character and form self assembled structures in water. This aggregation is explained by phase separation of the two blocks, and by the aggregation of the rigid polyisocyanide segments into (liquid-)crystalline domains. Block copolymers containing adenine functionalized isocyanides would be interesting candidates to form aggregated structures with numerous hydrogen bonding units (i.e., adenines) that are able to undergo interactions with complementary hydrogen bonding units (i.e., thymine).

This paragraph describes the aggregation behavior of block copolymer 33b (see Section 8.2.4).

8.3.1 Aggregation of 33 in water

Block copolymer 33b was dissolved in MeOH / THF (1:99 v/v). Methanol was needed as co-solvent to obtain a clear solution. Upon injection of this solution into Milli-Q water (injection volume / Milli-Q: 1/10) a cloudy suspension was formed. Drops of the solution were transferred onto a carbon grid and studied by transmission electron microscopy (TEM) and scanning electron microscopy (SEM).

The TEM and SEM images (Figure 4) revealed spherical aggregates. The spherical nature is supported by the shadowed image in Figure 4b, which shows that the objects have a height comparable to the width that is observed. The diameter of the aggregates ranges from 50 – 120 nm. Since block copolymer 33b in stretched conformation has a length of circa 17 nm (79 PS units of ~2 Å and 13 isocyanide units of ~1 Å) it is most likely that the observed aggregates correspond to vesicular structures, since micellar structures are not expected to be larger than circa 34 nm. To prove this, inclusion experiments with a fluorescent dye still need to be carried out.

Since the adenine polyisocyanide part of the block copolymer is more hydrophilic than the polystyrene it is expected that the polyisocyanide is situated on the outside of the vesicle bilayer (light part in Figure 4E) and the apolar polystyrene is shielded from the water on the inside of the bilayer (dark part in Figure 4E).
Figure 4: A–C) TEM images of aggregates of 33b on a carbon grid; (B) Pt shadowing was applied under an angle of 45°; D) SEM image of aggregates of 33b with Au staining; E) schematic representation of a vesicle.
8.3.2 Interaction studies of aggregates of 33b with thymine functionalized polymers

As explained above, the observed aggregates of 33b are expected to have many adenine groups on the outside of the spheres. It was therefore thought to be of interest to investigate whether the aggregates would interact with thymine functionalized polymers to form more complex structures. Three different thymine functionalized polymers were used in the following experiments: custom made single stranded thymine-DNA 6 (ss-T\textsubscript{100}) with a length of 100 repeating units, block copolymer PEG\textsubscript{45}-PT\textsubscript{10}, and triblock copolymer PEG\textsubscript{45}-PT\textsubscript{10}-PEG\textsubscript{45} (Scheme 9) that were synthesized and characterized by Spijker et al.\textsuperscript{345, 347, 349}

![Scheme 9](image)

The thymine functionalized polymers were added in different ratios to solutions containing the aggregates of 33b in Milli-Q water and in the case of the experiment with ss-T100 in a buffer of pH 7.4. The thymine functionalized polymers were added either one or four days after preparation of the solution of the 33b aggregates. Table 1 gives an overview of the performed experiments and the observations by TEM and SEM.

**Table 1: Overview of the amount of thymine polymers added to the aggregates of 33b. and the observations by TEM and SEM.**

<table>
<thead>
<tr>
<th>Equivalents of Thymine added</th>
<th>ss-T\textsubscript{100}</th>
<th>PEG\textsubscript{45}-PT\textsubscript{10}</th>
<th>PT\textsubscript{10}-PEG\textsubscript{45}-PT\textsubscript{10}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equivalents</td>
<td>0.01</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>Observations</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>

Experiments with “X” revealed no different aggregate architectures as compared to that of 33b only.
As shown in Table 1, only addition of five equivalents of PEG₄₅-PT₁₀ revealed a difference in the observed aggregates. By using SEM (EDX mode), the aggregates to which ss-T₁₀₀ was added were checked for the presence of phosphorus, which would prove the presence of DNA, however, no phosphorus could be detected.

The TEM and SEM micrographs of the aggregates to which five equivalents of PEG₄₅-PT₁₀ were added, revealed raspberry like aggregates, with diameters ranging from 300–800 nm (Figure 5). The smaller features on the outside of the aggregates have diameters in the range of 30–85 nm. The aggregates prepared here are much larger than those prepared from block copolymer of 3₃b alone (Section 8.3.1) or PEG₄₅-PT₁₀ alone. The latter polymer is known to form micellar structures with a diameter of circa 20 nm. [346, 349]

The images suggest that there is an interaction between the aggregates of 3₃b and PEG₄₅-PT₁₀. The observed structures are possibly micelles of PEG₄₅-PT₁₀ attached to the vesicles of 3₃b by base-pairing interactions between the adenines and the thymines (Figure 6). More investigations, however, are needed to learn more about the nature of these interactions and whether thymine-adenine base pairing is really playing a role in the aggregation (e.g., with IR and NMR spectroscopy). Inclusion experiments with fluorescent dyes can give insight into the aggregation structure of the spheres. For example, apolar dyes would be included in the micellar structures and within the bilayer of the vesicular structures, whereas polar dyes would be included in the interior of the vesicular structures. The structures could then be elucidated by fluorescence microscopy.

![Figure 5: TEM (A and B) and SEM (C and D) micrographs from solutions in which PEG₄₅-PT₁₀ was added to aggregates of block copolymer 3₃b.](image-url)
8.3.3 Aggregation of 33b in the presence of thymine functionalized polymers

In another set of experiments, 33b was injected into aqueous solutions containing the thymine functionalized polymers from Scheme 9. An overview of the experiments and the observation is given in Table 2. Experiments carried out with PT\textsubscript{10}-PEG\textsubscript{45}-PT\textsubscript{10} again revealed no different structures. Aggregates that were formed in the presence of PEG\textsubscript{45}-PT\textsubscript{10} did reveal different architectures, but the samples were found (SEM EDX mode) to be contaminated with NaCl and the results could therefore not be trusted. Due to shortage of material and time the experiments were not repeated.

<table>
<thead>
<tr>
<th>Equivalents of Thymine in solution</th>
<th>ss-T\textsubscript{100} in Buffer pH 7.4</th>
<th>PEG\textsubscript{45}-PT\textsubscript{10} in MilliQ</th>
<th>PT\textsubscript{10}-PEG\textsubscript{45}-PT\textsubscript{10} in MilliQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equivalents</td>
<td>0.01</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>Observations</td>
<td>X</td>
<td>Different</td>
<td>Different</td>
</tr>
</tbody>
</table>

For experiments with “?” the results were unclear due to contamination with salts. Experiments with “X” revealed no different aggregate architectures as compared to that of 33b.
The aggregates of 33b that were formed in the presence of one or ten equivalents of ss-T\textsubscript{100} were clearly different compared to the aggregates of 33b only. The SEM micrographs (Figure 7) revealed vesicular structures of circa 500–1200 nm with holes of circa 100–300 nm. The different structure of the aggregates is ascribed to the interaction of 33b with ss-T\textsubscript{100}. The buffer itself has no influence on the aggregation as can be concluded form the fact that no different structures were observed in the experiment in which only 0.01 equivalent of ss-T\textsubscript{100} was present in the buffer solution. It should be noted that in the presence of 1 and 10 equivalents of ss-T\textsubscript{100} there is a 70–700 fold excess of thymine present in solution. The nature of the interaction between the polymers is still unclear and could be the result of base pairing as well as of electrostatic interactions. Infrared and NMR spectroscopy could give more insight into this. One possibility to explain the holes is that the interacting ss-T\textsubscript{100} disrupts the spheres and stabilizes the holes by covering the apolar polystyrene and protect it from the water phase; the attraction between the adenines of 33b and the thymines of ss-T\textsubscript{100} should then overcome the repulsion between ss-T\textsubscript{100} and the polystyrene part of 33b.

**Figure 7:** A, B) SEM micrographs of 33b added to a solution containing one (A and B) and ten (C and D) equivalents of ss-T\textsubscript{100} in buffer pH 7.4.
8.4 Conclusion
Polyisocyanides functionalized with adenine (10 and 19) have been prepared. First steps in the synthesis towards thymine functionalized polyisocyanides have also been undertaken. Only short adenine functionalized polyisocyanides were formed due to fast precipitation of the polymer during polymerization. The polymers are therefore not very suitable as a template for other polymerization reactions or as a DNA mimic.

Block copolymers with polystyrene and adenine functionalized polyisocyanide 19 could be prepared due to the enhanced solubility, induced by presence of the polystyrene. From the \(^1\)H NMR spectrum it was estimated that circa 13 isocyanide units were incorporated into the block copolymer when the adenine protecting compound succinimide was added to the polymerization reaction.

The block copolymers were found to give vesicular structures in water as was demonstrated by TEM and SEM. When thymine functionalized block copolymers (PEG\(_{45}\)-PT\(_{10}\)) were added to the aggregates, modified structures were formed as seen by TEM and SEM, suggesting interactions between the adenine and thymine functionalized block copolymers. When aggregates of the adenine block copolymer were formed in the presence of single stranded thymine DNA (T\(_{100}\)) vesicular structures with holes were observed. More investigations are needed to elucidate the exact nature of the observed aggregates.
8.5 Experimental

8.5.1 General procedures

The following solvents were distilled prior to use under a nitrogen atmosphere at atmospheric pressure. CH$_2$Cl$_2$ and CHCl$_3$ were distilled from CaH$_2$ and CaCl$_2$ respectively, MeOH and THF from Na, and DMF from BaO. CHCl$_3$, CH$_2$Cl$_2$, and MeOH used for column chromatography were distilled (not dried) before use to remove high boiling stabilizers.

N-Formyl-L-alanine was prepared according to a literature procedure.[88] Amine functionalized polystyrene-79 (NH$_2$-PS$_{79}$) was obtained from Encapson. The nickel polystyrene complex Ni-PS$_{79}$ was synthesized according to a literature procedure.[36] All other chemicals were commercial products and used as obtained unless stated otherwise. Silica gel (0.035–0.070 mm, pore diameter 6 mm, Acros) was used for column chromatography and silica 60 F$_{254}$ coated glass plates (Merck) were used for thin layer chromatography.

$^1$H NMR were recorded on a Inova 400 MHz and $^{13}$C NMR spectra were recorded on a Bruker AC-300 MHz at room temperature. Chemical shift are reported in ppm relative to tetramethylsilane ($\delta = 0.00$ ppm). The following measurements were recorded at room temperature unless stated otherwise: FT-infrared on a ThermoMattson IR300 spectrometer equipped with a Harrick ATR unit where the compounds were measured as a solid; CD spectra on a Jasco J600 CD spectrometer equipped with a Peltier temperature control unit; electron impact ionization (EI) and chemical ionization (CI) mass spectra were recorded on a VG-7070E mass spectrometer; electrospray ionization (ESI) spectra on a Finnigan LCQ advantage max; MALDI-TOF spectra were measured on a Bruker Biflex III spectrometer.

The numbering of purine and pyrimidine rings in adenine and thymine, respectively, is shown in Figure 8.

![Figure 8: Numbering of the purine and pyrimidine rings adenine and thymine, respectively.](image)
8.5.2 Synthesis

**N-Boc 3-bromopropan-1-amine**

To a stirred solution of 3-bromopropylamine hydrobromide (10.00 g, 45.7 mmol) in CH$_2$Cl$_2$ (300 mL) at 0 °C, was added triethylamine (6.42 mL, 45.7 mmol). After 10 min di-tert-butyl dicarbonate (9.97 g, 45.7 mmol) was added. The reaction mixture was stirred overnight and then concentrated to a volume of 100 mL. The concentrated solution was washed with a saturated KHSO$_4$ solution (25 mL) and subsequently dried (Na$_2$SO$_4$). The organic layer was evaporated to dryness to yield N-Boc-3-bromopropan-1-amine as a yellow oil (10.87 g, 100%). Characterization corresponded to literature values.[356]

$^1$H NMR (δ ppm, CDCl$_3$): 4.67 (b, 1H, NH), 3.43 (t, 2H, CH$_2$-Br, $^3$J$_{HH}$ = 6.52 Hz), 3.26 (m, 2H, CH$_2$-N), 2.04 (m, 2H, CH$_2$CH$_2$CH$_2$), 1.43 (s, 9H, C(CH$_3$)$_3$).

FT-IR (cm$^{-1}$): 3249 (NH), 2970 (C-H), 1674 (amide), 1488, 1448, 1296, 1117, 1075.

**tert-Butyl-3-(adenin-9-yl) propylcarbamate (6)**

Adenine (3.00 g, 22.2 mmol) was stirred in DMF (300 mL) under argon for 2 h before a 60% oil dispersion of NaH (887 mg, 22.2 mmol) was added. The mixture was stirred for 1.5 h more and Boc 3-bromopropan-1-amine (5.72 g, 24.0 mmol) was added. After 15 h, the reaction mixture was evaporated to dryness and the crude product was purified by column chromatography (eluent: DCM / MeOH 95:5 v/v), yielding 6 (3.86 g, 60%) as a white powder.

$^1$H NMR (δ ppm, CDCl$_3$): 8.36 (s, 1H, purine H$_2$), 7.85 (s, 1H, purine H$_8$), 5.68 (br, 2H, NH$_2$), 5.32 (br, 1H, NH), 4.27 (t, 2H, N$_9$-CH$_2$, $^3$J$_{HH}$ = 6.53 Hz), 3.10 (m, 2H, CH$_2$-N), 2.04 (m, 2H, CH$_2$CH$_2$CH$_2$), 1.45 (s, 9H, C(CH$_3$)$_3$).

$^{13}$C NMR (δ ppm, CDCl$_3$, 75 MHz): 156.1 (C=O), 155.5 (C$_6$), 153.0 (C$_2$), 150.3 (C$_4$), 140.6 (C$_8$), 119.5 (C$_5$), 79.4 (C$_2$-(CH$_3$)$_3$), 49.0 (CH$_2$-NH), 37.1 (N$_9$-CH$_2$), 30.8 (CH$_2$CH$_2$CH$_2$), 28.4 (C-$(CH$_3$)$_3$).

FT-IR (cm$^{-1}$): 3318, 3178 (NH-stretch), 2973, 2932 (CH), 1690 (C(O)O), 1642 (amide I, NH$_2$), 1598 (NH$_2$), 1512 (amide II).[357]

**Adenin-9-yl-propan-1-amine (7)**

To a solution of 6 (2.85 g, 9.75 mmol) in CH$_2$Cl$_2$ (100 mL) was added TFA (5 mL, 67 mmol). The reaction was complete after stirring for 2 h as monitored by TLC (R$_f$ = 0, eluent: DCM / MeOH = 90:10 v/v). The reaction mixture was evaporated to dryness and the TFA salt of 7 was obtained as a green solid (2.98 g, 100%).

$^1$H NMR (δ ppm, DMSO-$d_6$): 8.31 (s, 1H, purine H-2), 8.30 (s, 1H, purine H-8), 8.10 (br, 2H, C$_5$-NH$_2$), 7.76 (br, 3H, CH$_2$-(NH$_3$)$^+$TFA$^{-}$), 4.27 (t, 2H, N$_9$-CH$_2$, $^3$J$_{HH}$ = 6.86 Hz), 2.80 (m, 3H, CH$_3$-(NH$_3$)$^+$TFA$^-$), 2.10 (m, 2H, CH$_2$CH$_2$CH$_2$).

FT-IR (cm$^{-1}$): 3060 (br) (NH$_3^+$; H$_2$O), 1676, 1201, 1133 (TFA).

**N-formyl-alanyl-(3-(adenin-9-yl)propyl)amine (8)**

To the TFA salt of 7 (502 mg, 1.64 mmol) in DMF (50 mL) was added DIPEA (0.5 mL, 3.02 mmol). After stirring the solution for 30 min, BOP (1267 mg, 2.86 mmol) and N-formyl-L-alanine (663 mg, 5.66 mmol) were added. After 2 days, according to TLC, all starting material had been consumed and the reaction mixture was evaporated to dryness. The crude product was
purified by column chromatography (Rf = 0.09, eluent: EtOAc / EtOH / H2O = 50:7.4 v/v/v), yielding 400 mg (53%) of 8 as a white solid.

1H NMR (δ ppm, DMSO-d6): 8.29 (d, 1H, NH-formyl, JHH = 7.47 Hz), 8.13 (s, 1H, purine H-2), 8.12 (s, 1H, purine H-8), 8.09 (t, 1H, CH2NH, JHH = 5.42 Hz), 7.99 (s, 1H, N-C(O)H), 7.19 (br, 2H, C6-NH2), 4.29 (m, 1H, CH2NH), 1.93 (m, 2H, CH2CH2CH2), 1.21 (d, 3H, CH3, JHH = 7.07 Hz).

13C NMR (δ ppm, DMSO-d6, 75 MHz): 171.7 (O=C-CHCH3), 160.6 (NCHO), 155.9 (C6), 152.3 (C2), 149.4 (C4), 140.8 (C8), 118.7 (C5), 46.9 (CHCH3), 40.6 (N9-CH2), 35.6 (CH2-NH), 29.3 (CH2CH2CH2), 18.3 (CH3).

FT-IR (cm−1): 3280, 3110 (NH-stretch), 2973, 2948 (C-H), 2875 (C-H-formyl), 1652, 1630 (amide I, NH2), 1609 (NH2), 1565, 1520 (amide II).

1-Isocyanoethylcarbonyl-(3-(adenin-9-yl)propyl)amine (9)

In a 3-necked flask under argon, equipped with a dropping funnel, formamide 8 (150 mg, 0.51 mmol) was dissolved in a THF / CH3CN mixture (30 mL, 2:1 v/v) and cooled to below -30°C using acetone / CO2. The solution was stirred and NMM (0.14 mL, 1.27 mmol) was added, followed by the dropwise addition of diphosgene (31 pL, 0.26 mmol) in dry THF (2 mL) over a period of 5 min. These last two steps were repeated two times until a total of 3.81 mmol NMM and 0.65 mmol diphosgene was added and the reaction mixture had turned yellow. According to TLC no starting material was left after the addition of the 1.3 equiv. of diphosgene. The reaction was warmed to 0 °C and quenched with 8 mL of an aqueous saturated NaHCO3 solution under vigorously stirring. After 10 min the reaction mixture was evaporated to dryness and directly purified by column chromatography (basic Al2O3, eluent: DCM / MeOH, 95:5 v/v). The isolated isocyanide fraction showed a spot on TLC at Rf = 0.10 (eluent: DCM / MeOH, 95:5 v/v), that turned yellow upon staining with a Ni(ClO4)2 solution in EtOH. Isocyanide 9 was obtained as a white powder in a yield of 32% (45.4 mg).

1H NMR (δ ppm, MeOD-d4): 8.23 (s, 1H, purine H-2), 8.15 (s, 1H, purine H-8), 4.42 (m, 1H, CH), 4.28 (t, 2H, N9-CH2, JHH = 6.83 Hz), 3.25 (t, 2H, CH2NH, JHH = 6.63 Hz), 2.10 (m, 2H, CH2CH2CH2), 1.57 (d, 3H, CH3, JHH = 6.94 Hz).

13C NMR (δ ppm, MeOD-d4): 169.4 (C=O), 159.7 (C=N), 157.4 (C6), 153.8 (C2), 150.8 (C4), 142.8 (C8), 120.1 (C5), 54.2 (CHCH3), 42.4 (CH2NH), 37.8 (N9-CH2), 30.7 (CH2CH2CH2), 20.3 (CH3).

FT-IR (cm−1): 3318 (br, NH-stretch), 2919 (CH), 2141 (C=N), 1658 (amide I, NH2), 1601 (NH2), 1571, 1545.

EI-MS: m/z = 288 [M+(CH3)]+, 273 [M]+, 219 [M−(CH3-NC)]+, 175, 148.

Polymerization of isocyanide 9 in CD2Cl2 (10a)

To isocyanide 9 (8.0 mg, 29.3 µmol) in CD2Cl2 (0.6 mL) was added an azide functionalized Ni(II) complex (13, Chapter 3, 0.84 mg, 1.22 µmol), which immediately resulted in precipitation of an orange solid. The mixture was evaporated to dryness, yielding an orange polymer that was only soluble in DMSO.
Nucleobase functionalized polyisocyanides

$^1$H NMR (δ ppm, DMSO-$d_6$): 8.13 (br, purine H-2/8), 7.19 (br, NH$_2$), 4.09 (br, CH ala; CH$_2$-N9), 2.89 (br, CH$_2$-NH), 1.91 (br, CH$_2$-CH$_2$-CH$_2$), 1.23 (br, CH$_3$).

FT-IR (cm$^{-1}$): 3360 (br, NH-stretch), 2102 (N$_3$), 1648 (amide I, NH$_2$), 1601 (NH$_2$), 1578, 1546.

Polymerization of isocyanide 10 in the presence of 5 equiv. succinimide in CD$_2$Cl$_2$ (10b)

To a solution of isocyanide 9 (8.0 mg, 29.3 pmol) in CD$_2$Cl$_2$ (0.6 mL) was added succinimide (15.1 mg, 152.4 pmol) and azide functionalized Ni(II) complex (13, Chapter 3(0.84 mg, 1.22 pmol)). Almost immediately an orange solid precipitated out of solution. Adding a larger excess (saturated) of succinimide, did not result in better solubility. The reaction mixture was evaporated to dryness. The solid was taken up in a small amount of DMSO, precipitated twice in MeOH, and collected by centrifugation for 15 min at 3500 rpm.

$^1$H NMR (δ ppm, DMSO-$d_6$): 8.14 (br, purine H-2/8), 7.19 (br, NH$_2$), 4.09 (br, CH ala; CH$_2$-N9), 2.89 (br, CH$_2$-NH), 1.92 (br, CH$_2$-CH$_2$-CH$_2$), 1.23 (br, CH$_3$).

FT-IR (cm$^{-1}$): 3361 (NH-stretch), 2098 (N$_3$), 1647 (amide I), 1601 (NH$_2$), 1578, 1546. [357] ESI-MS (with- and without ion trap) was unsuccessful.

Polymerization of isocyanide 9 in DMSO-$d_6$

To isocyanide 9 (8.4 mg, 30.7 pmol) in DMSO-$d_6$ (0.5 mL) was added azide functionalized Ni(II) complex (13,Chapter 3, 0.84 mg, 1.22 pmol)). The reaction was followed by $^1$H NMR spectroscopy, but no change in the $^1$H NMR spectrum was observed, even after 1 month.

3-Bromopropyl acetate

To 3-bromopropan-1-ol (12.01 g, 86.4 mmol) in CH$_2$Cl$_2$ (200 mL) was added acetic anhydride (41 mL, 433.7 mmol) and the solution was stirred for 16 h. After removal of the solvents, the product was isolated by vacuum distillation (42 °C, 20 mbar) to yield 3-bromopropyl acetate (10.89 g, 70%) as a colorless liquid.

$^1$H NMR (δ ppm, CDCl$_3$): 4.16 (t, 2H, CH$_2$O, $^3$J$_{HH}$ = 6.11 Hz), 3.43 (t, 2H, CH$_2$Br, $^3$J$_{HH}$ = 6.57 Hz), 2.14 (m, 2H, CH$_2$CH$_2$CH$_2$), 2.02 (s, 3H, CH$_3$).

FT-IR (cm$^{-1}$): 1280, 1275 (C-O-C stretch), 763, 751 (C-O-C def), 724 (C-Br).

3-(adenin-9-yl) propyl acetate (11)

Adenine (4.13 g, 30.6 mmol) in DMF (400 mL) under argon was stirred for 2h before a 60% oil dispersion of NaH (1.34 g, 33.5 mmol) was added. The mixture was stirred for 2 h more and 3-bromopropyl acetate (5.91 g, 32.6 mmol) was added. After 2 days the reaction mixture was evaporated to dryness and the crude product was purified by column chromatography (eluent: DCM / MeOH = 95/5; TLC: Rf = 0.20, eluent: DCM / MeOH, 90:10 v/v) yielding compound 11 (6.09 g, 85%) as a white powder.

Mp: 158 °C.

$^1$H NMR (δ ppm, CDCl$_3$): 8.36 (s, 1H, purine H-2), 7.81 (s, 1H, purine H-8), 5.67 (br, 2H, C6-NH$_2$), 4.31 (t, 2H, CH$_2$O, $^3$J$_{HH}$ = 6.93 Hz), 4.11 (t, 2H, N9-CH$_2$, $^3$J$_{HH}$ = 6.01 Hz), 2.26 (m, 2H, CH$_2$CH$_2$CH$_2$), 2.04 (s, 3H, CH$_3$).

$^{13}$C NMR (δ ppm, CDCl$_3$, 75 MHz): 170.4 (C=O), 155.2 (C6), 152.7 (C2), 149.8 (C4), 140.2 (C8), 119.6 (C5), 61.2 (CH$_2$O), 41.1 (N9-CH$_2$), 29.1 (CH$_2$CH$_2$CH$_2$), 21.0 (CH$_3$). FT-IR (cm$^{-1}$): 3312, 3106 (NH-stretch), 2937 (CH), 1729 (ester), 1660 (NH$_2$), 1601 (NH$_2$), 1575, 1243.
Chapter 8

CI-MS: $m/z = 264 \ [M+(C_2H_3)]^+$, 236 $[M+H]^+$, 192 $[M-(CH_2C=O)]^+$, 176 $[M-(CO_2CH_3)]^+$, 149, 136.

Elemental analysis: Calcd. for C$_{10}$H$_{13}$N$_5$O$_2$: C 51.06; H 5.57; N 29.77. Found: C 49.43; H 5.44; N 29.05.

Adenin-9-yl-1-propanol (12)

To 6.09 g (25.9 mmol) of 11 in 300 mL MeOH, 115 mg K$_2$CO$_3$ (0.88 mmol) was added and the solution was refluxed. After two hours, TLC ($R_f = 0.07$, eluent: DCM / MeOH, 90:10 v/v) indicated that no starting material was present and the reaction mixture was evaporated to dryness, yielding 4.89 g (quantitative) of 12 as a white powder.

Mp: 214 °C.

$^1$H NMR (δ ppm, DMSO-d$_6$): 8.13 (s, 1H, purine H-2), 8.10 (s, 1H, purine H-8), 7.17 (br, 2H, C$_6$-NH$_2$), 4.69 (br, 1H, CH$_2$OH), 4.19 (t, 2H, CH$_2$OH, $^3$J$_{HH} = 7.07$ Hz), 3.39 (t, 2H, N$_9$-CH$_2$, $^3$J$_{HH} = 6.13$ Hz), 1.94 (m, 2H, CH$_2$CH$_2$CH$_2$).

$^{13}$C NMR (δ ppm, DMSO-d$_6$, 75 MHz): 155.4 (C$_6$), 151.8 (C2), 149.0 (C4), 140.5 (C8), 118.4 (C5), 57.5 (CH$_2$OH), 40.2 (N$_9$-CH$_2$), 32.4 (CH$_2$CH$_2$CH$_2$).

FT-IR (cm$^{-1}$): 3270, 3100 (NH-stretch), 2934 (C-H), 1672 (C-O), 1602 (NH$_2$), 1574.

CI-MS: $m/z = 222 \ [M+(C_2H_3)]^+$, 194 $[M+H]^+$, 176 $[M-OH]^+$, 163 $[M-(CH_2O)]^+$, 149 $[M-(C_2H_5O)]^+$, 135 $[M-(C_3H_6O)]^+$.

Elemental analysis: Calcd. For C$_8$H$_{11}$N$_5$O: C, 49.73; H, 5.74; N, 36.25. Found: C, 49.60; H, 5.66; N, 36.37.

Boc-L-alanine-3-(adenin-9-yl) propanol ester (13)

To a solution of 12 (4.89 g, 25.3 mmol) in DMF (600 mL) was added DMAP (3.49 g, 28.6 mmol), HOBT (4.36 g, 28.5 mmol), Boc-L-alanine (9.81 g, 51.8 mmol), and finally DCC (5.85 g, 28.4 mmol). After 4 days of stirring the reaction mixture was evaporated to dryess and the resulting yellow product was subjected to column chromatography (eluent: DCM / MeOH = 95/5), yielding 13 (8.23 g, 89%) as a white powder (TLC: $R_f = 0.25$, eluent: DCM / MeOH = 90:10 v/v).

Mp: 124 °C.

$^1$H NMR (δ ppm, CDCl$_3$): 8.34 (s, 1H, purine H-2), 7.84 (s, 1H, purine H-8), 5.97 (br, 2H, C$_6$-NH$_2$), 5.24 (br, 1H, NH), 4.31 (m, 2H, CH$_2$-O), 4.31 (m, 1H, CH), 4.15 (m, 2H, N$_9$-CH$_2$), 2.27 (m, 2H, CH$_2$CH$_2$CH$_2$), 1.43 (s, 9H, C-(CH$_3$)$_3$), 1.38 (d, 3H, CH$_3$, $^3$J$_{HH} = 7.23$).

$^{13}$C NMR (δ ppm, CDCl$_3$, 75 MHz): 173.0 (CO$_2$-(CHCH$_3$), 155.2 (CO$_2$-N), 155.0 (C6), 152.3 (C2), 149.8 (C4), 140.5 (C8), 119.6 (C5), 80.0 (CO$_2$-(CH$_3$)$_3$), 61.6 (CH$_2$-O), 49.5 (CH), 40.7 (N$_9$-CH$_2$), 29.1 (CH$_2$CH$_2$CH$_2$), 28.5 (C-(CH$_3$)$_3$), 18.4 (CH$_3$).

FT-IR (cm$^{-1}$): 3330, 3201 (NH-stretch), 2975 (CH), 1744 (C=O ester), 1701, 1645 (amide I, NH$_2$), 1600 (NH$_2$), 1520 (amide II).

CI-MS: $m/z = 393 \ [M+(C_2H_5)]^+$, 365 $[M+H]^+$, 337 $[M+C_2H_3-Cd_8]^+$, 309 $[M+H^- (Cd_8)]^+$, 291 $[M+C_2H_3-(CO_2Cd_6H_8)]^+$, 264 $[M+H^- (CO_2Cd_6H_8)]^+$.

Elemental analysis: Calcd. For C$_{16}$H$_{24}$N$_6$O$_4$: C, 52.74; H, 6.64; N, 23.06. Found: C, 50.65; H, 6.68; N, 22.18.
Nucleobase functionalized polyisocyanides

L-Alanine-3-(adenin-9-yl) propanol ester (14)
To a solution of 13 (3.00 g, 8.23 mmol) in CH$_2$Cl$_2$ (100 mL) was added TFA (20 mL, 270 mmol). After stirring for 2h no starting material was present according to TLC (R$_f$ = 0 in DCM / MeOH, 90:10 v/v) and the reaction mixture was evaporated to dryness. The excess TFA was removed by three additional co-evaporations with MeOH (20 mL). Moreover, the product was taken up in H$_2$O and washed with CH$_2$Cl$_2$. The water layer was evaporated to dryness, yielding 4.50 g TFA salt of 14 as a sticky colorless solid. Without further characterization, this product was used in the synthesis of 15.

Boc-D-Alanyl-L-alanine-3-(adenin-9-yl) propanol ester (15)
To a solution of 14 (2.18 g, 8.23 mmol) in DMF (125 mL) was added DIPEA (4.1 mL 24.8 mmol) upon which the yellow/green solution turned yellow. Subsequently Boc-D-alanine (3.12 g, 16.5 mmol) and BOP (4.02 g, 9.07 mmol) were added to the reaction mixture. After 4 days, TLC showed that all starting material had reacted and the reaction mixture was evaporated to dryness and subjected to column chromatography (elucent: DCM / MeOH 95:5 v/v, TLC: R$_f$ = 0.19 in DCM / MeOH = 90:10 v/v) yielding a yellow oil. The oil was taken up in CHCl$_3$ (100 mL) and washed with an aqueous 10% (w/w) citric acid solution (20 mL), followed by a saturated aqueous NaHCO$_3$ solution (20 mL) and brine (20 mL). The organic layer was evaporated to dryness and 2.09 g (58%) of 15 was obtained as a white solid. Mp: 99 °C.

$^1$H NMR (δ ppm, CDCl$_3$): 8.35 (s, 1H, purine H-2), 7.86 (s, 1H, purine H-8), 6.93 (b, 1H, L-alanine-NH), 5.75 (d, 1H, D-alanine-NH, $^3$J$_{HH}$ = 7.66 Hz), 5.62 (br, 2H, C$_6$-NH$_2$), 4.51 (m, 1H, CH of L-ala), 4.33 (m, 2H, N$_9$-CH$_2$), 4.27 (m, 1H, CH of D-ala), 4.16 (m, 2H, CH$_2$-O), 2.27 (m, 2H, CH$_2$CH$_2$CH$_2$), 1.43 (s, 9H, C(CH$_3$)$_3$), 1.38 (d, 6H, CH$_3$ of L and D-ala, $^3$J$_{HH}$ = 7.09 Hz).

$^{13}$C NMR (δ ppm, CDCl$_3$, 75 MHz): 172.5 (CO$_2$-CHCH$_3$), 172.2 (O=C-CHCH$_3$), 155.6 (CO$_2$-N), 155.1 (C6), 152.2 (C2), 149.5 (C4), 140.7 (C8), 119.0 (C5), 80.2 (C$_3$-(CH$_3$)$_3$), 61.6 (N$_9$-CH$_2$), 49.9 (O=C-CHCH$_3$), 48.4 (CO$_2$-CHCH$_3$), 40.9 (CH$_2$-O), 29.0 (CH$_2$CH$_2$CH$_2$), 28.5 (C$_2$(CH$_3$)$_3$), 17.8 (CH$_3$ of L and D-ala).

FT-IR (cm$^{-1}$): 3319, 3198 (NH-stretch), 2978, 2935 (CH), 1738 (C=O ester), 1690, 1657 (amide I, NH$_2$), 1599 (NH$_2$), 1528 (amide II), 1163.

CI-MS: m/z = 436 [M+H$^+$], 362 [M–(C(CH$_3$)$_3$-OH)]$^+$, 336 [M–(CO$_2$-C–(CH$_3$)$_3$)]$^+$.  

D-Alanyl-L-alanine-3-(adenin-9-yl) propanol ester (16)
To a solution of 15 (1.98 g, 4.55 mmol) in CH$_2$Cl$_2$ (75 mL) was added TFA (10 mL, 135 mmol). After 2 h the reaction was completed according to to TLC (R$_f$ = 0, eluent: DCM / MeOH, 90:10 v/v). The reaction mixture was evaporated to dryness. The excess TFA was removed by two additional co-evaporations with MeOH (20 mL) to yield 16 as a brown oil. This product was used in the next reaction without any further characterization.

N-Formyl-D-alanyl-L-alanine-3-(adenin-9-yl) propanol ester (17)
To a stirred solution of 16 (1.98 g, 4.55 mmol) in ethyl formate (100 mL) was added NaOCOH (1.56 g, 22.9 mmol) was added and the reaction mixture was refluxed at 70 °C. After 2 days the reaction was completed (TLC: R$_f$ = 0.04 in DCM / MeOH = 90:10, v/v) and the reaction mixture was evaporated to dryness. The residue was dissolved in a small amount of MeOH and precipitated in CH$_2$Cl$_2$ (100 mL). The precipitate was further purified by column
chromatography (eluent: DCM / MeOH, 95:5 v/v) and formamide 17 was obtained as a white solid in 80% yield. Attempted recrystallizations in CH$_2$Cl$_2$ or THF were unsuccessful.

$^1$H NMR (δ ppm, DMSO-$d_6$): 8.43 (d, 1H, L-ala-NH, $^3$J$_{HH}$ = 6.97 Hz), 8.28 (s, 1H, purine H-2), 7.96 (s, 1H, N-formyl-OCH), 7.61 (br, 2H, C$_6$-NH$_2$), 4.43 (m, 1H, CH of D-ala), 4.23 (m, 3H, CH of D-ala and CH$_2$-O), 4.01 (t, 2H, N$_9$-CH$_2$, $^3$J$_{HH}$ = 6.12 Hz), 2.14 (m, 2H, CH$_2$CH$_2$CH$_2$), 1.27 (d, 3H, CH$_3$ of L-ala, $^3$J$_{HH}$ = 7.27 Hz), 1.21 (d, 3H, CH$_3$ of D-ala, $^3$J$_{HH}$ = 7.05 Hz).

$^{13}$C NMR (δ ppm, DMSO-$d_6$, 75 MHz): 172.2 (CO$_2$-CHCH$_3$), 171.8 (O=C-CHCH$_3$), 160.6 (N-formyl-O=CH), 158.1 (C$_6$), 157.7 (C4), 155.3 (C2), 151.5 (C$_8$), 118.8 (C5), 61.4 (N$_9$-CH$_2$), 47.7 (CO$_2$-CHCH$_3$), 46.4 (O=C-CHCH$_3$), 28.3 (CH$_2$CH$_2$CH$_2$), 18.6 (CH$_3$ of D-ala), 16.7 (CH$_3$ of L-ala).

S-(1-Isocyano)ethylcarbonyl-L-alanine-3(adenin-9-yl) propanol ester (18)

To a 3-necked flask equipped with a dropping funnel was added 17 (200 mg, 0.55 mmol) in THF (25 mL) and the solution was cooled below -30 °C with an acetone / CO$_2$ bath under argon. To the stirred solution NMM (0.15 mL, 1.4 mmol) was added, followed by the drop wise addition of diphosgene (33.2 pL, 0.28 mmol) in dry THF (2 mL) over a period of 5 min. These last two steps were repeated twice until a total of 4.1 mmol of NMM and 0.66 mmol of diphosgene were added to the reaction mixture that turned dark yellow. No starting material was left after addition of the 1.2 equiv. of diphosgene (according to TLC) and the reaction was warmed to 0 °C and quenched with an aqueous saturated NaHCO$_3$ solution (8 mL) under vigorously stirring. After 10 min of stirring, the reaction mixture was evaporated to dryness and directly purified by column chromatography (basic Al$_2$O$_3$, eluent: DCM / MeOH, 95:5 v/v; TLC: R$_f$ = 0.25, eluent: DCM / MeOH, 90/10 v/v, coloring agent Ni(ClO$_4$)$_2$ in EtOH). Isocyanide 18 was obtained as a white solid in a yield of 27% (51.8 mg). Recrystallization experiments from Et$_2$O, Et$_2$O / EtOH mixtures, CH$_2$Cl$_2$, and hexane were unsuccessful.

$^1$H NMR (δ ppm, CDCl$_3$): 8.34 (s, 1H, purine H-2), 7.83 (s, 1H, purine H-8), 7.11 (br, 1H, NH), 5.64 (br, 2H, NH$_2$), 4.54 (m, 1H, CH L-ala), 4.33 (m, 3H, CH D-ala, CH$_2$-O), 4.15 (m, 2H, CH$_2$-N9), 2.30 (m, 2H, CH$_2$CH$_2$CH$_2$), 1.68 (d, 3H, CH$_3$ D-ala, $^3$J$_{HH}$ = 7.12 Hz), 1.47 (d, 3H, CH$_3$ L-ala, $^3$J$_{HH}$ = 7.22 Hz).

$^{13}$C NMR (δ ppm, CDCl$_3$, 75 MHz): 171.8 (CO$_2$-CHCH$_3$), 168.6 (O=C-CHCH$_3$), 165.9 (C=N), 155.4 (C6), 153.0 (C2), 150.1 (C4), 140.6 (C8), 62.1 (N9-CH$_2$), 53.3 (O=C-CHCH$_3$), 48.7 (CO$_2$-CHCH$_3$), 40.5 (CH$_2$-O), 28.9 (CH$_2$CH$_2$CH$_2$), 19.6 (CH$_3$ of D-ala), 17.8 (CH$_3$ of L-ala).

FT-IR (cm$^{-1}$): 3322 (NH-stretch), 2989 (C-H), 2143 (C=N), 1737 (ester), 1642 (amide I, NH$_2$), 1598 (NH$_2$).


Polymerization of isocyanide 18 (19)

To a solution of 18 (10.3 mg, 29.8 µmol) in CHCl$_3$ (1.0 mL) was added a Ni(ClO$_4$)$_2$ solution (0.99 mL of 1mM Ni(ClO$_4$)$_2$·6H$_2$O in CHCl$_3$ / EtOH 94:6 v/v, 1.0 µmol), which immediately resulted in the precipitation of an orange solid. TLC indicated that most of isocyanide 18 was still present and was not further consumed. The addition of succinimide (14.8 mg, 142.1 µmol) or a large excess (saturated), did not result in a better solubility and no product was obtained from the reaction.
3-(Thymin-1-yl) propyl acetate (20)
Under microwave irradiation thymine (1.96 g, 16 mmol) was stirred with sodium hydride (2.0 equiv.) in DMF (50 mL) for 2 min (6 x 20 s, P = 300 W), after which time 3-bromopropyl acetate (2.3 g, 35.6 mmol, 2.3 equiv.) was added. The resulting solution was stirred and irradiated for 2 min (6 x 20 s, P = 300 W). The excess of NaH was quenched with water and the reaction mixture was evaporated in vacuo. The obtained solid was taken up in chloroform, the remaining salts were filtered off, and the filtrate was subjected to column chromatography (1% MeOH in CHCl3) to yield 0.59 g (43%) of a white solid.

\[ \text{1H NMR (δ ppm, CDCl3): 9.99 (s, 1H, NH), 6.97 (s, 1H, pyrimidine H-6), 4.08 (t, 2H, OCH}_2 \], 3.76 (t, 2H, NCH}_2 \], 2.01 (m, 2H, CH}_2CH}_2CH}_2 \), 1.85 (s, 6H, thymine CH}_3 \), C(O)CH}_3 \].

\[ \text{13C NMR (δ ppm, CDCl3): 170.7 (O=CH}_3 \), 164.6 (pyrimidine C-4), 152.6 (pyrimidine C-2), 140.4 (pyrimidine C-6), 110.5 (OCH}_2 \), 45.7 (NCH}_2 \), 27.7 (CH}_2CH}_2CH}_2 \), 20.6 (O=CH}_3 \), 12.1 (thymine CH}_3 \). \]

\[ \text{FT-IR (cm}^{-1} \): 3178 (N-H), 1735, 1662, 1661 (C=O), 1225 (C-O). \]

3-(Thymin-1-yl) propanol (21)
Compound 20 (0.526 g, 2.33 mmol) was refluxed in MeOH (100 mL) with a catalytic amount of K}_2CO}_3 (0.03 equiv.). After 3 h the reaction was complete according to TLC. The reaction mixture was evaporated to dryness and used directly in the synthesis of 22.

\[ \text{1H NMR (δ ppm, MeOD-d}_4 \): 7.17 (s, 1H, pyrimidine H-6), 3.84 (t, 2H, OCH}_2 \), 3.60 (t, 2H, NCH}_2 \), 1.93 (m, 2H, CH}_2CH}_2CH}_2 \), 1.85 (s, 3H, thymine CH}_3 \).

Boc-L-alanine-3-(thymin-1-yl) propanol ester (22)
To compound 21 (0.46 g, 2.5 mmol) in DMF (100 mL) was added Boc-L-alanine (1.0 g, 5.0 mmol, 2 equiv.), HOBt (0.37 g, 2.7 mmol, 1.1 equiv.), DMAP (0.03 g, 0.25 mmol, 0.1 equiv.), and finally DCC (0.58 g, 2.7 mmol, 1.1 equiv.). The reaction mixture was stirred for 4 days. DCU was filtered off and the filtrate was evaporated in vacuo. The solid was taken up in diethyl ether (Et}_2O \), filtered off, and any remaining DCU was filtered off again. The filtrate was evaporated to dryness and purified by column chromatography (5% MeOH in CHCl3) to yield 0.13 g (15%) of 22 as a colourless oil.

\[ \text{1H NMR (δ ppm, CDCl3): 9.37 (s, 1H, pyrimidine NH), 7.02 (s, 1H, pyrimidine H-6), 5.16 (d, 1H, ala-NH \], 3J_HH = 6.9 Hz), 4.20 (q, 1H, CHCH}_3 \], 3J_HH = 6.7 Hz), 4.12 (t, 2H, OCH}_2 \), 3.75 (t, 2H, NCH}_2 \), 3J_HH = 5.7 Hz), 2.03 (m, 2H, CH}_2CH}_2CH}_2 \), 1.83 (s, 3H, thymine CH}_3 \), 1.40 (s, 9H, C(CH}_3}_3 \), 1.35 (d, 3H, CHCH}_3 \), 3J_HH = 7.2 Hz).

\[ \text{13C NMR (δ ppm, CDCl3): 165.27 (O=C-ala), 151.54 (pyrimidine C-1), 141.52 (O=C-Boc), 135.73 (pyrimidine C-2), 126.09 (pyrimidine C-6), 110.40 (pyrimidine C-5), 78.89 (C(CH}_3}_3 \), 57.98 (OCH}_2 \), 45.39 (CH-ala), 37.49 (NCH}_2 \), 30.99 (C(CH}_3}_3 \), 27.88 (CH}_2CH}_2CH}_2 \), 17.81 (CH}_3-ala \), 12.29 (thymine CH}_3 \). \]

\[ \text{FT-IR (cm}^{-1} \): 3317 (N-H), 1685, 1683, 1650, 1627 (C=O), 1250, 1247 (C-O). \]

L-Alanine-3-(thymin-1-yl) propanol ester (23)
Boc protected amine 22 (0.13 g, 0.30 mmol) was dissolved in CHCl3 (50 mL) with an excess of TFA (10 mL). After 3 h TLC analysis (eluent: CH}_2Cl}_2/MeOH, 9:1 vv; ninhydrine staining)
showed complete conversion of 22 to free amine 23. The reaction mixture was evaporated to dryness. Without further characterization this product was used in the next coupling reaction.

**Boc-L-alanyl-L-alanine-3-(thymin-1-yl) propanol ester (24)**

Boc-L-alanine (0.12 g, 0.41 mmol, 1.1 equiv.) was added to 23 (0.17 g, 0.37 mmol) in DMF (50 mL). BOP (0.18 g, 0.41 mmol, 1.1 equiv.) and DIPEA (0.2 mL, 1.11 mmol, 3.0 equiv.) were subsequently added. The mixture was stirred for 8 h and evaporated to dryness. The crude product was taken up in CH$_2$Cl$_2$ and washed with Milli Q water. The organic layer was dried (Na$_2$SO$_4$), concentrated, and subjected to column chromatography (eluent: 2% MeOH in CHCl$_3$) yielding 17% of 6 as a white solid.

$^1$H NMR (5 ppm, MeOD-d$_4$): 7.22 (s, 1H, pyrimidine H-6), 4.17 (m, 4H, OCH$_2$CH$_2$CH$_2$CH$_2$CH-ala (2x)), 3.82 (t, 2H, NCH$_2$, $^3$J$_{HH}$ = 6.9 Hz), 2.06 (m, 2H, CH$_2$CH$_2$CH$_2$CH$_2$), 1.91 (s, 3H, thymine CH$_3$), 1.45 (s, 9H, C(CH$_3$)$_3$), 1.35 (d, 6H, CH$_3$ ala (2x), $^3$J$_{HH}$ = 7.0 Hz).

$^{13}$C NMR (5 ppm, MeOD-d$_4$, 75 MHz): 170.07 (2C, O=C-ala), 164.80 (pyrimidine C-4), 151.79 (O=C-Boc), 140.01 (pyrimidine C-3), 135.70 (pyrimidine C-6), 108.61 (pyrimidine C-5), 80.10 (C(CH$_3$)$_3$), 66.95 (OCH$_2$), 58.72 (CH-ala), 57.73 (CH-ala), 37.95 (NCH$_2$), 26.88 (CH$_2$CH$_2$CH$_2$), 16.29 (C(CH$_3$)$_3$), 11.04 (thymine CH$_3$).

**5-Methyl-2,4-bis(trimethylsilyloxy)pyrimidine (26)**

In a 100 mL two-necked round-bottom flask thymine (3.18 g, 25.2 mmol), 1,1,1,3,3,3-Hexamethylsilazane (16 mL, 75.8 mmol, 3.0 equiv.) and chlorotrimethylsilane (1.6 mL, 12.6 mmol, 0.5 equiv.) were sirred under reflux for 12 h under an N$_2$ atmosphere. After cooling to room temperature the solid was filtered off and the solvent was evaporated to dryness to give a colourless liquid in quantitative yield.

$^1$H NMR (5 ppm, CDCl$_3$): 7.97 (s, 1H, pyrimidine H-6), 1.96 (s, 3H, CH$_3$), 0.32 (s, 18H, Si(CH$_3$)$_3$ (2x)).

**3-(Thymin-1-yl)-1-bromopropane (27)**

Under a N$_2$ atmosphere, 26 (6.8 g, 25 mmol) and 1,3-dibromopropane (8 mL, 78.8 mmol, 3 equiv.) were dissolved in DMF (10 mL). The reaction was stirred at 80 °C. After 14 h, ice water (150 mL) was added to the reaction mixture and the solution was stirred for 30 min. The aqueous solution was extracted with CH$_2$Cl$_2$ (2 × 200 mL). The organic layers were combined, dried (Na$_2$SO$_4$), and the solvent was evaporated. The product, in a small amount of CHCl$_3$, was precipitated in heptane to give, after filtration, 27 as a white solid (3.3 g, 46%).

mp: 138°C.

$^1$H NMR (5 ppm, CDCl$_3$): 7.94 (br, 1H, NH), 7.06 (s, 1H, pyrimidine H-6), 3.88 (t, 2H, BrCH$_2$, $^3$J$_{HH}$ = 6.9 Hz), 3.44 (t, 2H, NCH$_2$, $^3$J$_{HH}$ = 6.0 Hz), 2.26 (m, 2H, CH$_2$CH$_2$CH$_2$), 1.93 (s, 3H, CH$_3$).

$^{13}$C NMR (5 ppm, CDCl$_3$): 163.3 (Pyrimidine C-4), 150.2 (Pyrimidine C-3), 140.1 (Pyrimidine C-6), 110.4 (Pyrimidine C-5), 46.8 (NCH$_2$), 30.7 (BrCH$_2$), 29.3 (CH$_2$CH$_2$CH$_2$), 11.8 (CH$_3$).

FT-IR (cm$^{-1}$): 3321 (N–H), 3031 (CH), 1674 (C=O), 616 (C–Br).

CI-MS: m/z= 247, 249 [M+H$^+$], 169 [M–Br+H$^+$].
Nucleobase functionalized polyisocyanides

3-(thymin-1-yl)-1-azidopropane (28)
Compound 27 (2.02 mg, 8.1 mmol) was dissolved in DMF (100 mL) and NaN₃ (3.2 mg, 49.7 mmol, 6 equiv.) was added. The mixture was refluxed at 80°C for 2 hours. After evaporation of the solvent, the compound was dissolved in CH₂Cl₂ (50 mL) and extracted with water (3 x 50 mL). The combined organic layers were dried (Na₂SO₄) to yield 97% (1.6 g) of compound 28 as a white solid.

1 H NMR (δ ppm, CDCl₃): 8.87 (br, 1H, NH), 6.99 (s, 1H, pyrimidine H-6), 3.79 (t, 2H, N₃CH₂, 3JHH = 6.9 Hz), 3.40 (t, 2H, NCH₂, 3JHH = 6.3 Hz), 1.94 (qn, 2H, CH₂CH₂CH₂, 3JHH = 6.6 Hz), 1.25 (s, 3H, pyrimidine CH₃).

13C NMR (δ ppm, CDCl₃): 164.0 (pyrimidine C-4), 150.7 (pyrimidine C-3), 140.3 (pyrimidine C-6), 110.9 (pyrimidine C-5), 48.2 (N₃CH₂), 46.0 (NCH₂), 28.0 (CH₂CH₂CH₂), 12.21 (CH₃).

FT-IR (cm⁻¹): 3365 (N-H), 3031 (CH), 2094 (N₃), 1670 (C=O).


mp: 96 °C.

3-(thymin-1-yl)-1-aminopropane (29)
To a mixture of THF / Water / NaOH (1 M) (10:1:0.1 v/v/v), 28 (630 mg, 3.0 mmol) was added. The solution was cooled to 0 °C and a solution of Me₃P / THF (1 M, 4.0 mL, 45.8 mmol, 15 equiv.) was added dropwise. The reaction was followed by regularly measuring samples with infrared spectroscopy. When no azide signal was observed (1.5 h), the mixture was evaporated to dryness. The residue was taken up in ethyl acetate and the product was extracted with water (3 x 50 mL). The aqueous layer was washed with CHCl₃ and Et₂O before being neutralized with a solution of NaHSO₄·H₂O (0.5M). Finally the solvent was removed by freeze drying the aqueous solution. The yield could not be recorded due to the presence of salts.

1 H NMR (δ ppm, D₂O): 7.51 (s, 1H, pyrimidine H-6), 3.89 (t, 2H, 4, 3JHH = 6.9 Hz), 2.09 (qn, 2H, CH₂CH₂CH₂, 3JHH = 7.8 Hz), 1.90 (s, 3H, CH₃).

13C NMR (δ ppm, D₂O): 166.9 (pyrimidine C-4), 152.4 (pyrimidine C-3), 142.1 (pyrimidine C-6), 110.7 (pyrimidine C-5), 44.9 (NCH₂), 36.1 (NH₂CH₂), 26.0 (CH₂CH₂CH₂), 10.8 (CH₃).

FT-IR (cm⁻¹): 3373, 3269 (NH, NH₂), 1648, 1631 (C=O).

Poly(styrene-block-18) (33a)
A solution of isocyanide 18 (3.85 mg, 11.1 μmol) in CD₂Cl₂ (1 mL) was added to an NMR tube containing a polystyrene functionalized Ni(II) complex (Ni-PS₇₉, 3.35 mg, 0.37 μmol). The reaction mixture turned orange, but no precipitation was observed. The reaction was followed by 1 H NMR spectroscopy and during time the color of the solution became darker orange. After 98 h no further significant changes in the NMR spectrum were observed. The CDCl₃ was evaporated from the reaction mixture and the remaining orange solid was dissolved in CHCl₃ (1 mL) with a drop of MeOH and subsequently precipitated in MeOH (25 mL). After centrifugation for 10 minutes at 3500 rpm, the supernatant was removed and the solid was purified by size exclusion chromatography (Sephadex LH20, eluent: CH₂Cl₂ / MeOH, 90:10 v/v). The orange compound was precipitated again in MeOH as described before and 3.0 mg of block copolymer 33a was obtained (42% yield).

1 H NMR (δ ppm, CDCl₃): 8.22 (br, purine H-2), 7.92 (br, purine H-8), 7.05 (br, PS-Harom), 6.58 (br, PS-Harom), 4.4-4.0 (br, CH-ala; CH₂-O; CH₂-N-9), 2.3-2.0 (br, CH₂CH₂CH₂-CH₂) 1.85 (br, CH-styrene), 1.45 (br, CH₂-styrene; CH₃-ala); 1.25 (br CH₃-ala).
Poly(styrene-block-18) (33b)

To a solution of isocyanide 18 (20 mg, 58 pmol) in CD$_2$Cl$_2$ (2 mL) were added succinimide (30 mg, 300 pmol) and a polystyrene functionalized Ni(II) complex (Ni-PS$_{79}$, 17.3 mg, 1.9 pmol). The reaction was followed by $^1$H NMR spectroscopy over which time the solution became darker orange. After 67 h the reaction mixture was evaporated to dryness. The crude product was dissolved in CHCl$_3$ (1 mL) with a drop of MeOH and precipitated (2x) in MeOH (25 mL). The solid was collected after centrifugation for 10 min at 3500 rpm. This material was subjected to size exclusion chromatography (2x, Sephadex LH20, eluent: CH$_2$Cl$_2$ / MeOH, 90:10 v/v) and again precipitated (2x) in MeOH following the same procedure as described above. This yielded 33b (1.0 mg, 3%) as an orange solid.

$^1$H NMR (δ ppm, CDCl$_3$): 8.22 (br, purine H-2), 7.92 (br, purine H-8), 7.05 (br, PS-H$_{arom}$), 6.58 (br, PS-H$_{arom}$) 4.4-4.0 (br, CH-ala; CH$_2$-O; CH$_2$-N9), 2.3-2.0 (br, CH$_2$-CH$_2$-CH$_2$) 1.85 (br, CH-styrene), 1.45 (br, CH$_2$-styrene; CH$_3$-ala); 1.25 (br CH$_3$-ala).

Maldi-tof experiments on 33b were unsuccessful. Different polymer matrix samples were prepared from the following solutions:

33b (1 mg mL$^{-1}$ in THF / MeOH 99:1 v/v) mixed 1:1 (v/v) with:
1) dithranol in THF (40 mg mL$^{-1}$);
2) trans 1,4-diphenyl-1,3-butadiene in THF (40 mg mL$^{-1}$);
3) trans-3-indole-acrylic acid in THF (40 mg mL$^{-1}$).

The samples were prepared with- and without the addition of 1:10 (v/v polymer) Ag-triflate solution (5 mg mL$^{-1}$).

8.5.3 Aggregation experiment with block copolymer 33b

Aggregates of 33b

In a typical aggregation experiment 50 µL of a solution of 33b (1 mg mL$^{-1}$; M$_w$$\sim$13200; from integration, $\sim$76µM) in THF / MeOH (99:1 v/v) was injected into ultra pure MilliQ water (0.5 mL). For the experiments in which ssT$_{100}$ was added to the aggregates, the aggregates were prepared by injecting the 33b solution (50 µL) into a buffer solution pH 7.4 (25 mM TRIS, 2 mM EDTA, and 50 mM NaCl in MilliQ water).

Addition of thymine functionalized polymers to the aggregates of 33b

To a solution with aggregates of 33b (0.55 mL, ca. 3.8 nmol) a thymine polymer (ssT$_{100}$, PEG$_{45}$-PT$_{10}$, or PT$_{10}$-PEG$_{45}$-PT$_{10}$) solution (5–130 µL) was added with concentrations (3–350 µM) to match the 33b-thymine polymer ratios shown in Table 1. The ss-T$_{100}$ polymer was dissolved in buffer pH7.4, PEG$_{45}$-PT$_{10}$ in THF, and PT$_{10}$-PEG$_{45}$-PT$_{10}$ in THF / MeOH / water (90:5:5 v/v). The thymine polymer solutions were added after 33b-aggregate preparation in aqueous solution.

Aggregate formation of 33b in the presence of thymine functionalized polymers

Thymine polymer (ssT$_{100}$, PEG$_{45}$-PT$_{10}$, or PT$_{10}$-PEG$_{45}$-PT$_{10}$) solutions (5–130 µL) were added to 0.5 mL of ultra pure water or buffer pH7.4 (in case of ss-T$_{100}$) in order to match the 33b-thymine polymer ratios in Table 2 corresponding to 3.8 nmol (contents of 50 µL of a 1 mg mL$^{-1}$ solution)
of 33b. When the aqueous solution was homogenized, 50 μL of the 1 mg mL\(^{-1}\) solution of 33b was slowly injected.

**TEM and SEM sample preparation**

TEM and SEM samples were prepared after 30 min or one day of injection by putting droplets of the solutions on pieces of parafilm using a Pasteur pipet. Cu/C grids were positioned on top of these drops for 1 min, and the excess of solvent was removed with filter paper. The grids were dried overnight prior to measurement. Samples measured by SEM were coated with a 1.5 nm thick Au-layer. To visualize the heights of the object on the grid the TEM samples were coated with Pt.
Appendices

Appendix 1: Definitions in the field of photovoltaics

External quantum efficiency (EQE)

External quantum efficiency (EQE) = incident photon to current efficiency (ICPE).
This value includes the efficiency of absorption, charge generation, and charge collection and is
defined as:

\[ EQE = ICPE = \frac{\# \text{ incident electrons}}{\# \text{ incident photons}} \]  

which for a certain wavelength (\( \lambda \)) is equal to:

\[ EQE(\lambda) = \frac{J_{sc}}{P_{in} \cdot \lambda} \]  

This formula can be derived from the following equations:

\[ P_{in} = h \cdot c \cdot (\# \text{ incident photons / sec}) = h \cdot \frac{c}{\lambda} \cdot (\# \text{ incident photons / sec}) \]

\[ \iff (\# \text{ incident photons / sec}) = \frac{1}{h \cdot c} \cdot \frac{\lambda}{P_{in}} \]  

and

\[ J_{sc} = (\# \text{ generated electrons/sec}) \cdot e \]

\[ \iff (\# \text{ generated electrons/sec}) = \frac{J_{sc}}{e} \]  

Combining (3) and (4) with (1) gives:

\[ \frac{\# \text{ generated electrons}}{\# \text{ incident photons}} = \frac{h \cdot c \cdot J_{sc}}{e \cdot P_{in} \cdot \lambda} \]

with \( \frac{h \cdot c}{e} \cdot 10^9 \approx 1240 \) (multiplying by a factor 10^9 gives \( \lambda \) in nanometers).

\( J_{sc} \) is the short circuit current density (mA cm\(^{-2}\)), \( P_{in} \) is the incident light power per cm\(^2\) (mW cm\(^{-2}\)), \( h \) is Planck’s constant, \( c \) the speed of light, and \( e \) is the elementary charge.

Power conversion efficiency (\( \eta \))

Power conversion efficiency (\( \eta \)) = \( \frac{P_{out}}{P_{in}} = \frac{(J \cdot V)_{mp}}{P_{in}} = \frac{J_{sc} \cdot V_{oc} \cdot FF}{P_{in}} \)

where \( (J \cdot V)_{mp} \) is the product of the voltage (V) and current density (J) at the maximum power point mp (the point in the J-V curve where the product of J and V is maximal), \( J_{sc} \) is the short
Apendices

circuit density (A cm\(^{-1}\)), \(V_{oc}\) the open circuit voltage, \(FF\) the fill factor (\(FF=\frac{(J \cdot V)_{mp}}{J_{sc} \cdot V_{oc}}\)), and \(P_{in}\) is the incident light power per cm\(^2\) (see Figure A.1).

A standardized \(P_{in}\) equals the average spectrum of the sun with a power of 100 mW cm\(^{-2}\) = 1000 W m\(^{-2}\) and is referred to as AM\(_{1.5}\).

\[\text{Figure A.1: Illustration of the characteristic values of a solar cell in a typical J-V plot.}\]

Appendix 2: Concepts in Photovoltaics

Figure A.2 shows the energy levels for a typical solar cell system with aluminum and ITO electrodes and an active layer consisting of an electron donor and acceptor. Figure A.2A shows the situation for an open circuit and B for a closed circuit. Going from the open to the closed circuit, electrons will flow from the aluminum (high work function) to the ITO (low work function) electrode giving an internal electric field. The electric field places the HOMO and LUMO levels of the active layer in a gradient. Under illumination electrons will flow, along the electric field gradient, to the aluminum electrode and a current is generated in a counterclockwise direction (according to the situation in Figure A.2B).

The potential of the cell that is built up under illumination in the open circuit (\(V_{oc}\)) is determined by the energy difference between the LUMO of the acceptor and the HOMO of the donor. The efficiency of charge separation is determined by the energy difference between the two HOMO levels, in cases where the donor is excited, and by the energy difference of the LUMO levels, in cases where the acceptor is excited. An acceptor with a higher LUMO level (less good acceptor) or a donor with a lower HOMO level (less good donor) will therefore lead to less efficient charge separation but also to a higher voltage.
Appendix 3: Experiments carried out to prove the azide end-functionalization of polymer 2.

The following experiments were undertaken to prove that by using nickel initiator complex 13 for the polymerization of isocyanides, the polymer contains a terminal azide functionality that can be used in a Huisgen [3 + 2] cycloaddition reaction with a compound that has an acetylene group (“click” reaction).[358]

In a test reaction isocyano-L-alanyl-D-alanine methyl ester (l,d-IAA) was polymerized with 13 (using the same procedure as described for the synthesis of polymer 2 in Chapter 4) with catalyst/monomer ratios of 1/500, 1/50 and 1/10 yielding polymers abbreviated as l,d-PIAA(500), l,d-PIAA(50), and l,d-PIAA(10), respectively (Scheme A.1).

**Figure A.2:** Energy diagram of an Al-ITO solar cell with an active layer of an electron donor and acceptor material (illuminated) under open (A) and closed circuit (B) circumstances.
NMR spectroscopy (\(^1\)H NMR and COSY) did not give any conclusive information about the presence of the azide group for any of the synthesized polymers. Although the polymer \(\text{L}_{,D}\text{-PIAA}(10)\) is expected to be relatively short, it is known that, because of the relatively fast propagation compared to initiation, the polymer is most likely much longer than 10 repeat units.\(^{[89]}\) Signals of the initiator functionality therefore are difficult to detect. Infrared spectroscopy, however, revealed for \(\text{L}_{,D}\text{-PIAA}(50)\) a very small and for \(\text{L}_{,D}\text{-PIAA}(10)\) a clear signal at 2097 cm\(^{-1}\) characteristic for the azide functionality (see Figure A3). Extra purification steps were taken to ensure that only \(\text{L}_{,D}\text{-PIAA}(10)\) was isolated and that the observed signal in IR was not caused by remaining initiator (see Experimental Section).

**Figure A.3: Infrared spectrum of \(\text{L}_{,D}\text{-PIAA}(10)\)**

To obtain further evidence \(\text{L}_{,D}\text{-PIAA}(500)\) was reacted with an acetylene-functionalized zinc protoporphyrin (ZnPP-acetylene, Scheme A.2).\(^{[359]}\) ZnPps have very high extinction coefficients (~10\(^5\) mol\(^{-1}\) L cm\(^{-1}\)) and therefore are ideal to use as probe molecules for detection with UV-Vis spectroscopy.\(^{[360]}\) \(\text{L}_{,D}\text{-PIAA}(500)\) and ZnPP-acetylene were reacted under Schlenk conditions with CuBr as catalyst and \(N, N', N''\text{-trimethyl- 1,2-ethanediamine (PMDETA)}\) as copper ligand in THF as solvent. After the reaction the unreacted ZnPP-acetylene was removed by precipitation, i.e., by pouring the reaction mixture into MeOH and subsequent washing of the solid with MeOH until the filtrate was colorless.

**Scheme A.2**
Absorption spectroscopy on the obtained solid in CHCl₃ clearly showed an absorption band at λ = 420 nm. The product and unreacted L,D-PIAA(500) were injected onto GPC column and the retention times were recorded at λ = 310 nm (absorption polymer) and λ = 420 nm (Soret band ZnPP). At both wavelengths the two polymers were detected at a retention time of ~500 s. The signals at 420 nm (Figure A.4A) were corrected for the polymer concentration by dividing the obtained signal by the area of the peaks measured at λ = 310 nm (Figure A.4A) resulting in the graph shown in Figure A.4B. The higher signal at λ = 420 nm for L,D-PIAA-ZnPP (PP-PIAA) compared to L,D-PIAA (PIAA) is a good indication that at least part of the polymer is attached to ZNPP-acetylene and hence part of the L,D-PIAA is functionalized with an azide group.
Finally, polymer 2 (Chapter 3) was reacted with 1,3,5-triethynylbenzene using CuBr and PMDETA as catalyst (Scheme A.3). This reaction could yield dimers and trimers of polymer 2 and was chosen because it will give higher mass that can more easily be detected by GPC. After 7 days, the reaction mixture was analyzed by GPC and compared with a solution of polymer 2 in THF. Differences between the GPC traces (Figure A.5, reaction mixture in black, polymer 2 in grey) were observed, however, the fractions collected from GPC and analyzed by AFM did not provide a clear indication of a higher mass product (dimer or trimer).

\[ \text{Scheme A.3} \]

**Figure A.4**: A) Baseline-corrected GPC traces of PIAA and PP-PIAA (detection at $\lambda = 420$ nm and 310 nm). B) Traces in (A) at 420 nm after correction for the polymer concentration as measured by the signal at 310 nm.

**Figure A.5**: GPC trace of the product of the reaction shown in scheme A.3 (reaction time 7 days, black) compared to the GPC trace of polymer 2 (grey).
**Experimental**

**l,d-PIAA**

The l,d-PIAA polymers (500, 50, 10) were synthesized using the same procedure as described for the synthesis of polymer 2 (catalyst complex 13). The l,d-PIAAs (50, 500) were isolated by precipitating the polymers from CHCl3 into MeOH / H2O (2:1 v/v). l,d-PIAA(10) was worked up by a different method. First, the polymer (20 mg) in CHCl3 (1 ml) was precipitated in a mixture of MeOH (15 mL) and EDTA in water (0.04 M, 13 mL). Subsequently, precipitation was repeated by pouring a chloroform solution of the polymer into MeOH / H2O (2:1 v/v, 20 mL). Finally, the precipitate in chloroform (10 mL) was washed with 10% (w/w) citric acid solution (10 mL) followed by 10% saturated bicarbonate solution (10 mL) mixed with 0.065 M EDTA solution (5 mL). The organic layer was dried (Na2SO4) to give the polymer as a solid (yield not determined).

The polymer was characterized by 1H NMR spectroscopy and found to have identical physical properties as previously reported.[88]

**FT-IR (cm⁻¹, ATR):** 3267 (NH), 2951 (C-H stretch), 2097 (N₃), 1746 (C=O ester), 1655 (amide I), 1531 (amide II).

**l,d-PIAA-ZnPP**

The reaction was performed under Schlenk conditions. To a suspension of l,d-PIAA(500) (18.3 mg, M > 93500 (500 units), < 0.2 μmol) and ZnPP-acetylene (1.4 mg, 2.17 μmol) in THF (1.5 mL) was added CuBr (2.3 μmol) and PMDETA (2.3 μmol, 100 μL of a stock solution containing CuBr (3.2 mg) and PMDETA (3.8 mg) in THF (1 mL)). After stirring for 50 hrs, the reaction mixture was diluted with CHCl3 (10 mL) and washed with an aqueous 0.065M EDTA solution (2×10 mL) and water (2×10 mL). The chloroform solution was concentrated (1 mL) and poured into MeOH (10 mL). The precipitate was washed with MeOH until the filtrate was colorless.

**UV-Vis (CHCl3):** λmax = 317, 418, 547 nm

**Di- or trimerization of polymer 2**

The reaction was performed under Schlenk conditions. To a solution of polymer 2 (5.8 mg, M < 3.5 × 10⁶ D (5000 units), >1.6 nmol) in THF (1 ml) was added 1,3,5-triethynylbenzene (6.9 × 10⁻⁵ mg, 0.46 nmol, < 1/3equiv., 20 μL from 0.023 mM solution in THF). To the mixture a 20-fold excess of CuBr and PMDETA was added (27 nmol, 100 μL from a 0.27 mM solution). The mixture was stirred for 7 days, diluted with CHCl3 (10 mL) and washed with a 0.065M EDTA solution (2×10 mL) and water (2×10 mL). The chloroform solution was concentrated 1 mL and poured into MeOH (10 mL) to give a red solid after drying. The solid was analyzed by GPC (see above).
Appendix 4: Comparison of the absorption and fluorescence spectra of H-aggregated PBIs with a dimer model compound.

The exciton model has been worked out qualitatively for perylene dimer U-PDI$_2$, which contains two PDIs precisely on top of each other (H-aggregate) (Figure A.6).

![Ref-PDI and U-PDI$_2$](image)

*Figure A.6: Chemical structure and cartoon of Ref-PDI and U-PDI$_2$.*

Figure A.7A shows the absorption spectra of Ref-PDI and U-PDI$_2$. The spectrum of the latter compound displays roughly the same features as the spectrum of polymer 2. Figures A.7B and C give a qualitative explanation for the observed absorption bands of Ref-PDI and U-PDI$_2$. In Figure A.7C the excitonic and all vibronic couplings are taken into account to explain the absorptions A–D and their relative strengths for U-PDI$_2$. The blue shifted transitions (C, D) have higher oscillation strengths according to the exciton model, but are also intensified due to the overlap with red shifted vibronic bands.

The same model can also explain the excimer-like emission observed in the dimer although the excimer formation probably also involves some lower lying exited states stabilized by charge transfer interaction. As shown in Figure A.8, the emissions to the ground state are of low intensity, because they are forbidden according to exciton theory, with relatively higher emission strengths to the vibronic levels. Therefore, as for polymer 2, a low fluorescence quantum yield $\Phi_f$ is observed with a high fluorescence lifetime $\tau$. 
Figure A.7: A) Absorption spectrum of Ref-PDI (grey) and U-PDI\textsubscript{2} (black); B) scheme of the vibronic $S_0$-$S_1$ transitions in the absorption spectrum of Ref-PDI; C) scheme of the vibronic transitions in the absorption spectrum of the exciton coupled system of U-PDI\textsubscript{2}.

Figure A.8: A) Fluorescence emission spectrum of Ref-PDI (grey) and U-PDI\textsubscript{2} (black); B) Scheme of the vibronic transitions in the emission spectrum of the excitonically coupled system of U-PDI\textsubscript{2}.
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enthousiasme is een mooi stuk onderzoek neergezet. Het plaatje op de achterkant van het
proefschrift is het beeldende bewijs van je creativiteit. Roy, bedankt voor al je inzet en heel
veel succes met je eigen promotieonderzoek.
Dankwoord

In mijn laatste jaar kwam Irene Gonzales bij Erik en mij stage lopen. Dear Irene, when you started your internship my life was really full of “peace”: At home there was Irene my girlfriend, back home Irene my mother and in the lab Irene my great Spanish student. You truly are a very peaceful person: always relaxed and full of joy. You started to work on the difficult thymine chemistry and later on you worked on bulky perylenes attached to polyisocyanides. At the very end of your internship we even succeeded, due to your enthusiasm and perseverance, to prepare and test solar cells of these perylene functionalized polyisocyanide. It was great to hear that you started a PhD in Spain in the field of photovoltaics. Irene it was fantastic to work with you!

Mijn laatste twee studenten volgden een stage van 10 weken. Als eerste kwam Wouter, die samen met Richard en mij gewerkt heeft aan een trimere van perylenen, een variant op de porphyrinetrimer van Richard’s onderzoek. In 10 weken heb jij heel veel bereikt en wij hebben alle drie erg veel uitdaging en lol gehad.

Gijs, jij was de allerlaatste student die bij mij kwam stagelopen. Samen met Johan hebben we geprobeerd perylene-polymeren op een siliciumoppervlak vast te zetten. Dit bleek erg moeilijk, maar tijdens jouw 10 weken stage heb je wel een enorme berg werk verzet. Met de vracht polymeren die jij hebt gemaakt (en niet aan een oppervlak vast zaten) hebben ze in Cambridge nog een paar jaar plezier gehad. Ik ben benieuwd wat je na je studie gaat doen, maar met jouw enthousiasme voor zonnecellen kunnen we alle energieproblemen in Nederland wellicht oplossen.

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Enzo, thanks for the great time in Bologna and for the fruitful collaboration. I’m really happy with our Kelvin Probe publication in JACS and I wish you all the best in your further career. Andrea, thanks for all your answers to my questions on KPFM.

Also Mariangela from Sicily I want to thank for the light scattering measurements.

In Leuven heb ik samengewerkt met de groep van Johan Hofkens. Johan, Els en Hiroshi, jullie waren enorm gastvrij en het verblijf in Heverlee was elke keer weer een groot feest. Els, ik weet nog goed dat we met de fluorescentiemicroscoop voor het eerst onze polymeren zagen bewegen. Wat een leuk stuk onderzoek hebben wij gedaan!

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Dankwoord

Wanneer je moleculen maakt voor een toepassing, is niets zo leuk dan dat je ze ook werkelijk kunt testen. René Janssen en Martijn Wienk van de TU in Eindhoven hebben het mogelijk gemaakt dat ik mijn peryleenpolymeren heb kunnen testen in zonnecellen. Behalve voor het onderzoek dat ik met, en bij jullie mocht doen, wil ik jullie enorm bedanken voor alle tijd die jullie genomen hebben om mij alle in’s en out’s van zonnecellen te vertellen.

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Dankwoord

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Dankwoord

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Matthijs
Publications


Curriculum vitae

English
Matthijs Otten was born on January 6, 1978 in Nijmegen. In 1996 he graduated at ‘Het Dominicus College’ in Nijmegen and in the same year he started to study chemistry at the Radboud University Nijmegen.

He did his minor internship in the macromolecular physics group of Prof. J. Rabe at the Humboldt Universität zu Berlin under supervision of Prof. P. Samori an Prof. J.P. Rabe. During this internship he studied the physical properties of polymers on a surface by means of scanning probe techniques. His did his major in organic chemistry at the Radboud University Nijmegen in the group of Prof. R.J.M. Nolte under supervision of Dr. P. A.J. de Witte, Prof. A.E. Rowan and Prof. R.J.M. Nolte. The topic of his major was the synthesis and characterization of porphyrin functionalized polyisocyanides. In 2002 he obtained his masters degree in chemistry and started his PhD research at the organic chemistry department at the Radboud University Nijmegen. He conducted the research described in this thesis under supervision of Prof. A.E. Rowan and Prof. R.J.M. Nolte. Since May 2007 Matthijs is working as a researcher/consultant at CE Delft and is involved in developing innovative solutions to environmental problems.

Nederlands

He deed z'n bijvakstage in de macromoleculaire fysica groep van Prof. Rabe aan de Humboldt Universiteit zu Berlin onder begeleiding van Prof. P. Samori en Prof. J.P. Rabe. Tijdens deze stage heeft hij de fysische eigenschappen van polymeren op een oppervlak bestudeerd met scanning probe technieken. Zijn hoofdvakstage in organische chemie heeft hij afgerond in de groep van Prof. R.J.M. Nolte aan de Radboud Universiteit onder begeleiding van Dr. P.A.J. de Witte, Prof. A.E. Rowan en Prof. R.J.M. Nolte. Het onderwerp betrof de synthese en karakterisering van polyisocyanides met porfyrinegroepen. In 2002 haalde behaalde hij zijn docteraal examen scheikunde waarna hij werd aangesteld als junior onderzoeker aan de afdeling organische chemie. Het onderzoek beschreven in dit proefschrift heeft hij uitgevoerd onder supervisie van Prof. A.E. Rowan en Prof. R.J.M. Nolte. Sinds mei 2007 is Matthijs werkzaam bij CE Delft als onderzoeker/adviseur en houdt hij zich bezig met het zoeken naar oplossingen voor milieuvraagstukken.