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Synthesis of small molecules and π -conjugated polymers and their applications in organic solar cells

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Synthesis of small molecules and π -conjugated polymers and their applications in organic solar cells

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University of Groningen, The Netherlands

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Synthesis of small molecules and π -conjugated polymers and their applications in organic solar cells

PhD thesis

to obtain the degree of PhD at the
University of Groningen
on the authority of the
Rector Magnificus prof. C. Wijmenga
and in accordance with
the decision by the College of Deans.

This thesis will be defended in public on

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1

Introduction

1.1. Organic photovoltaic devices

Organic electronics has been the focus of a growing body of investigation in the fields of physics and chemistry for more than 50 years. Up to only a short time ago, organic electronic and optical phenomena have been the domain of “pure research”, somewhat removed from practical application.[1] The attraction of this field has been the ability to modify chemical structure in ways that could directly impact the properties of the materials when deposited in thin film form. While there was always a hope that organic materials would ultimately have uses in applications occupied by “conventional” semiconductors, for a long time their stability and performance fell well short of those of devices based on materials such as silicon or gallium arsenide. That situation changed dramatically in the mid-1980s, with the demonstration of a low voltage and efficient thin film light emitting diode by Ching Tang and Steven van Slyke at Kodak.[2] Although that particular first demonstration was not of sufficiently high performance to replace existing technologies, it nevertheless opened the door to the possibility of using organic thin films as a foundation for a new generation of optoelectronic devices.

Organic photovoltaic devices, based on π -conjugated small molecules or polymers, offer great opportunities for low-cost solar energy conversion, due to several technological advantages of organic materials.[3–7] The π -conjugation in these organic molecules and polymers results in typical energy gaps of 1 to 3 eV between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO), leading to semiconducting behavior and strong interactions with visible and near-infrared light. The maximum absorption coefficients of typical organic semiconductors are in the order of 10^5 cm^{-1} , which suggests that the use of 100 nm thick films can absorb most of the incident light. Compared to their inorganic counterparts, these organic electronic materials generally have significantly lower material costs and can be made into thin films using inexpensive room-temperature processes.[1, 8, 9] Organic materials are intrinsically compatible with flexible substrates and high-throughput, roll-to-roll manufacturing processes; hence they are ideally suited for the fabrication of large-area electronic and optoelectronic devices with low cost.[3],[6],[10, 11] Moreover, the electronic and optical properties of organic semiconductors can be tuned to a large extent with appropriate structure modifications during synthesis, leading to tailored materials properties for specific applications.[6] With low-cost materials and processes, some statistical studies have shown that photovoltaic modules based on organic semiconductors are expected to have a much shorter energy payback time and better environmental

sustainability with less greenhouse gas (CO_2) emission than inorganic photovoltaic technologies.[10],[12] In recent years, the performance of organic photovoltaic devices, including the efficiency and stability, has steadily improved, resulting from the development of new active materials and material processing/treatment methods, novel device architectures and internal/external optical structures to manage the light. In addition to PV applications, organic semiconductors have been used to produce organic light-emitting devices for lighting and displays,[2],[13, 14] field-effect transistors,[15] photodetectors,[16–18] and memory devices,[19] some of which have already been commercialized.[6]

1.2. π -conjugated polymers

A conjugated polymer is a carbon-based macromolecule through which the valence π -electrons are delocalized. *Trans*-polyacetylene, illustrated in Figure 1.1, is a linear polyene, whose ground state structure is composed of alternating long and short bonds. Also shown in Figure 1.1 are two other linear polyenes, *cis*-polyacetylene and polydiacetylene. The light emitting polymers, for example, poly(para-phenylene) (or PPP) and poly(para-phenylene vinylene) (or PPV), are characterized by containing a phenyl ring in their repeat units. PPP and PPV are illustrated in Figure 1.2.

trans-polyacetylene

cis-polyacetylene

polydiacetylene

Figure 1.1: The carbon backbone of some linear polyenes. The hydrogen atoms are not shown.

Research into the electronic, optical, and magnetic properties of conjugated polymers began in the 1970s after a number of seminal experimental achievements.

poly(*para*-phenylene) poly(*para*-phenylene-vinylene)

Figure 1.2: The carbon backbone of some phenyl-based light emitting polymers.

First, the synthesis of polyacetylene thin films (Itô et al. 1974) and the subsequent success in doping these polymers to create conducting polymers (Chiang et al. 1977) established the field of synthetic metals. Second, the synthesis of the phenyl-based polymers and the discovery of electroluminescence under low voltages in these systems (Burroughes et al. 1990) established the field of polymer optoelectronics. The interest in π -conjugated polymers increased considerably after the discovery that their electrical conductivity increases substantially upon electrochemical doping.[20, 21] This discovery led to the 2000 Nobel Prize in Chemistry awarded to Alan Heeger, Alan MacDiarmid, and Hideki Shirakawa. In comparison with inorganic materials and small-molecule organic semiconductors, conjugated polymers provide several advantages including low cost, light weight, and good flexibility. More importantly, soluble polymer semiconducting materials can be readily processed and easily printed, removing the conventional photolithography for patterning, which is a critical issue for the realization of large-scale roll-to-roll processing of printed electronics[22].

A large library of polymer semiconductors have been synthesized and investigated, since poly(*p*-phenylenevinylene) (PPV)-based polymer light-emitting diodes (PLEDs) were reported in 1990[23]. Organic chemists have developed huge amounts of building blocks, such as fluorene, carbazole, thiophene and its fused derivatives, benzothiadiazole and its derivatives, rylene diimides, and diketopyrrolopyrrole (see structures in Figure 1.3), which have been employed to design various polymers according to individual demands for specific applications. One particular approach

was the application of alternating donor (D) and acceptor (A) units to steer the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels, as well as the band gap of the resulting copolymers (so-called D–A polymers), which is an efficient strategy for tailoring the properties of conjugated polymers for applications in organic field-effect transistors (OFETs) and polymer solar cells (PSCs)[24].

Figure 1.3: Typical building blocks as fluorene, carbazole, thiophene and its fused derivatives, benzothiadiazole, diketopyrrolopyrrole, and rylene diimides.

To design conjugated polymers for different applications several general principles should be kept in mind, including (1) side chains to enhance the solubility and processibility, (2) high molecular weights, (3) band gap and absorption behavior, (4) HOMO and LUMO energy levels, and (5) suitable morphology with low barriers. These factors are dependent on each other and must be comprehensively considered for specific applications. For instance, side chains play a significant role for improving the solubility and the obtainable molecular weight of conjugated polymers, but also influence their intermolecular interactions through changes in morphology and thereby the charge carrier mobility. Tuning the energy band gap for obtaining the desired absorptions will usually change the HOMO and LUMO energy levels, and thus change the emitting color in an organic light-emitting diode (OLED) or influence the open-circuit voltage (V_{oc}) in a polymer solar cell (PSC). Therefore it is necessary to fully account for these designing principles and balance the guiding concepts in pursuit of ideal polymers for specific applications.

1.3. The synthesis of π -conjugated polymers

1.3.1. Introduction

As shown in the previous paragraphs π -conjugated polymers as semiconducting materials have attracted broad academic and industrial interest for various organic photovoltaic devices. To suit the particular needs of such a wide range of applications, tailor-made conjugated polymers must be designed and prepared. A critical aspect of conjugated polymers lies in their preparation as their optical and electronic properties are intrinsically linked to their extended conjugation pathway. Parameters such as molecular weight,[25–28] molar-mass dispersity,[29, 30] and the presence of structural defects[31, 32] are known to affect these properties, which in turn impact their performance in organic photovoltaic devices. Robust, reproducible, and reliable polymerization methods are therefore of utmost importance.

To obtain high molecular weight polymers with extended π -conjugation, multiple C–C bond couplings between two sp^2 or sp hybridized carbon atoms are necessary. Initial examples included the Ziegler–Natta polymerization of acetylene[33] and oxidative polymerization for the synthesis of poly(phenylene)s, poly(thiophene)s, poly(pyrrole)s, and poly(aniline)s.[34–37] Following these early methods, synthesis of poly(hetero-arene)s has increasingly relied on transition metal-catalyzed cross-couplings[38] such as Heck,[39] Kumada,[40] Negishi,[41] Suzuki,[42], Stille[43] and Sonogashira[44] polycondensations (Figure 1.4). The next paragraphs will give a short introduction of the most commonly used cross-coupling reactions for the synthesis of π -conjugated polymers.

The development of novel polymerization methods for producing conjugated materials is an ongoing topic. Prime candidates for improved synthetic methods are cross-coupling reactions which bypass the need for preactivated organometallic arenes and heteroarenes. The most recent example is direct (hetero)arylation polymerization (DHAP)[45], featuring palladium-catalyzed cross-coupling between (hetero)-aromatic C–H and C-halogen bonds (Figure 1.5). DHAP has imposed itself as an attractive method to procure well-defined and high molecular weight conjugated polymers and will be also discussed in this thesis.

1.3.2. Kumada cross-coupling

One of the first and most common cross-coupling reactions for C–C bond formation is the Kumada cross-coupling. The Kumada cross-coupling allows the rapid stere-

Figure 1.4: Overview of traditional C–C coupling techniques for the preparation of π -conjugated polymers.

Figure 1.5: Direct (hetero)arylation polymerization reaction.

oselective coupling between alkenyl- and aryl- halides or pseudohalides and aryl-, alkenyl-, and alkyl- Grignard or organolithium reagents, catalyzed by a nickel (or palladium) complex.[46] Although it is still not completely understood, a general mechanism[47, 48] of the Kumada cross-coupling is given in Figure 1.6.

To start the catalytic cycle the $Ni^{(II)}$ complex first has to be transformed, in situ, to the active $Ni^{(0)}$ complex through the transmetalation step which the R exchanges Mg for Ni and the reductive elimination step, leading to the active $Ni^{(0)}$. During this activation a small amount of Grignard reagent is lost and undesired homo-coupled products are formed. The yield of this homo-coupled side product is low ($< 1\%$) because of the low catalyst loading of these reactions. Next the active $Ni^{(0)}$ complex is oxidized to the $Ni^{(II)}$ complex by the addition of an organo-halide ($R'X$), which is called oxidative addition. Then again it is the transmetalation step which is found to be the rate determining step although the whole mechanism is not well understood. The organo-halide subsequently coordinates to the $Ni^{(II)}$ complex, and follows a reductive elimination step to release the homo-coupled product and the

Figure 1.6: General reaction mechanism for the Kumada cross-coupling reaction.

active $Ni^{(0)}$ and then oxidative addition of the organo-halide, leading to the $Ni^{(II)}$ complex, and completing the catalytic cycle.

From the catalytic cycle (Figure 1.6), the use of the Kumada coupling to synthesize conjugated polymers via the step-growth mechanism is very common, although the reaction can be limited by ineffective magnesium-halogen exchange or ineffective addition of the organic compound to the Grignard reagent. Slow magnesium-halogen exchange occurs in general when the aryl-halide contains more than two aromatic rings, leading to an increase in unwanted side reactions like homo-coupling.[49] Regioselectivity (regioregularity) in the polymerization of 3-alkylthiophenes has profound influence on the conductivity of the formed polymers. Regioregular polymers usually display much higher conductivity than their regioran-

dom forms. It is worth mentioning that McCullough et al. reported that 2-bromo-3-hexyl-5-bromomagnesiumthiophene formed *in situ* could be polymerized using $\text{NiCl}_2(\text{dppp})$ ($\text{dppp} = 1,2\text{-bis(diphenylphosphino)propane}$), producing head-to-tail coupled P3HT.[50] NMR showed that the polymers were 93–98% of the desired regio-chemistry.

In 2004, Yokozawa et al. found that Ni(dppp)Cl_2 ($\text{dppp} = 1,3\text{-bis(diphenyl phosphino)propane}$) catalyzed Kumada polymerization of 2-bromo-5-chloromagnesium-3-hexylthiophene followed chain-growth mechanism.[51] Since then, this new polymerization method, named Kumada chain growth polycondensation (KCGP), evolves very fast under the effort of researchers all over the world. Conjugated polymers with diversity of architectures, such as conjugated homo-polymers with well controlled molecular weights and chain-ends, rod-rod and rod-coil block co-polymers, and functional polymer brushes, have been prepared. Furthermore, KCGP will provide various new polymers with well-defined architectures for understanding the structure-property relationship of conjugated polymers, constructing novel functional nanostructures, and improving the performance of optoelectronic devices.

A major drawback of the Kumada cross-coupling is the low tolerance to reactive functional groups, such as amino-, nitrile-, ester- or carbonyl- groups and the sensitivity of the reaction to water.

1.3.3. Negishi cross-coupling

Negishi cross-coupling may be loosely defined as the palladium or nickel catalyzed cross-coupling reaction of organometals containing metals of intermediate electronegativity represented by Zn, Al, and Zr with organic electrophiles such as organic halides and sulfonates.[52] Since its discovery in the middle to late 1970s,[53, 54] Negishi cross-coupling has become a frequently used C–C bond formation method in modern organic synthesis.[55–58] Negishi cross-coupling, particularly with the use of organozinc reagents, has enabled cross coupling of all types of carbon atoms, namely sp , sp^2 , and sp^3 carbons, and essentially all possible combinations of various types of organozincs and electrophiles to form carbon–carbon bonds.[59] The generally accepted mechanism for Negishi coupling with organozinc reagents is shown in Figure 1.7. The reaction involves the oxidative addition of an organic electrophile, typically a halide or a sulfonate ester, to palladium⁽⁰⁾, transmetalation with an organozinc reagent, and reductive elimination to release the cross-coupling product and regenerate the catalyst.

Negishi coupling becomes the method of choice mainly because of a few bene-

$R, R' = \text{alkyl, alkenyl, aryl and alkynyl} \quad X = \text{Cl, Br, I, OTf, OAc}$

Figure 1.7: Mechanism of Negishi coupling with organozinc reagents.

facial factors to organic synthesis which distinguish it from other cross couplings using organometals of Sn (Stille coupling), B (Suzuki coupling), and Mg (Kumada coupling). First, Negishi coupling proceeds with generally high efficiency, namely high yields and high selectivities. Second, Negishi coupling has optimal balance between reactivity and chemoselectivity. Organozinc reagents are more reactive than their Sn and B counterparts, and can tolerate more functional groups than Grignard reagents. Third, Negishi coupling often proceeds under mild conditions. Unlike the Suzuki and Stille couplings, the cross coupling with organozinc reagents typically does not require a base or other additives. Another feature of Negishi coupling is its operational simplicity. The organometals (Al, Zr, and Zn) used in Negishi coupling can be generated in situ and used directly in the subsequent cross couplings. Last but not least, there are multiple convenient and inexpensive accesses to organozinc reagents including transmetalation with organolithiums and Grignard reagents, and particularly, direct zinc insertion in organic halides.[60–65] Unlike Stille coupling which uses toxic organostannes, Negishi coupling with organozincs is environmentally benign.

Negishi cross-coupling has been widely used for the synthesis of π -conjugated polymers such as polythiophenes, polyphenylenes and polyfluorenes. Regioregular, head-to-tail poly(3-alkylthiophenes) (P3AT) can also be prepared with excellent selectivity from the Ni-catalyzed cross coupling of the corresponding thiophenylzinc reagents.[66, 67] The polycondensation of these bifunctional organozinc reagents in the presence of catalyst $\text{NiCl}_2(\text{dppe})$ ($\text{dppe} = 1,2\text{-bis(diphenylphosphino)ethane}$) produced P3AT in greater than 97% head-to-tail regio-selectivity.

It was well accepted that Negishi cross-coupling using for synthesis of conjugated polymers proceeded by step-growth mechanism.[51, 68] However, following the report of Yokozawa in 2004,[51] McCullough and coworkers also reported a similar chain-growth polymerization of 2-bromo-5-chlorozincio-3-hexylthiophene, instead of the Grignard-type monomer, via the Negishi coupling reaction.[69] Later on a universal chain-growth polymerization protocol was developed and demonstrated for the synthesis of both homo-polymers and block-co-polymers.[70] Chain-growth catalyst-transfer Negishi polycondensation has recently been successfully applied for the co-polymerization of electron-rich and electron-deficient monomers.[71] A recent study demonstrates that Negishi polycondensation can offer several critical advantages such as higher reactivity, lower catalyst loading, and higher molecular weight (MW), although π -conjugated polymers are often synthesized by the Stille[43] and Suzuki[42] polycondensations.[72] Moisture and oxygen-free conditions seem to be the limitation of Negishi cross-coupling.

1.3.4. Stille cross-coupling

The Stille cross-coupling reaction between organostannanes and organic halides, triflates or phosphates, to form new carbon-carbon bonds has become a versatile synthetic methodology and has been widely applied to the syntheses of numerous organic compounds.[73–75] The major advantages of the Stille cross-coupling are the growing availability of organostannanes, the high stability towards moisture and air, its compatibility with a variety of functional groups and mild reaction conditions. The Stille cross-coupling reaction encompasses $\text{Pd}^{(0)}$ -mediated cross-coupling of organohalides, triflates, and phosphates with organostannanes.[74] The general mechanism of the Stille cross-coupling reaction shown in Figure 1.8 follows closely that of other $\text{Pd}^{(0)}$ -mediated reactions, involving an oxidative addition step, a transmetalation step, and reductive elimination step, which yields the product and regenerates the catalyst.

The active catalyst is believed to be a 14-electron $\text{Pd}^{(0)}$ -complex which can be

Figure 1.8: General mechanism of the Stille cross-coupling reaction.

generated *in situ*. Palladium(0)-catalysts such as $Pd(PPh_3)_4$ and $Pd(dba)_2$ with or without an added ligand, are often used. Alternatively, $Pd^{(II)}$ -complexes such as $Pd(OAc)_2$, $PdCl_2(MeCN)_2$, $PdCl_2(PPh_3)_2$, $BnPdCl(PPh_3)_2$, etc. are also used as precursors for the catalytically active $Pd^{(0)}$ species, as these compounds are reduced by the organostannane[76] or by an added phosphine ligand prior to the main catalytic process. The first step in the catalytic cycle, oxidative addition, occurs when the organohalide or triflate oxidatively adds to the $Pd^{(0)}$ active catalyst, forming a $Pd^{(II)}$ intermediate $[PdL_nR^2X]$ (L = ligand; R^2 = alkenyl, aryl, acyl; X = Br, I, Cl, OTf or OPO(OR)₂). The second major step in the process, transmetalation, is generally regarded to be the rate-determining step.[74],[77, 78] Different groups on the tin coupling partner transmetallate to the $Pd^{(II)}$ intermediate at different rates and the order of migration is: alkynyl > vinyl > aryl > allyl ~ benzyl >> alkyl. The very slow migration rate of the alkyl substituents allows the transfer of aryl or vinyl groups when mixed organostannanes containing three methyl or butyl groups are used. Reductive elimination is the final step in the process, which generates the desired product and allows the palladium catalyst to reenter the catalytic cycle.

A variety of different organometallic reactions have been utilized in the formation of sp^2-sp^2 carbon-carbon bonds, as typically found in semiconducting polymers, including the Heck,[39] Suzuki-Miyaura,[79] Sonogashira,[80] and Yamamoto[81] reactions. However, the Stille coupling reaction is one of the most versatile. Advantages include the fact that the Stille reaction is stereospecific, regioselective, and typically gives excellent yields. Organotin and organohalide compounds can be

conveniently prepared, typically without the requirement for protecting functionalities present in the monomers, and are far less oxygen- and moisture-sensitive than many of their other organometallic counterparts, e.g., Grignard reagents, organolithium reagents, and others. With its mild reaction conditions, high monomer solubility, tolerance for a wide range of functional groups, and facile preparation of monomers, the Stille reaction represents one of the most versatile protocols in the arsenal of organometallic chemistry.[74]

While there are many advantages to the Stille methodology for polymerization, one of the most important disadvantages is the formation of highly toxic SnR_3X , halogenated tin byproducts, which are known to be harmful to the environment. Additionally, complete removal of tin from the final product is difficult, presenting another key disadvantage. Another potential drawback has been the use of highly expensive and potentially also toxic phosphine ligands as stabilizers for the active catalyst. Additionally, the low reactivity of aryl chlorides under these conditions presents another challenge. In addition, the synthesis of distannane monomers requires use of reactive organometallic compounds, such as organolithium or Grignard reagents, which impose problems in monomer functional group compatibility. The distannane monomers are usually difficult to purify when they are not crystallizable. Palladium catalysts are relatively expensive and palladium black formed during polymerization could be detrimental to electrical properties of the resulting polymers if they are not properly removed. The methodology still gives only low molecular weight polymers, quite often, only oligomers. Side reactions such as homo-coupling of distannane compounds exist in the Stille coupling reaction, which change the stoichiometric balance of monomers and may be one of the reasons for low molecular weight observed in many reports.

1.3.5. Suzuki cross-coupling

Very similar to the Stille cross-coupling is the Suzuki cross-coupling. The Suzuki cross-coupling reaction is a palladium catalyzed reaction between organic halides and organoborane compounds. The reaction is suitable for aryl and alkenyl halides and aryl and alkenyl borane compounds. There are several advantages to this method: 1) mild reaction conditions; 2) commercial availability of many boronic acids; 3) the inorganic by-products are easily removed from the reaction mixture, making the reaction suitable for industrial processes; 4) boronic acids are environmentally safer and much less toxic than organostannanes; 5) starting materials tolerate a wide variety of functional groups, and they are unaffected by water;

6) the coupling is generally stereo- and regioselective; and 7) sp^3 -hybridized alkyl boranes can also be coupled by the *B-alkyl Suzuki-Miyaura cross-coupling*.

The mechanism of the Suzuki cross-coupling[82–86] is analogous to the catalytic cycle for the other cross-coupling reactions and has four distinct steps (Figure 1.9). The first step is the oxidative addition of an organic halide to the $Pd^{(0)}$ -species to form $Pd^{(II)}$. Next is the exchange of the anion attached to the palladium for the anion of the base (metathesis). The third step is the transmetalation between $Pd^{(II)}$ and the alkylborate complex. Although organoboronic acids do not transmetalate to the $Pd^{(II)}$ -complexes, the corresponding ate-complexes readily undergo transmetalation. The quaternization of the boron atom with an anion increases the nucleophilicity of the alkyl group and it accelerates its transfer to the palladium in the transmetalation step. Final step is the reductive elimination to form the C-C sigma bond and regeneration of $Pd^{(0)}$. Very bulky and electron-rich ligands (e.g., $P(t-Bu)_3$) increase the reactivity of otherwise unreactive aryl chlorides by accelerating the rate of the oxidative addition step.

R^1 = alkyl, allyl, alkenyl, alkynyl, aryl R = alkyl, OH, O-alkyl
 R^2 = alkenyl, aryl, alkyl X = Cl, Br, I, OTf, OPO(OR)₂ (enol phosphate)

Figure 1.9: General mechanism of the Suzuki cross-coupling reaction.

Among this variety of cross-couplings, the Suzuki cross-coupling has attracted the greatest attention, as it is compatible with a wider range of functional groups than the Kumada or Negishi cross-couplings, while the organoboronates used have much lower toxicity than the organotin compounds used in the Stille cross-coupling. The organoboronates also possess high thermal and chemical stability, are relatively inert toward moisture and oxygen, and can generally be prepared efficiently from readily available halide precursors under mild conditions. These features of organoboronates combined with very high efficiency of Suzuki cross-coupling reaction in terms of C–C bond formation between aryl moieties has turned Suzuki polycondensation (SPC) into one of the most powerful tools for synthesis of conjugated polymers, which have potential applications in emerging technologies such as organic thin-film transistors (OTFTs), organic light-emitting diodes (OLEDs)[87], and organic photovoltaics (organic solar cells, OPVs)[88].

Potential side reactions of the Suzuki cross-coupling include oxygen-induced homocoupling of organoboron compounds, B–C bond cleavage, ipso-coupling, and participation of phosphine ligands. In some specific cases, dehalogenation[89], β -hydride elimination[90], and cleavage of some functional groups (e.g., amino group[91]) are also possible. In order to reveal the full scope of SPC for the synthesis of high molar mass conjugated polymers, the reaction conditions must be optimized in terms of choice of monomers, catalyst, and solvent, based on careful consideration of the mechanism of the reaction. While much progress has been made, there still remains much scope to further improve these reactions.

The polymers made by SPC often contain significant traces of the Pd catalysts. These have been shown to have adverse effects on the conjugated polymers' performance in transistors[92] and in solar cells[93]. The levels can be reduced by appropriate treatment, but total removal may be difficult or impossible without damaging the polymer. This is a problem with all metal-catalyzed polymerizations, and so SPC is not disadvantaged compared with other methods, but clearly procedures which minimize the amount of catalyst used or aid in its removal are to be preferred.

1.3.6. Direct (hetero)arylation polymerization (DHAP)

Conventional (hetero)aryl-(hetero)aryl cross-coupling reactions for C–C bond formation after Suzuki, Stille, Negishi, or Kumada are of highest relevance in organic and macromolecular chemistry. One disadvantage of these reactions is, however, the use of various organometallic reagents (or related anion equivalents) that produces stoichiometric amounts of by-products during coupling. These reagents and the re-

sulting by products are, in addition, often toxic or environmentally risky, especially in the case of stannyl derivatives. Syntheses of these organometallic monomers often require multistep procedures as well as expensive purification steps. As example, purification of arylboronic acids/esters or aromatic trialkylstannyl derivatives is often challenging. In order to overcome these shortcomings new synthetic schemes, so-called direct (hetero)arylation schemes without use of organometallic reagents came into the focus of attention and have been much improved during the last two decades.[94–98] This new coupling involved C-C bonds formation between sp^2 C-H bonds of (hetero)aryl derivatives as coupling partners directly. As a result, this synthetic procedure could improve atom economy, reduce synthetic steps, avoid defects and contamination introduced by organometallic (hetero)aryl derivatives.[99] (Figure 1.10)

Figure 1.10: Comparison of traditional cross-coupling reactions with direct (hetero)arylation.

Most transition-metal-catalyzed cross-coupling reactions involving (hetero)-aryl molecules generally follow a catalytic cycle consisting of three main steps: oxidative addition, transmetalation and reductive elimination.(Figure 1.11) It is worth mentioning among these steps oxidative addition is often the rate-determining step,[100] though other steps can be rate limiting. For example, transmetalation is frequently reported as the slowest step for Stille couplings.[101],[74] The transmetalation step is generally what differentiates the various cross-coupling reactions from one another. The mechanism involved during this step varies depending upon the nature of the ligands, precatalyst, solvent, and organometallic compounds utilized.[100], [79], [77], [102]

Direct (hetero)arylation reactions proceed using this same general catalytic cycle, with the key difference being that they do not involve a transmetalation step but rather a metallation step proceeding via the direct cleavage of a C–H bond. Sev-

where, R_1 and R_2 are arene derivatives

X represents an halogen or a pseudo-halogen

M represents an organometallic functional compound

Figure 1.11: General mechanism of Pd-catalyzed cross-coupling reactions.[100]

eral mechanisms have been proposed for this process. The most studied are concerted metallation-deprotonation (CMD); aromatic electrophilic substitution (S_EAr) and Heck-type arylation (see Figure 1.12). The elucidation of the reaction mechanisms of direct (hetero)-arylation has been undertaken by combining experimental data and theoretical calculations, revealing that CMD is involved in most direct (hetero)arylation processes through the use of carbonate or carboxylate bases.[103] In-depth mechanistic studies generally dismiss the S_EAr mechanism as DFT calculations fail to isolate the key cationic Wheland intermediate. Interestingly, recent reports have demonstrated that the competing Heck-type mechanism is at play when using specific reaction conditions, thereby offering alternative reaction selectivity when compared to the CMD process.[104–108]

On the basis of studies performed on small molecules, DHAP, which involves the coupling of a (hetero)arene and a (hetero)aryl halide, has been improved dramatically over the last decade and can now be used to prepare some of the most

Figure 1.12: Transition states for the carboxylate-assisted concerted metalation-deprotonation (CMD), aromatic electrophilic substitution ($\text{S}_{\text{E}}\text{Ar}$) and Heck-type reaction mechanisms using benzene as a model.[108]

highly performing organic electronic materials reported in the literature.[109–114] In many instances, DHAP represents a competitive alternative to traditional organo-metallic polycondensation reactions when one considers the reduction of synthetic steps and the absence of stoichiometric quantities of organometallic byproducts. Many well-defined, nearly defect-free polymeric materials[111],[115–121] can now be obtained. For instance, highly regioregular P3HTs have been obtained (over 99% HT-HT coupling) via a DHAP protocol.[116],[122] Analysis of side-reactions has helped to identify the reaction conditions best suited to given families of monomers. In the vast majority of studies, C–H/C–H, C–Br/C–Br homo-couplings and β -defects have been found to be the major source of chain alternation defects. Two distinct approaches have emerged for efficient and selective C–C bond formation by DHAP: (1) phosphine-assisted conditions in nonpolar solvents (e.g., toluene and THF)[123, 124] and (2) phosphine-assisted or phosphine-free conditions in aprotic polar solvents (e.g., DMAC and DMF).[112, 113, 125] Nonpolar approaches, once optimized, offer both greater selectivity and high molecular weights.[126] Polar systems, on the other hand, use inexpensive reagents and can give rise to higher catalyst activity even at low (ppm) concentrations of palladium.[127] Mixed solvent phosphine-assisted conditions have been recently explored and may be an avenue to balance reactivity, solubility, and selectivity, thereby retaining

some of the characteristics of both methods.[128] More recently, oxidative C-H/C-H arylation polymerization, consisting of the coupling of two nonhalogenated (hetero)arenes, has become a viable technique for the synthesis of synthetically meaningful materials.[129]

Although direct (hetero)arylation and oxidative C-H/C-H arylation may still be perceived as “immature” polymerization techniques, it is clear that their advantages make it wholly worthwhile to develop and optimize synthetic routes that employ these reactions for the production of the next generations of conjugated polymers.

1.4. Determination of the molecular weight of conjugated polymers via GPC

Accurate measurements of molecular weights and molar-mass dispersity of conjugated polymers are primordial, for this influences the conjugation length and their ability to self-organize. And these parameters are known to affect their optical and electronic properties, which in turn impact their performance in organic devices. By far the most common and convenient way to measure molecular weights is by gel permeation chromatography (GPC), also known as size exclusion chromatography (SEC). The polymer to be analyzed is dissolved and injected into a column containing a porous gel. Molecules with a small hydrodynamic volume get stuck in the small holes in the gel, while with a larger hydrodynamic volume run through more freely. At the end of the column one or more detectors determine when and how much of (concentration) a particular fraction elutes from the column. Several detectors can be used but a UV-VIS detector is commonly used for conjugated polymers. The raw data obtained from GPC is an apparent molecular size distribution, which needs to be converted to true molecular weight distribution using a calibration curve (usually, obtained from polystyrene). This calibration method is a relative calibration, meaning that the molecular weight of the polymers that are analyzed is based on the relative molecular weight of the polymers used for the calibration. If the relationship between hydrodynamic volume and the molecular weight of the analyzed polymers is very different compared to polystyrene, the value obtained can be wrong. As conjugated polymers can have strong aggregation properties, care must be taken to fully solubilize them, as aggregates will cause gross overestimation of both molecular weights and molar mass dispersity. More and more research shows that GPC gives an overestimation of the molecular weight up to a factor four when analyzing conjugated polymers. To achieve more accurate GPC

results for these materials, high temperature analysis with solvents such as 1,2-dichlorobenzene and 1,2,4-trichlorobenzene are recommended.[130] Superheated chloroform has also demonstrated superior performances for breaking conjugated polymer aggregates.[131]

1.5. Aim and outline of this thesis

The research described in this thesis is centered on π -conjugated polymers. The aim of this project was to develop new reaction and polymerization methodologies for the synthesis of π -conjugated polymers and to study the performance of π -conjugated molecules and polymers based on organic photovoltaic devices. The project crossed the boundaries of many fields and was therefore performed in both organic synthesis and organic materials group and with close collaboration with the photophysics and optoelectronics group of Prof. Jan Anton Koster. Our goal was to simplify the synthetic routes of π -conjugated polymers, better understand polymerization mechanism and improve the performance of organic materials used as optoelectronics.

In Chapter 2, the synthesis of ene-yne-enes by nickel-catalyzed double S_N2' substitution of 1,6-dichlorohexa-2,4-diyne will be discussed. The established reaction methodology here is formally an extension of the well-described S_N2' -allylic and -propargylic substitution reactions. A more complex mechanism is proposed as well. The corresponding products might be used as building blocks for conjugated polymers.

In Chapter 3, we performed a mechanistic study of a polymerization methodology for the synthesis of thiophene-based, π -conjugated co-polymers directly from the bis-bromide monomer by generating the active boronate species for a Suzuki polymerization *in situ* from bis(pinacolato)diboron (BiPi) via the Miyaura reaction. Upon selection of the model reaction and with aid of GPC measurement of the polymerization process, it was found that this polymerization methodology underwent a chain-growth mechanism at the beginning and then switched to a step-growth mechanism. A brief explanation of the mechanism was proposed as well.

Chapter 4 describes the development of homo-polymerization methodology for the synthesis of thiophene-based π -conjugated polymers. This $t\text{BuLi}$ -mediated polymerization catalyzed by palladium gives high molecular weight and low polymer dispersity index. This is a new and significant contribution to the field of transition-metal catalyzed cross-coupling polymerization, without the need of toxic organometallic reagents and with high efficiency.

In Chapter 5, we conduct a systematic UV-degradation study on a set of PBDDT-TT polymers: fullerene solar cells. Through this work, it shows clearly the relationship between the polymer chemical structure and the UV-stability of the solar cells. We find that solar cells of polymers with alkoxy side chains are more stable than those with alkylthienyl side chains. Through combined experimental techniques, the effects of both the polymer chemical structure and additives 1,8-diiodooctane (DIO), chloronaphthalene (CN) and 1,8-octanedithiol (ODT) on the UV-stability of the solar cells are further explored. It shows DIO acts as photo-acid and leads to accelerated degradation of the solar cells and CN does not. The mechanisms behind the effect of DIO are explained as well, paving the way for the design of new, efficient as well as stable materials and additives.

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2

Synthesis of Ene-yne-enes by Nickel-Catalyzed Double S_N2' substitution of 1,6-Dichlorohexa-2,4-diyne

Abstract: 1,6-Dichlorohexa-2,4-diyne undergoes nickel catalyzed double substitution with aryl and alkenyl Grignard reagents to provide substituted ene-yne-enes. The reaction is formally an extension of the well-described S_N2' -allylic and -propargylic substitution reactions but the mechanism is considerably more complex. The products might function as building blocks for conjugated polymers.

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2.1. Introduction

Transition metal-catalyzed S_N2' -allylic and -propargylic substitution reactions with organometallic reagents as nucleophiles have been deeply studied in the last twenty years. In particular, copper-catalyzed allylic substitution of allylic halides and esters with organozinc, boron, aluminum and Grignard reagents is well understood and has developed into a powerful tool in organic synthesis as it provides a carbon–carbon single bond and a new carbon–carbon double bond.[1] As often a chiral center is formed in these reactions, both substrate control and catalyst control have been used to provide the products enantio-enriched.[2] The corresponding S_N2' -propargylic substitution reaction has received much less attention although in particular the groups of Alexakis, Lipshutz, and Krause have convincingly shown that this reaction provides a versatile entry into (enantio-enriched) allenes.[3–6] Both reactions have now evolved to such an extent that more complex substrates with larger conjugated systems and alkenes and alkynes with two leaving groups have come within reach. Thus, on the one hand, dienes and ene-yne[7, 8] equipped with a leaving group at the allylic position have been studied and, on the other hand, alkenes and alkynes with leaving groups at the 1 and 4 positions,[9, 10] next to gemdisubstituted allylic systems,[11, 12] have been successfully used as substrates (Figure 2.1).

Figure 2.1: Substrates for S_N2' -allylic and -propargylic substitution reactions.

In the case of 1,4-dichlorobut-2-ene,[10] allylic substitution takes place once, providing a homo-allylic product suitable for further functionalization. This has been cleverly used for desymmetrization as well.[13–16] In the case of 1,4-disubstitut-

ed but-2-yne, the reaction takes place twice,[17–24] as the initially formed 4-substituted 1,2-butadiene again acts as a substrate for the reaction, to provide disubstituted 1,3-butadienes. This reaction has been extensively exploited as the products, in turn, are starting materials for subsequent Diels–Alder reactions[25–35] (Figure 2.2).

Figure 2.2: Double $\text{S}_{\text{N}}2'$ reactions of 1,4-disubstituted 2-butyne.

After an initial report of Mkryan and co-workers,[25] this double substitution reaction has been carried out mainly using organocuprates based on Grignard or organozinc reagents (Figure 2.2).

Although less far developed than that catalyzed by copper, nickel-catalyzed allylic and propargylic substitution is also well known.[36] In addition, palladium catalysis has been employed in this double $\text{S}_{\text{N}}2'$ substitution, in particular with less reactive organometallics such as organotin and organoboron compounds together with alkyne dicarbonates. Here, satisfactory yields of 1,3-dienes were obtained as well, although the advantages compared to the use of copper and “hard” organometallics seemed somewhat limited (Figure 2.3).

Figure 2.3: The application of organoboron and tin compounds to form 2,3-disubstituted 1,3-butadienes.

Very recently, however, this reaction was extended to the direct use of readily available propargylic diols.[37] This adds considerably to the applicability of the reaction as this procedure is essentially (pseudo) halogen-free (Figure 2.4).

The reaction has been used in particular for the preparation of dendralenes. This was carried out by reacting vinyl Grignard reagents with 1,4-dichlorobut-2-yne using Ni as a catalyst (Figure 2.2, $\text{RM} = \text{vinyl MgBr}$).[38] This methodology gives rapid access to novel substituted dendralenes and addressed the deficiency of the

Figure 2.4: Direct cross-coupling reactions of propargylic diols

synthesis of these compounds. As an example of selective S_N2 substitution, instead of S_N2' substitution, the iron-catalyzed coupling of bulky Grignard reagents to propargylic and allylic halides is mentioned.[39]

We were curious to determine whether the S_N2' - propargylic substitution reaction could be extended to a diyne as the substrate with leaving groups at the 1 and 6 positions. Surprisingly, this motif seems to have escaped attention although the starting material, 1,6-dichlorohexa-2,4-diyne, is readily prepared by chloro-substitution of 1,6- dihydroxyhexa-2,4-diyne, which in turn is prepared by Glaser coupling of propargyl alcohol. We report here that the nickel-catalyzed reaction of 1,6-dichlorohexa-2,4-diyne with aryl or alkenyl Grignard reagents leads to the formation of 2,5- disubstituted hexa-1,5-dien-3-yne via formal double S_N2' substitution (Figure 2.5).

Figure 2.5: Nickel-catalyzed formal double S_N2' substitution of 1,6- dichloro-hexa-2,4-diyne with Grignard reagents.

2.2. Results and Discussion

Partly based on literature precedents in the double substitution of 1,4-dichlorobut-2-yne, we focused on the reaction of phenylmagnesium bromide with 1,6-dichloro- hexa-2,4-diyne (**2**), prepared from hexa-2,4-diyne-1,6-diol (**1**), in the presence of nickel catalysts (Table 2.1). In the Kumada–Tamao–Corriu reaction, a cross-coupling reaction of Grignard reagents catalyzed by nickel, the catalysts

Table 2.1: Defining a suitable Ni-catalyst and catalyst loading for the double S_N2' propargylic substitution^a

Entry	Catalyst (mol %) ^c	Yield ^b (%)	Conversion of 2 (%)
1	Ni(dppp)Cl ₂ (2.5)	52	100
2	Ni(dppe)Cl ₂ (2.5)	38	100
3	Ni(dppf)Cl ₂ (2.5)	30	100
4	Pd(PPh ₃) ₄ (2.5)	6	98
5	IPrNiCl ₂ (PPh ₃) (2.5)	n.d. ^d	74
6	Ni(dppp)Cl ₂ (5.0)	48	100
7	Ni(dppp)Cl ₂ (1.0)	73	100
8	Ni(dppp)Cl ₂ (0.5)	62	100
9	Ni(dppp)Cl ₂ (1.0) ^e	63	100
10	—	Trace	53

^aReaction conditions: **2** (1.0 mmol), PhMgBr (3.0 mmol, 3.0 mL, 1.0 M in THF), the addition rate of **2** was 10 mmol h⁻¹, the reaction was performed at a final concentration of 0.1 M of **2**. ^bThe yield of the desired product was determined by q-¹H-NMR. ^cdppp, 1,3-bis-(diphenylphosphino)propane; dppe, 1,2-bis-(diphenylphosphino)ethane; dppf, 1,1'-bis-(diphenylphosphino)ferrocene; PPh₃, triphenylphosphine; IPr, 1,3-bis(2,6-diisopropylphenyl) imidazol-2-ylidene. ^dn.d., not detected. ^e2 mol% PPh₃ was added.

Ni(dppp)Cl₂, Ni(dppe)Cl₂ and Ni(dppf)Cl₂ are often effective so these were initially selected. It turned out that although all catalysts led to full conversion of the starting material, in particular Ni(dppp)Cl₂ provided an acceptable NMR yield of a product that turned out to be diphenyl ene-yne-ene **3** (Table 2.1, entry 1). In addition, an *N*-heterocyclic carbene Ni catalyst was investigated, but this did not lead to an identifiable product (Table 2.1, entry 5). The structure of diphenyl ene-yne-ene **3** was established by ¹H- and ¹³C-NMR, mass spectrometry, and comparison of these spectra with the literature, as **3** has been prepared once before via another route.[38] Apart from homo-coupling of the Grignard reagent, we were unsuccessful in the identification of other products in addition to **3**. In addition to **3**, NMR and

Table 2.2: Optimization of the stoichiometry of the Grignard reagent in the double S_N2' -propargylic substitution^a

Entry	Equiv. of PhMgBr	Yield ^b (%)	Conversion of 2 (%)
1	2.5	60	100
2	3.0	73	100
3	3.5	68	100
4	4.0	65	100

^aReaction conditions: **2** (1.0 mmol), PhMgBr (1.0 M in THF), Ni(dppp)Cl₂ (0.01 mmol), the addition rate of **2** was 10 mmol h⁻¹, the reaction was performed at a final concentration of 0.1 M **2** ^bThe yield of the desired product was determined by q⁻¹H-NMR.

Table 2.3: Defining the optimal solvent in the double S_N2' -propargylic substitution^a

Entry	Solvent	Yield ^b (%)	Conversion of 2 (%)
1	THF	73	100
2	Et ₂ O	49	100
3	MTBE	56	100
4	1,4-Dioxane	31	98

^aReaction conditions: **2** (1.0 mmol), PhMgBr (3.0 mmol, 3.0 mL, 1.0 M in THF), Ni(dppp)Cl₂ (0.01 mmol), the addition rate of **2** was 10 mmol h⁻¹, the reaction was performed at a final concentration of 0.1 M **2** ^bThe yield of the desired product was determined by q⁻¹H-NMR.

GC indicated the formation of oligomers, likely because of subsequent reactions of the product (vide infra).

Upon selection of Ni(dppp)Cl₂ as the catalyst, we varied its loading (Table 2.1, entries 1 and 6–8). The results indicated that 0.5 mol% Ni(dppp)Cl₂ was sufficient

Table 2.4: Defining the optimal reaction temperature in the double S_N2' -propargylic substitution^a

Entry	Temperature/°C	Yield ^b (%)	Conversion of 2 (%)
1	-25	42	100
2	-15	73	100
3	5	49	100
4	rt	45	100

^aReaction conditions: **2** (1.0 mmol), PhMgBr (3.0 mmol, 3.0 mL, 1.0 M in THF), Ni(dppp)Cl₂ (0.01 mmol), the addition rate of **2** was 10 mmol h⁻¹, the reaction was performed at a final concentration of 0.1 M **2** ^bThe yield of the desired product was determined by q⁻¹H-NMR.

Table 2.5: Defining the optimal addition rate of **2** in the double S_N2' -propargylic substitution^a

Entry	Addition rate of 2 (mmol h ⁻¹)	Yield ^b (%)	Conversion of 2 (%)
1	10	73	100
2	5	57	100
3	20	64	100

^aReaction conditions: **2** (1.0 mmol), PhMgBr (3.0 mmol, 3.0 mL, 1.0 M in THF), Ni(dppp)Cl₂ (0.01 mmol), the reaction was performed at a final concentration of 0.1 M **2** ^bThe yield of the desired product was determined by q⁻¹H-NMR.

to fully convert the starting material (Table 2.1, entry 8) but 1 mol% catalyst gave the highest NMR yield (Table 2.1, entry 7). The addition of PPh₃ to the reaction led to a slight decrease in yield (Table 2.1, entry 9), possibly due to decomposition of the product by nucleophilic attack of PPh₃. Without a catalyst, only a trace of product was detected with 53% conversion of **2** after 1 h (Table 2.1, entry 10), demonstrating the necessity of the catalyst in this reaction.

Table 2.6: Defining the optimal reaction time in the double S_N2' -propargylic substitution^a

2			3
Entry	Time/h	Yield ^b (%)	Conversion of 2 (%)
1	0.5	66	100
2	1.0	73	100
3	1.5	50	100

^aReaction conditions: **2** (1.0 mmol), PhMgBr (3.0 mmol, 3.0 mL, 1.0 M in THF), Ni(dppp)Cl₂ (0.01 mmol), the addition rate of **2** was 10 mmol h⁻¹, the reaction was performed at a final concentration of 0.1 M **2**. ^bThe yield of the desired product was determined by q-¹H-NMR.

With a suitable catalyst system selected, our attention turned to the optimization of the amount of the Grignard reagent required (Table 2.2). It turned out that also with 2.5 equiv. of phenylmagnesium bromide the starting material was fully converted, but the NMR yield was higher when 3 equiv. was used. A further increase in the amount of the Grignard reagent lowered the yield to some extent.

Subsequently, several solvents commonly used for the Kumada–Tamao–Corriu reaction were evaluated for the reaction on hand (Table 2.3), and THF showed to be optimal (Table 2.3, entry 1). As 1,4-dioxane leads to a shift in the Schlenk equilibrium because it complexes to MgBr₂, thereby forming diphenylmagnesium,^[39] the NMR yield probably decreased although the conversion was only slightly lower (Table 2.3, entries 1–4).

The yield of the reaction is surprisingly sensitive to the reaction temperature. Carrying out the reaction in a temperature range of –10 to –20 °C led to the highest NMR yields, whereas both lower and higher temperatures caused a significant drop in yield (Table 2.4, entry 1–4). Variation in the order and rate of addition showed that adding **2** slowly at an approximate rate of 10 mmol h⁻¹ for a reaction on a 1 mmol scale led to acceptable isolated yields (Table 2.5, entry 1). At a considerably higher addition rate, the yields dropped (Table 2.5, entry 3). The reaction was complete in approximately 1 h, whereas prolonged reaction times led to significantly lower yields, most probably because the product decomposed under the influence of the remaining Grignard reagent (Table 2.6, entry 1–3).

Figure 2.6: Scope of the double S_N2' propargylic substitution reaction in terms of the Grignard reagent. Reaction conditions: 1,6-dichlorohexa-2,4-diyne (2.0 mmol, 2.0 mL, 1 M in THF), Grignard reagent (6.0 mmol, 6.0 or 12.0 mL, 1.0 or 0.5 M in THF), $Ni(dppp)Cl_2$ (0.02 mmol), THF (12 or 6 mL). ^a6.0 mL of a 1.0 M solution of 4-chlorophenylmagnesium bromide in 2-methyl-THF and 12.0 mL THF were used. Crude yield is the yield as determined by q-NMR before column purification. ^bDirect double S_N2 substitution product was obtained.

With the reaction conditions optimized, our next efforts focused on the scope of applicable Grignard reagents (Figure 2.6). For aryl Grignard reagents, modest to good crude yields are obtained, more or less regardless of the presence of electron-donating or electron-withdrawing substituents and the substitution pattern (**3**, **4**, **5**, **6**, **7**). Nevertheless, the isolated yields after purification by column chromatography strongly varied due to the instability of the various products. It turned out that, although decomposing in the reaction and upon column purification, the products could be stored as solutions in pentane at $-10^\circ C$ for several weeks. Unfortunately, the crude yield in the reaction with *cis*-2-butenylmagnesium bromide

Figure 2.7: Complex **10**, = **3**.Co₂(CO)₆. CCDC deposition number: 1519007.

was low, although the yield of **8** after purification nearly equaled the crude yield, indicating that this compound is stable. We assume that the oligomerization of **8** is slow because it is less prone to act as an activated alkene. When the more reactive benzyl Grignard reagent was used, only the double S_N2 product (**9**) was obtained. This corresponds to the reaction with methylmagnesium bromide that also produced solely the double S_N2 product as shown by the ^1H -NMR of the reaction mixture (the product was too volatile to isolate).

In order to obtain rigorous proof of the structure of these unstable ene-yne-enes, the diphenyl ene-yne-ene product **3** was treated with dicobalt octacarbonyl (see the Experimental section and Figure 2.7). This led to a stable solid that was purified by column chromatography and subsequent crystallization. Crystals suitable for X-ray analysis were obtained in this way and this showed unambiguously the structure of the dicobalt complex **10** and thereby the structure of diphenyl ene-yne-ene **3**.

2.3. Proposed mechanism

The mechanism of the Kumada–Tamao–Corriu reaction, the Ni-catalyzed cross-coupling of Grignard reagents with aryl halides, is reasonably well understood.[40–46] Based on this mechanism, we propose the following pathway for the formation of diphenyl ene-yne-ene **3** (Figure 2.8). The precatalyst is reduced to Ni(0) by

Figure 2.8: Proposed mechanism for the double S_N2' reaction. Figure 2.9: Derailing pathway of the double S_N2' reaction.

the homo-coupling of the Grignard reagent leading to the formation of biphenyl. The $\text{Ni}(0)$ catalyst undergoes oxidative insertion into one of the C–Cl bonds of 1,6-dichlorohexa-2,4-diyne **2** to give propargylic nickel(II) intermediate **In1**. Re-

arrangement gives allenyl nickel(II) complex **In3**, either via intermediate **In2** or directly. **In3** undergoes transmetalation with the Grignard reagent to give phenyl-allenyl nickel(II) intermediate **In4**. Reductive elimination would then lead to the formation of **P1** (route a), although this compound was not observed.

Subsequent oxidative insertion of Ni(0) into the C–Cl bond of **P1** would produce intermediate **In5**. A more likely hypothesis is that **In4** undergoes intramolecular transfer of nickel(0) to the terminal C–Cl bond to yield **In5** directly (route b). Similar rearrangements are well precedent in so-called catalyst-transfer (poly)-condensations, also for Ni(dppp). In those cases, association of Ni(II) with the π -system of an aromatic ring, however, is mostly involved.[47] Rearrangement of **In5** gives complex **In7**, either via intermediate **In6** or directly. Subsequently, **In7** undergoes transmetalation with the Grignard reagent, and final reductive elimination of **In8** produces diphenyl ene-yne-ene **3**.

It is clear that this complex pathway can derail at several places (Figure 2.9). First of all, considerably more biphenyl (around 20%) is observed than can be accounted for by the initial reduction of the precatalyst (1 mol%). This can be explained by side reactions that lead to the regeneration of the Ni(II) species. So **In1**, **In2**, **In3** and in principle **In4** can undergo elimination to provide cumulene **11** and Ni(II)Cl₂. Cumulene **11** is most probably so unstable that it escapes observation. This elimination is known and forms the basis for the synthesis of radialenes according to Iyoda et al.[48] We speculate that the elimination in the latter case is very fast because of the formation of a fully substituted double bond, whereas in the current reaction, a 1,1-disubstituted double bond is formed and the cross-coupling reaction can apparently compete. Magnesium halogen exchange with the substrate is also possible and leads to dimer and oligomer formation of the substrates. Within 0.5 h, half of the starting material was consumed also in the absence of catalyst, whereas biphenyl formation was observed. Finally, it is clear that the product **3** is unstable under the reaction conditions, and might be sensitive to nucleophilic attack by the Grignard reagent.

2.4. Conclusion

It has been shown that 1,6-dichlorohexa-2,4-diyne undergoes nickel-catalyzed disubstitution with Grignard reagents to provide diaryl- or dialkenyl-substituted ene-yne-enes. This is a new and significant contribution to the field of transition metal-catalyzed allylic and propargylic substitution reactions in which the mechanism is considerably more complex and involves extensive rearrangements of the inter-

mediate nickel species. The products can be isolated, purified, and characterized either as such or as the corresponding dicobalt hexacarbonyl complex. Although the application of these eneyne-ene systems might be hampered by their instability, it is definitely worthwhile to pursue. Prepared efficiently from low-cost starting materials and catalysts, these compounds might function as building blocks for conjugated polymers. Ene-yne-enes resemble the repeating unit in polydiacetylenes, which have important applications in organic films.[48, 49] Olefin metathesis of these ene-yne-enes could provide an alternative way to produce these polymers with better control over their chain length and processability.

2.5. Experimental section

2.5.1. General experimental details

All reactions were performed using oven-dried glassware and dry solvents unless otherwise specified. THF, Et₂O, MTBE and DCM were taken from an MBraun solvent purification system (SPS-800). All other reagents were purchased from Sigma-Aldrich, TCI Europe, Strem Chemicals or Acros Organics and were used without further purification unless noted otherwise. CuI was purified before use according to the literature procedure.[50] IR spectra were recorded on a Perkin-Elmer FTIR spectrometer. ¹H NMR, ¹³C NMR and ¹⁹F NMR spectra were recorded on a Varian AMX400 (400, 100.6 and 376 MHz, respectively). Chemical shift values are reported in ppm with the solvent resonance as the internal standard. Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = double doublet, dq = double quartet, qd = quarter doublet, m = multiplet), coupling constants (Hz), and integration. GC-MS measurements were performed with an HP 6890 series gas chromatography system with an HP1 or HP5 column (Agilent Technologies, Palo Alto, CA), equipped with an HP 5973 mass-sensitive detector. Flash chromatography: Merck silica gel type 9385, 230–400 mesh. TLC: Merck silica gel 60, 0.25 mm. Compounds were visualized using UV, Seebach's reagent (phosphomolybdic acid, 25 g; cerium sulfate, 7.5 g; H₂O, 500 mL; H₂SO₄, 25 mL) and potassium permanganate staining.

2.5.2. General procedure for quantitative NMR experiments

Exactly 0.50 mL of the reaction mixture was sampled using a syringe and added to a mixture of 1 mL of HPLC grade pentane and 2 mL of 0.1 M HCl_{aq}. The mixture was shaken, the organic layer was separated and the volatiles were removed

in vacuo. To the residue was added 0.5 mL of 0.1 M mesitylene in $CDCl_3$ as an internal standard. Then, the solution was measured through a quantitative NMR experiment.[50] The spectra were obtained with a sufficiently long acquisition time (3 s) and processed using MestReNova version 10.2. The crude yield of the desired product was determined based on the ratio between the signals of the double bond hydrogens of the product and the signals of the internal standard.

2.5.3. Synthesis of the starting material

Hexa-2,4-diyne-1,6-diol (1).[51] To a dried 500 mL threenecked flask with a stirring bar were added 1.43 g (7.5 mmol) of CuI, 1.78 g (7.5 mmol) of $NiCl_2 \cdot 6H_2O$, 4.5 mL (30 mmol) of TMEDA and 62.8 mL (450 mmol) of Et_3N in 340 mL of dry THF at room temperature under air. The solution was stirred until the solution was bright dark green and 8.41 g (150 mmol) of propargyl alcohol was slowly added to the reaction mixture while bubbling O_2 through the solution via a glass inlet over 45 min. After 24 h, the THF and the remaining Et_3N were removed in vacuo and the residue was dissolved in 500 mL of EtOAc. This mixture was filtered and the filtrate was carefully washed with saturated NH_4Cl (3×100 mL). The aqueous phase was separated and further extracted with EtOAc (3×100 mL). Then, the combined organic layers were washed with brine (100 mL), dried over anhydrous Na_2SO_4 , filtered, and concentrated under vacuum. The pure product was obtained as a white solid through flash precipitation of the residue with EtOAc and *n*-pentane (7.85 g, 95%). 1H NMR (400 MHz, acetone- d_6) δ 4.27 (d, $J = 6.0$ Hz, 4H), 4.38 (t, $J = 6.0$ Hz, 2H). ^{13}C NMR (101 MHz, acetone- d_6): δ 50.8, 69.0, 79.5. The spectroscopic data corresponded to the literature.[52]

1,6-Dichlorohexa-2,4-diyne (2).[53] To a dry 250 mL threenecked flask were added 3.04 g (28 mmol) of hexa-2,4-diyne-1,6-diol, 5.6 mL (70 mmol) of pyridine and 100 mL of dry DCM at room temperature under a N_2 atmosphere. The flask was then cooled to 0 °C with an ice bath and a solution of 5.1 mL (70 mmol) of $SOCl_2$ in 20 mL of dry DCM was added dropwise to the reaction mixture. After the addition, the ice bath was removed and the reaction mixture was stirred overnight. Then, the reaction mixture was poured into 300 mL of crushed ice and extracted with Et_2O (3×100 mL). The organic layer was washed with saturated $NaHCO_3$ (3×100 mL) and brine (150 mL), and the organic layer was dried over Na_2SO_4 and decolorized using activated carbon. The solvent was removed in vacuo at 0 °C and the residue was purified by means of a short silica column using *n*-pentane as the eluent. The fractions containing the product were collected and evaporated

in vacuo at 0 °C to give the pure product as a colorless liquid (2.91 g, 71%). As the product decomposed over time, it was stored as a 1 M solution in dry THF at –80 °C and used quickly. ¹H NMR (400 MHz, CDCl₃): δ 4.21 (s, 4H). ¹³C NMR (101 MHz, CDCl₃): δ 30.4, 70.0, 74.7. The spectroscopic data corresponded to the literature.[54]

2.5.4. General procedure for the double S_N2' reaction of 1,6-dichlorohexa-2,4-diyne

A 50 mL Schlenk flask, flame-dried three times and placed under a N₂ atmosphere, was charged with 10.8 mg (0.02 mmol) of Ni(dppp)Cl₂ and 6 or 12 mL of dry THF. The reaction mixture was subsequently cooled to –15 °C using a cold acetone bath. A solution of 6.0 mmol of the Grignard reagent (0.5 or 1.0 M in dry THF) was added to the reaction mixture. After the addition, the solution was stirred for 10 min at –15 °C. Then, a solution of 2 mL of 1,6-dichlorohexa-2,4-diyne (1.0 M in THF) was added over 12 min using a syringe pump. After the addition, the solution was left to stir at –15 °C for an additional 10 min. After this time, the acetone bath was removed and the reaction mixture was left to stir for another 1 h. Then, a quantitative NMR was taken to determine the crude yield of the desired product. The reaction mixture was subsequently poured into a mixture of 150 mL of H₂O, 10 mL of 2 M HCl and 150 mL of *n*-pentane. The organic layer was separated, washed with H₂O (2 × 100 mL) and brine (150 mL), dried over anhydrous MgSO₄, filtered, and concentrated under vacuum at 0 °C. The resulting residue was purified using flash silica column chromatography using *n*-pentane as the eluent. The fractions containing the product were collected and evaporated in vacuo at 0 °C to give the pure product as a colorless oil or white solid. As the product polymerized quickly over time, yields were lower than expected based on q-NMR. The isolated product was stored at –80 °C in *n*-pentane.

Hexa-1,5-dien-3-yne-2,5-diyl dibenzene (3). Phenylmagnesium bromide was used as the Grignard reagent (1.0 M in THF). Crude yield, 72%. The pure product was obtained as a colorless oil (0.20 g, isolated yield, 44%). ¹H NMR (400 MHz, CDCl₃): δ 5.78 (d, *J* = 0.8 Hz, 2H), 6.00 (d, *J* = 0.8 Hz, 2H), 7.41–7.31 (m, 6H), 7.72–7.69 (m, 4H). ¹³C NMR (101 MHz, CDCl₃): δ 90.1, 121.2, 126.3, 128.5, 128.6, 130.7, 137.4. GC-MS: *m/z* (relative intensity, %) = 230 (100, M⁺), 229 (54), 228 (44), 215 (36). The analytical data were in accordance with the literature.[38]

4,4'-(Hexa-1,5-dien-3-yne-2,5-diyl) bis(methylbenzene) (4). *p*-Tolylmagnesium bromide was used as the Grignard reagent (1.0 M in THF). Crude yield,

68%. The pure product was obtained as a white solid (0.11 g, isolated yield, 22%). ^1H NMR (400 MHz, CDCl_3): 2.37 (s, 6H), 5.71 (d, $J = 0.8$ Hz, 2H), 5.95 (d, $J = 0.8$ Hz, 2H), 7.18 (d, $J = 8.0$ Hz, 4H), 7.60 (d, $J = 8.0$ Hz, 4H). ^{13}C NMR (101 MHz, CDCl_3): δ 21.3, 90.0, 120.2, 126.1, 129.3, 130.5, 134.6, 138.4. GC-MS: m/z (relative intensity, %) = 258 (100, M^+), 228 (55), 243 (48), 129 (33).

4,4'-(Hexa-1,5-dien-3-yne-2,5-diyl)bis(chlorobenzene) (5). A 50 mL Schlenk flask, flame-dried three times and placed under a N_2 atmosphere, was added to 10.8 mg (0.02 mmol) of $\text{Ni}(\text{dppp})\text{Cl}_2$ and 12 mL of dry THF. The reaction mixture was then cooled to -15°C using a cold acetone bath. A solution of 6.0 mmol of (4-chlorophenyl)magnesium bromide (1.0 M in 2-methyltetrahydrofuran) was added to the reaction mixture. After the addition, the solution was stirred for 10 min at -15°C . Then, a solution of 2 mL of 1,6-dichlorohexa-2,4-diyne (1.0 M in THF) was added over 12 min using a syringe pump. After the addition, the solution was left to stir at -15°C for an additional 10 min. After this, the acetone bath was removed and the reaction mixture was left to stir for another 1 h. Then, a quantitative NMR was taken to determine the crude yield of the desired product (50%). The reaction mixture was subsequently poured into a mixture of 150 mL of H_2O , 10 mL of 2 M HCl and 150 mL of *n*-pentane. The organic layer was separated, washed with H_2O (2×100 mL) and brine (150 mL), dried over anhydrous MgSO_4 , filtered, and concentrated under vacuum at 0°C . The resulting residue was purified using flash silica column chromatography using *n*-pentane as the eluent. The fractions containing the product were collected and evaporated in vacuo at 0°C to give the pure product as a white solid (0.15 g, 26%). As the product polymerized quickly over time, some of the product was lost in the column and the isolated product was stored at -80°C in *n*-pentane. ^1H NMR (400 MHz, CDCl_3): δ = 5.76 (s, 2H), 5.98 (s, 2H), 7.36–7.33 (m, 4H), 7.62–7.59 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3): δ = 89.9, 121.8, 127.5, 128.8, 129.5, 134.5, 135.7. GC-MS: m/z (relative intensity, %) = 298 (52, M^+), 263 (41), 228 (100), 226 (40).

5,5'-(Hexa-1,5-dien-3-yne-2,5-diyl)bis(1,3-dimethylbenzene) (6). (3,5-Dimethylphenyl)magnesium bromide was used as the Grignard reagent (0.5 M in THF). Crude yield, 56%. The pure product was obtained as a white solid (0.17 g, isolated yield, 30%). ^1H NMR (400 MHz, CDCl_3): δ = 2.35 (s, 12H), 5.72 (d, $J = 0.8$ Hz, 2H), 5.96 (d, $J = 1.2$ Hz, 2H), 6.98 (s, 2H), 7.33 (s, 4H). ^{13}C NMR (101 MHz, CDCl_3): δ = 21.5, 90.2, 120.8, 124.2, 130.2, 130.9, 137.4, 138.0. GC-MS: m/z (relative intensity, %) = 287 (23), 286 (100, M^+), 271 (45), 256 (62).

4,4'-(Hexa-1,5-dien-3-yne-2,5-diyl)bis(fluorobenzene) (7). (4-Fluorophenyl)

enyl)magnesium bromide was used as the Grignard reagent (1.0 M in THF). Crude yield, 60%. The pure product was obtained as a white solid (0.19 g, isolated yield, 36%). ^1H NMR (400 MHz, CDCl_3): 5.75 (s, 2H), 5.93 (s, 2H), 7.10–7.04 (m, 4H), 7.69–7.63 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3): δ 90.0, 115.5 (d, $J = 21.7$ Hz), 121.1 (d, $J = 1.9$ Hz), 128.0 (d, $J = 8.0$ Hz), 129.6, 133.4 (d, $J = 3.4$ Hz), 163.0 (d, $J = 248.4$ Hz). ^{19}F NMR (376 MHz, CDCl_3): δ –113.51 to –113.58 (m, 2F). GC-MS: m/z (relative intensity, %) = 266 (100, M^+), 265 (35), 264 (30), 133 (48).

(2E,8E)-3,8-Dimethyl-4,7-dimethylenedeca-2,8-dien-5-yne (8). (*E*)-But-2-en-2-ylmagnesium bromide was used as the Grignard reagent (0.5 M in THF). Crude yield, 25%. The pure product was obtained as a white solid (74.5 mg, isolated yield, 20%). ^1H NMR (400 MHz, CDCl_3): 1.75 (dq, $J = 7.2$ Hz, 1.5 Hz, 6H), 1.88–1.87 (m, 6H), 5.30 (d, $J = 2.0$ Hz, 2H), 5.43 (dq, $J = 7.0$ Hz, 1.4 Hz, 2H), 5.58 (d, $J = 2.0$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3): δ 15.0, 23.5, 89.4, 123.4, 123.5, 130.7, 134.5. GC-MS: m/z (relative intensity, %) = 186 (18, M^+), 171 (92), 156 (100), 141 (86), 128 (80).

1,8-Diphenylocta-3,5-diyne (9). A 50 mL Schlenk flask, flame-dried three times and placed under a N_2 atmosphere, was added to 10.8 mg (0.02 mmol) of $\text{Ni}(\text{dppp})\text{Cl}_2$ and 13.7 mL of dry THF. The reaction mixture was then cooled to -15°C using a cold acetone bath. A solution of 6.0 mmol of benzylmagnesium chloride (1.4 M in dry THF) was added to the reaction mixture. After the addition, the solution was stirred for 10 min at -15°C . Then, a solution of 2 mL of 1,6-dichlorohexa-2,4-diyne (1.0 M in THF) was added over 12 min using a syringe pump. After the addition, the solution was left to stir at -15°C for 10 min more. After the stirring, the cold acetone bath was removed and the reaction mixture was left to stir for another 1 h. Then, a quantitative NMR was taken to determine the crude yield of the desired product (43%). The reaction mixture was poured into a mixture of 150 mL of H_2O , 10 mL of 2 M HCl and 150 mL of *n*-pentane. Then, the organic layer was separated, washed with H_2O (2×100 mL) and brine (150 mL), dried over anhydrous MgSO_4 , filtered, and concentrated under vacuum at 0°C . The resulting residue was purified using flash silica column chromatography using *n*-pentane as the eluent. The fractions containing the product were collected and evaporated in vacuo at 0°C to give the pure product as a white solid (0.20 g, 38%). This product was relatively stable at room temperature. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): 2.58 (t, $J = 7.2$ Hz, 4H), 2.75 (t, $J = 7.2$ Hz, 4H), 7.24–7.19 (m, 6H), 7.31–7.27 (m, 4H). ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$): δ 20.4, 33.7, 65.7, 77.6, 126.2, 128.3, 128.4, 140.0. GC-MS: m/z (relative intensity, %) = 258 (17, M^+), 167 (33),

165 (26), 91 (100), 65 (24).

(Hexa-1,5-dien-3-yne-2,5-diylidibenzene) (dicobaltoctacarbonyl) complex (10). A 50 mL Schlenk flask, flame-dried three times and placed under a N₂ atmosphere, was charged with 10.8 mg (0.02 mmol) of Ni(dppp)Cl₂ and 12 mL of dry THF. The reaction mixture was then cooled to −15 °C using a cold acetone bath. A solution of 6.0 mmol of phenylmagnesium bromide (1.0 M in THF) was added to the reaction mixture. After the addition, the solution was stirred for 10 min at −15 °C. Then, a solution of 2 mL of 1,6-dichlorohexa-2,4-diyne (1.0 M in THF) was added over 12 min using a syringe pump. After the addition, the solution was left to stir at −15 °C for an additional 10 min. After this, the acetone bath was removed and the reaction mixture was left to stir for another 1 h. Then, the reaction mixture was poured into a mixture of 150 mL of water, 10 mL of 2 M HCl and 150 mL of *n*-pentane. Afterwards, the organic layer was separated, washed with water (2 × 100 mL) and brine (150 mL), dried over anhydrous MgSO₄, filtered, and concentrated under vacuum at 0 °C. To a 50 mL round-bottom flask, a solution of the resulting residue in 12 mL of dry THF was added followed by 0.82 g of Co₂(CO)₈ (2.4 mmol). The reaction mixture was left to stir overnight. After this, the reaction mixture was concentrated under vacuum. The resulting residue was purified using flash silica column chromatography using *n*-pentane as the eluent. The fractions containing the product were collected and evaporated in vacuo at 0 °C to give the pure product as a red brown solid (0.18 g, 17%). ¹H NMR (400 MHz, CD₃CN): δ = 5.75 (d, *J* = 0.8 Hz, 2H), 5.84 (d, *J* = 1.2 Hz, 2H), 7.36–7.30 (m, 6H), 7.52–7.49 (m, 4H). ¹³C NMR (101 MHz, CD₂Cl₂): δ = 98.7, 118.9, 127.6, 128.8, 128.9, 141.4, 148.1, 199.7. IR (neat): ν_{max} 2924, 2854, 2091, 2025, 2009, 1995, 1975, 1958, 1617, 1595, 1572, 1493, 1444, 1399, 1383, 890, 843, 773, 740, 721, 699, 628 cm^{−1}.

2.5.5. X-ray structure determination of dicobalt complex 10

A single crystal of compound **10** was mounted on top of a cryoloop and transferred into the cold nitrogen stream (100 K) of a Bruker-AXS D8 Venture diffractometer. Data collection and reduction was done using the Bruker software suite APEX3.[55] The final unit cell was obtained from the xyz centroids of 9770 reflections after integration. A multiscan absorption correction was applied, based on the intensities of symmetry-related reflections measured at different angular settings (SADABS). The structures were solved by direct methods using SHELXT[56] and refinement of the structure was performed using SHELXL.[57] The hydrogen atoms were generated

Figure 2.10: Molecular structure of compound **10**, showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

by geometrical considerations, constrained to idealised geometries and allowed to ride on their carrier atoms with an isotropic displacement parameter related to the equivalent displacement parameter of their carrier atoms. Crystal data and details on data collection and refinement are presented in Table 2.7. The structure was deposited in the CCDC deposition number: 1519007.

Table 2.7: Crystallographic data for dicobalt complex **10**

chem formula	C ₂₄ H ₁₄ Co ₂ O ₆
M _r	516.21
cryst syst	Triclinic
color, habit	red, block
size (mm)	0.24 × 0.29 × 0.32
space group	P -1
a (Å)	8.4376(11)
b (Å)	10.1022(12)
c (Å)	13.0614(15)
α, deg	98.593(4)
β, deg	92.973(4)
γ, deg	100.142(4)
V (Å ³)	1080.1(2)
Z	2
ρ _{calc} , g.cm ⁻³	1.587
μ(Mo Kα), cm ⁻¹	1.574
F(000)	520
temp (K)	100(2)
θ range (deg)	3.245 – 27.925
data collected (h,k,l)	-11:11, -13:13, -17:17
no. of rflns collected	44480
no. of indepndt rflns	5140
observed rflns	4915 (F _o ≥ 2 σ(F _o))
R(F) (%)	1.78
wR(F ²) (%)	4.78
GooF	1.057
Weighting a,b	0.0228, 0.5470
params refined	289
restraints	0
min, max resid dens	-0.294, 0.361

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3

Insights into the mechanism of bis(pinacolato)diboron- mediated polymerization for conjugated co-polymers

Abstract: *The mechanism of bis(pinacolato)diboron-mediated polymerization for conjugated co-polymers was investigated via analysis of the whole polymerization process of a model reaction. It was found out the polymerization followed a step-growth mechanism. With understanding the mechanism better, it would be beneficial for designing new controlled polymerization methodologies.*

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3.1. Introduction

π -Conjugated (semiconducting) polymers have become an important class of materials for applications in polymer solar cells, field-effect transistors, and light emitting diodes.[1] Almost all π -conjugated polymers are prepared using transition metal catalyzed cross coupling reactions.[2, 3] In short, these reactions consist of an oxidative addition (OA), followed by a transmetalation (TM) and, finally, a reductive elimination (RE), after which the cycle restarts. Such polymerizations are clearly polycondensations and one can assume that those polymerizations proceed in a step-growth fashion. Conventionally, π -conjugated polymers synthesized via a step-growth condensation mechanism typically results in poor control over crucial properties, such as kinetics, molecular weight (MW), polydispersity ($\mathcal{D}$), and end groups.[4] The development of synthetic routes to π -conjugated polymers using controlled polymerizations⁵ is of great importance as it gives access to conjugated polymers with well-defined structures and conjugated block co-polymers.

In 2004, Yokozawa[5] and McCullough[6] independently discovered that a particular polymerization, i.e. poly(3-alkylthiophene) (P3AT) obtained with a Ni(dppp)Cl₂ catalyst (dppp = 1,3- bis(diphenylphosphino)propane), proceeds in a controlled chain-growth fashion. This discovery marked the beginning of the exploration of the controlled nature of the polymerization of π -conjugated polymers. In general, there are two ways to realize a controlled polymerization of π -conjugated polymers. The first and by far most used way relies on the complexation of the catalyst to the π -system of the growing polymer chain. In this way the catalyst remains complexed to the growing polymer chain after reductive elimination and is transferred to a terminal C-X bond where it oxidatively inserts. This type of polymerization is called a catalyst transfer polymerization (CTP). Termination can occur if the catalyst diffuses away prior to oxidative addition or by disproportionation. If termination and transfer reactions are retarded, one catalyst/initiator moiety polymerizes one polymer chain and a controlled polymerization is realized. The association of the catalyst with the polymer chain is crucial. Several coupling reactions have been utilized in CTP, including the initially investigated Kumada catalyst transfer polymerization (KCTP) that uses Kumada couplings, Suzuki-Miyaura catalyst transfer polymerization (SCTP) using the Suzuki-Miyaura reaction[7] and, more recently, CTPs that exploit Sonogashira[8], Stille[8, 9], Negishi[6] and Murahashi[10] couplings.

A second way to realize a controlled polymerization of CPs is inspired by Yokozawa's controlled polymerization of aromatic amides[11]. It uses AB-type monomers and the key to success is the deactivation of one functional group by the other in the

monomer. However, after reaction this deactivation is lost. As a consequence, growth is only possible on the growing polymer chains. The catalyst can decomplex, but, since reaction with monomer is impossible, it must perform an oxidative addition on a (dormant) polymer chain and restart the polymerization. The choice of the catalyst is crucial: it must be stable when dissociated and oxidatively insert very easily into a dormant polymer chain. The catalyst that has been used is Pd(Ruphos)[12]. The advantage of this procedure is that the controlled nature of the polymerization does not depend on the complexation of the catalyst with the growing polymer chain, which is system-dependent. Moreover, the independence of this complexation has also additional advantages, like the more easy formation of block and gradient copolymers.

Previously our group[13] developed a polymerization methodology for the synthesis of thiophene-based, π -conjugated co-polymers directly from the bis-bromide monomer by generating the active boronate species for a Suzuki polymerization *in situ* from bis(pinacolato)diboron (BiPi) via the Miyaura reaction.[14–18] This “BiPi method” combines the more facile syntheses of the co-polymerization route with the reproducibility and higher quality polymers of the co-monomer route by enabling the direct homo-polymerization of a symmetric co-monomer[19, 20] to form a co-polymer. This method obviates the synthesis of Sn- or B-containing monomers and retains the versatility and tolerance for functional groups of the standard Suzuki polymerization. It produces higher-quality polymers in fewer synthetic steps and with less variation in end-groups than the same co-polymers prepared by Stille co-polymerizations.

In order to better understand this polymerization methodology, we explored its polymerization mechanism by analyzing the whole polymerization process of a model reaction. And it was found out that the polymerization went through in a step-growth mechanism. With the investigation of the mechanism, it would be beneficial to people to establish controlled polymerization.

3.2. Results and discussion

3.2.1. Model reaction for polymerization mechanism

In order to study the mechanism of this polymerization methodology, first we select the following polymerization reaction as the model reaction, under the conditions according to the literature[13] (Figure 3.1).

Before the investigation of the mechanism, the monomer was synthesized according

Figure 3.1: Selected model reaction to investigate the mechanism of the BiPi-mediated polymerization methodology.

to previously reported procedures[13], [21–23]. The synthetic route was illustrated in Figure 3.1 (details seen in experimental section).

Figure 3.2: The synthetic route to the monomer.

3.2.2. Analysis of the whole polymerization process

With the monomer in hand, the polymerization reaction for the synthesis of **PTBT** was carried out under the conditions as shown in Figure 3.1. Molecular weight of the reaction mixture was analyzed continuously via GPC during the whole polymerization process. Conversion of the monomer was simultaneously traced through HPLC using naphthalene as an internal standard. Both of these results were shown in Table 3.1. It was found out that most of the monomer was consumed in the first 2 h of the polymerization. It also showed that after 6 h there was no conversion of the monomer and molecular weight didn't increase anymore, which indicated polymerization time needed of this methodology much less than previously reported[13].

Table 3.1: Monomer conversion^a and molecular weight^b during the whole polymerization process

Entry	Reaction time (h)	Monomer conversion (%)	Mn ^c (Da)	Mw ^d (Da)	Đ ^e (Mw/Mn)
1	0.03	4.3	1755	3725	2.12
2	0.07	12.4	2197	4368	1.99
3	0.10	28.6	2022	4247	2.10
4	0.13	36.8	2274	4730	2.08
5	0.17	42.9	2421	5156	2.13
6	0.22	45.4	2546	5812	2.28
7	0.25	49.2	2110	3725	2.21
8	0.50	61.3	2404	6899	2.87
9	0.75	67.8	2741	7676	2.80
10	1.0	72.5	2739	7308	2.67
11	1.5	79.4	3327	10228	3.07
12	2.0	83.5	3605	9475	2.63
13	2.5	86.8	3603	9627	2.67
14	3.0	91.1	3490	12092	3.47
15	3.5	94.0	4919	15775	3.21
16	4.0	96.4	3844	11351	2.95
17	4.5	98.0	5407	16219	3.00
18	5.0	98.6	4824	14841	3.08
19	6.0	98.9	4640	12887	2.78
20	7.0	98.9	3787	11195	2.96

^a Monomer conversion was determined by HPLC using naphthalene as an internal standard.^b Molecular weight was measured by GPC with sample prepared in THF at 1.6 mg/mL concentration.^cMn, number average molecular weight.^dMw, weight average molecular weight.^eĐ, dispersity.

3.2.3. Mechanism study and explanation

The relationship between the monomer conversion and Mn was present in Figure 3.3 along with Đ. As shown in Figure 3.3 the reaction proceeded rapidly at the beginning but the molecular weight increased only slowly and high molecular weights were only attained at the end of the process by long oligomers reacting with each-other. This was also consistent with that large quantities of monomers were consumed early in the reaction as shown in Table 3.1. Moreover, the poly-

mer chain length distribution broadened with increasing reaction time as illustrated by the $\bar{M}_w/\bar{M}_n$ trend. All of these results indicated this polymerization went through a step-growth mechanism.

Figure 3.3: The molecular weight and dispersity change over the conversion of the monomer.

The coupling mechanism of this BiPi polymerization methodology was also proposed in the previous report^[13] (Figure 3.4). The likely mechanism consisted of two palladium-catalyzed cycles. Asymmetric organoborane reagent BrArB was formed through Miyaura cycle. And BrArB underwent a Suzuki cycle in a step-wise fashion, which also reasonably explained why the BiPi polymerization methodology followed a step-growth mechanism. On the other hand, it also revealed that $\text{Pd}(\text{dppf})\text{Cl}_2$ catalyst dissociated from the growing polymer chain each time after reductive elimination.

Figure 3.4: The proposed coupling mechanism of the BiPi polymerization methodology.

3.3. Conclusions

In this Chapter, the mechanism of the previously reported BiPi polymerization methodology was investigated through analysis of the polymerization process from the molecular weight change over the monomer conversion. The results showed

that large quantities of monomers were consumed early in the reaction but the molecular weight increased only slowly and high molecular weight needed a long reaction time. The polymer dispersity broadened over the polymerization process as well. Based on these above analysis, we proposed the BiPi polymerization methodology proceeded in a step-growth mechanism. With understanding the mechanism better, it gives people more information to design controlled polymerization methodologies.

3.4. Experimental Section

3.4.1. General Experimental details

All reactions were performed using oven-dried glassware and dry solvents unless otherwise specified. Et₂O, toluene and *n*-hexane were taken from an MBraun solvent purification system (SPS-800). All other reagents were purchased from Sigma–Aldrich, TCI Europe, Strem Chemicals or Acros Organics and were used without further purification unless noted otherwise. ¹H-NMR, ¹³C-NMR and were recorded on a Varian AMX400 (400 and 100.6, respectively). Chemical shift values are reported in ppm with the solvent resonance as the internal standard. Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = double doublet, dq = double quartet, qd = quarter doublet, m = multiplet), coupling constants (Hz), and integration. HPLC measurements were performed with a Shimadzu LC-10ADVP HPLC equipped with a Shimadzu SPD-M10AVP diode array detector. GPC measurements were done on a Spectra Physics AS 1000 series machine equipped with a Viskotek H-502 viscometer and a Shodex RI-71 refractive index detector. The columns (PLGel 5 μ mixed-C) (Polymer Laboratories) were calibrated using narrow disperse polystyrene standards (Polymer Laboratories). Samples were made in THF at concentration of 1.6 mg/ml. Flash chromatography: Merck silica gel type 9385 230–400 mesh. TLC: Merck silica gel 60, 0.25 mm. Compounds were visualized by UV, Seebachs reagent (phosphomolybdic acid, 25 g, cerium sulfate, 7.5 g, H₂O, 500 mL, H₂SO₄, 25 mL) and potassium permanganate staining.

3.4.2. Synthesis of the Monomer

3-decylthiophene (1): To a 250 mL three necked round-bottom flask equipped with a cool condenser, dropping funnel and stirring egg were added 6.52 g (40 mmol) of 3-bromothiophene and 0.33 g (0.6 mmol) of Ni(dppp)Cl₂ in 40 mL Et₂O

at room temperature under N_2 . A solution of 48 mmol of decylmagnesium bromide (1.0 M in dry Et_2O) was added dropwise to the reaction mixture through dropping funnel. After the addition, the reaction mixture was stirring under reflux overnight. Then the reaction was quenched with 5 mL of 1N HCl, poured into 150 mL of H_2O and extracted with Et_2O (3×50 mL). The combined organic layer was washed with H_2O (150 mL), brine (150 mL) and dried over $MgSO_4$. After filtration and removal of the solvent under vacuum, the resulting residue was purified via Kugelrohr distillation to give 6.86 g of compound **1**, 76.0%. 1H -NMR (400 MHz, $CDCl_3$) δ 7.24 - 7.22 (m, 1H), 6.94 - 6.92 (m, 2H), 2.62 (t, $J = 7.6$ Hz, 2H), 1.65 - 1.58 (m, 2H), 1.35 - 1.20 (m, 14H), 0.88 (t, $J = 6.8$ Hz, 3H).[21]

2-bromo-3-decylthiophene (2): To a 100 mL round-bottom flask was added 5.61 g (25 mmol) of **1** in a solution of $CHCl_3$ (25 mL) and CH_3COOH (25 mL). 4.45 g (25 mmol) of *N*-Bromosuccinimide was added in portions to the reaction mixture over a period of 1 h under ice bath. After the addition, the reaction mixture was continued to stir under ice bath for 1 h and reacted at room temperature overnight. Then the reaction mixture was poured into 80 mL of H_2O and extracted with $CHCl_3$ (3×60 mL). The combined organic layer was washed with H_2O (2×60 mL), 1N NaOH (100 mL), brine (100 mL) and dried over $MgSO_4$. After filtration and removal of the solvent under vacuum, the resulting residue was purified via Kugelrohr distillation to give 6.93 g of compound **2**, yield 91.0%. 1H -NMR (400 MHz, $CDCl_3$) δ 7.18 (d, $J = 5.6$ Hz, 1H), 6.79 (d, $J = 5.6$ Hz, 1H), 2.55 (t, $J = 7.6$ Hz, 2H), 1.60 - 1.53 (m, 2H), 1.33 - 1.25 (m, 14H), 0.88 (t, $J = 6.8$ Hz, 3H).[22]

2,5-bis(tributylstannyl)thiophene (3): To a 250 mL three necked round-bottom flask equipped with a cool condenser, dropping funnel and stirring egg were added 1.68 g (20 mmol) of thiophene and 4.65 g (40 mmol) of TMEDA in 40 mL *n*-hexane under N_2 . A solution of 40 mmol of *n*-BuLi (1.6 M in hexanes) was added dropwise to the reaction mixture through dropping funnel under ice bath. After the addition, the reaction mixture was stirring under reflux for 45 min. A solution of 13.02 g (40 mmol) of tributylchlorostannane was added dropwise via dropping funnel after cooling down the reaction mixture to 0 °C. After the addition, the reaction was continued to stir at room temperature overnight. Then the reaction was quenched with saturated NH_4Cl solution (60 mL), extracted with Et_2O (3×60 mL). The combined organic layer was washed with brine (2×50 mL) and dried over $MgSO_4$. After filtration and removal of the solvent under vacuum, 13.2 g of crude product **3** was obtained, directly used for next step without further purification.[23]

3,3''-didecyl-2,2':5',2''-terthiophene (4): To a 250 mL three necked round-

bottom flask equipped with a cool condenser and stirring egg were added 2.46 g (8.1 mmol) of **2**, 3.31 g (5 mmol) of **3** and 173 mg (0.15 mmol, 3 mol%) of Pd(PPh₃)₄ in a solution of 120 mL toluene and 40 mL DMF. The reaction mixture was then sparged with N₂ for 15 min. After this, the reaction mixture was heated to 110 °C and continued to stir for 16 h. The reaction mixture was poured into ice after cooling down to room temperature, extracted with CHCl₃ (4 × 70 mL). The combined organic layer was washed with 1 N HCl (2 × 100 mL), brine (1 × 150 mL) and dried over MgSO₄. After filtration and removal of the solvent under vacuum, the resulting residue was purified via flash silica column chromatography using *n*-hexane as eluent to give 1.22 g of compound **4**, yield 56.7%. ¹H NMR (400 MHz, CDCl₃) δ 7.18 (d, *J* = 5.2 Hz, 2H), 7.06 (s, 2H), 6.94 (d, *J* = 5.2 Hz, 2H), 2.79 (t, *J* = 7.8 Hz, 4H), 1.69 – 1.62 (m, 4H), 1.42 – 1.26 (m, 28H), 0.88 (t, *J* = 6.8 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 139.9, 136.2, 130.6, 130.2, 126.2, 123.9, 32.1, 30.9, 29.8, 29.73, 29.65, 29.50, 29.45, 22.8, 14.3.[13]

5,5''-dibromo-3,3''-didecyl-2,2':5',2''-terthiophene (5): To a 100 mL round-bottom flask was added 1.52 g (2.9 mmol) of **4** in a solution of CHCl₃ (6 mL) and CH₃COOH (6 mL). 1.02 g (5.8 mmol) of *N*-Bromosuccinimide was added in portions to the reaction mixture over a period of 20 min under ice bath. After the addition, the reaction mixture was continued to stir under ice bath for 1 h and reacted at room temperature overnight. Then the reaction mixture was poured into 50 mL of H₂O and extracted with CHCl₃ (3 × 20 mL). The combined organic layer was washed with H₂O (2 × 30 mL), 1N NaOH (30 mL), brine (30 mL) and dried over MgSO₄. After filtration and removal of the solvent under vacuum, the resulting residue was purified by flash silica column chromatography using *n*-hexane as eluent and recrystallized from *n*-hexane/isopropanol (v/v = 3:1) to give 1.58 g of compound **5**, yield 80.2%. ¹H NMR (400 MHz, CDCl₃) δ 6.98 (s, 2H), 6.90 (s, 2H), 2.7 (t, *J* = 7.8 Hz, 4H), 1.64 – 1.57 (m, 4H), 1.39 – 1.21 (m, 28H), 0.88 (t, *J* = 6.6 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 140.6, 135.3, 132.9, 131.8, 126.6, 110.8, 32.1, 30.7, 29.8, 29.7, 29.6, 29.5, 29.4, 22.8, 14.3.[22]

3.4.3. Model reaction for polymerization mechanism

To a 100 mL two necked round bottom flask was added with 0.48 g (0.7 mmol) of monomer **5** in 70 mL of dry DMF. 90 mg (0.7 mmol) of naphthalene was added as an internal standard for tracking conversion by HPLC. A first aliquot was taken (~0.3 mL) prior to heating as a HPLC reference. 0.18 g (0.7 mmol) of bis(pinacolato)-diboron, 0.74 g (3.5 mmol) of crushed K₃PO₄ and 25 mg (5 mol%) of Pd(dppf)Cl₂

were added subsequently. After three times of freeze pump thaw cycling, the reaction was heated to 110 °C. A aliquot (~ 0.3 mL) of the reaction mixture were taken at different reaction time. Each aliquot was first analyzed by HPLC to track the conversion of the monomer. The aliquot was precipitated by pouring slowly into 100 mL of CH₃OH afterwards. To facilitate the precipitation, 5 mL of 1N HCl was then added. The resulting slurry was filtered by hydrophilic filter membranes. The crude polymer was analyzed via GPC measurement.[22]

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4

Establishment of a green and atom-economical polymerization methodology for π -conjugated polymers

Abstract: 5,5"-dibromo-3,3"-didodecyl-2,2':5',2"-terthiophene goes through ^tBuLi-mediated homo-polymerization with palladium catalyst to π -conjugated polymers. The polymerization methodology is formally an extension of transition-metal catalyzed cross-coupling polymerization with mild conditions and very narrow polymer dispersity. The methodology might be applicable for other more different π -conjugated polymers.

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4.1. Introduction

π -conjugated polymers are an attractive class of materials due to their potential applications in electronic devices such as solar cells[1–4], transistors[5, 6], light-emitting diodes[7, 8], memory devices[9, 10], and sensing technologies[11–14]. Over the years, transition-metal catalyzed cross-couplings have attracted considerable attention in polymer synthesis and material science.[15, 16] However, to date, n -conjugated polymers have primarily been prepared by Miyaura–Suzuki and Migita–Stille cross-coupling techniques, which require multiple steps and unstable or toxic organometallic intermediates[17]. The Negishi and Kumada–Corriu polymerizations, on the other hand, involve in situ organozinc and organomagnesium intermediates, respectively, and are limited to homo-polymer synthesis.(Figure 4.1) The two major methods used for the synthesis of semiconducting polymers Migita–Stille and Miyaura–Suzuki cross-coupling, are popular for their versatility and predictable reactivity. However, there are key setbacks to each of these techniques[18–22].

The challenges of Miyaura–Suzuki polymerization, in addition to the high cost of boronic ester precursors, are tied to the lack of reproducibility of reactions in biphasic conditions. As the polymerization occurs at the interface of the organic and aqueous phases, contact between the phases and degree of mixing depends heavily on glassware and stirring methods used. While this poses fewer problems in small molecule couplings, in polymerization this can lead to unexpected molecular weight-limiting events which are highly dependent on the reaction conditions. An example of this is gelation of the polymer mixture, which impedes the reaction before polymerization is complete. Other side-reactions related to protodeboronation can lead to by-products in the reactions mixture, such as boric acid, which may react with functional groups elsewhere on the monomers or growing polymer chain.

Although the Migita–Stille polymerization is in most cases a robust and dependable method for the cross-coupling synthesis of thiophene-based conjugated polymers, the applicability of Migita–Stille coupling to polymer synthesis is severely limited by the need for organostannanes. Aside from their inherent toxicity, the most common organostannanes used for polymerization, trimethylstannyl and tributylstannyl, each come with their own synthetic difficulties. Monomers with tributylstannyl groups almost exclusively form oils, making purification via crystallization unfeasible, while trimethylstannyl groups are more volatile and susceptible to decomposition. The instability of the C–Sn bond seldom makes column chromatography a feasible technique for the purification of monomers and the use of distillation is

often limited for the same reasons. A further consequence of this instability and volatility is that all glassware used for synthesis, purification, and solvent evaporation must be decontaminated with an oxidizing agent (i.e., bleach) after every manipulation.

Recently Direct (hetero)arylation polymerization (DHAP or DArP) and oxidative C-H/C-H arylation polymerization (oxi-DArP) make accessible the synthesis of both conjugated homo- and co-polymers by means of palladium-catalyzed C-H activation, thereby avoiding many of the setbacks inherent to other polymerization techniques such as the reduction of synthetic steps and the absence of stoichiometric quantities of organometallic byproducts.[23–25] However, homo-coupling is observed during polymerization process and β -defects cause polymer insolubility and loss of yield. Substrate limitations is another setback.(Figure 4.1)

So far very few examples[15] have been reported for the synthesis of n -conjugated polymers by using organolithium reagents as organometallic species because of its high reactivity. Mostly organotin and organoboron reagents are prepared from organolithium reagents. Thus one synthetic step can be saved when using organolithium reagents directly. In addition, organolithium reagents are non-toxic and atom-economical compared to organotin and organoboron reagents. All of these lead us to explore the potential of organolithium for synthesis of conjugated polymers. We report hereby a Pd/Ni-catalyzed organolithium reagents mediated polymerization methodology for the synthesis of n -conjugated polymers in this chapter.(Figure 4.1)

Figure 4.1: A schematic comparison of the various pathways leading to regioregular conjugated polymers

4.2. Results and Discussion

4.2.1. Exploration of polymerization conditions

Based on the literature[26, 27] reported on the direct catalytic cross-coupling of organolithium reagents for the synthesis of small molecules, initially we directly focused on the polymerization between a terthiophene dibromide monomer and the alkylated-DPP organolithium reagent. (Figure 4.2) 5,5''-dibromo-3,3''-didodecyl-2,2':5',2''-terthiophene was synthesized according to literature.[28],[29],[30] The alkylated-DPP organolithium reagent was obtained by direct lithiation of the alkylated-DPP following the procedure of literature.[31] (details seen in **Experimental section**) With these two starting materials in hand, two optimal reaction conditions used for direct catalytic cross-coupling of organolithium compounds[26, 27] were chosen for the polymerization. (Figure 4.2) Unfortunately, polymers were not formed from both the working-up of the reaction solution and ^1H -NMR analysis of the reaction mixture. The reaction system became extremely messy as well with difficulties of further analysis.

Figure 4.2: A test of polymerization using reaction conditions for the direct catalytic cross-coupling of organolithium compounds

Considering the complex structure and the unstable property of the alkylated-DPP organolithium reagent, we selected the alkylated-DPP dibromide which can be easily prepared through bromination[32] and commercially available organolithium reagent 2-thienyllithium as starting materials to build a model reaction for achieving optimal polymerization conditions. (Figure 4.3) In this case, the reaction system was simplified and easier to be analyzed. Again several reaction conditions used for direct catalytic cross-coupling of organolithium compounds[26],[33],[34]

Figure 4.3: Designed model reaction for achieving optimal polymerization conditions

were employed for the designed model reaction. The reaction didn't proceed and none of the product was observed in the presence of the selected reaction conditions based on the ^1H -NMR measurement of the reaction mixture. Meanwhile, the alkylated-DPP dibromide was consumed during the reaction.

To further understand details behind these results, a control reaction without any catalyst system was carried out under the same reaction conditions. After being analyzed by ^1H -NMR and TLC, the alkylated-DPP dibromide was not observed anymore and none of Li-Br exchange product was formed during the reaction process. We concluded that 2-thienyllithium was incompatible with the alkylated-DPP dibromide and was able to ruin the structure.

4.2.2. $^t\text{BuLi}$ -mediated polymerization

According to reported literature, one easy and fast method to generate an organo-metallic compound in situ from an aryl bromide is the formation of the corresponding aryllithium reagent via lithium-halogen exchange. With previous results, *tert*-butyllithium ($^t\text{BuLi}$) was the lithiation agent of choice because of its bulky steric hindrance and weak nucleophilicity, which was tolerant with the backbone unit of DPP. Thus the polymerization of the alkylated-DPP dibromide and $^t\text{BuLi}$ was carried out under the conditions which was used for $^t\text{BuLi}$ -mediated one-pot direct highly selective cross-coupling of two distinct aryl bromides. (Figure 4.4) However, there was no polymerization undergoing but just recovery of the alkylated-DPP dibromide,

which illustrated that no Li-Br exchange happened through $t\text{BuLi}$.

Figure 4.4: A test of $t\text{BuLi}$ -mediated polymerization of the alkylated-DPP dibromide

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In order to make the Li-Br exchange accessible, the alkylated-DPP dibromide was replaced by 5,5''-dibromo-3,3''-didodecyl-2,2':5',2''-terthiophene (Table 4.1). Initially the previous reaction conditions were also selected for this polymerization. It turned out that the polymerization worked with 50.3% yield and a relatively low dispersity ($\bar{D}$) (Table 4.1, entry 3). Subsequently we varied the loading of the catalyst. The results indicated that 0.5 mol% Pd-PEPPSI-IPr was sufficient to trigger the polymerization (Table 4.1, entry 1) but 5 mol% catalyst gave the highest yield and lowest $\bar{D}$ (Table 4.1, entry 4).

Table 4.1: Defining a suitable catalyst loading for the $t\text{BuLi}$ -mediated polymerization^a

The reaction scheme shows the polymerization of compound **5**, 5,5''-dibromo-3,3''-didodecyl-2,2':5',2''-terthiophene, with $t\text{BuLi}$ (1.2 eq.) and $[\text{Pd-PEPPSI-IPr}]$ in toluene (0.1 M) at room temperature for 1 hour. The product is a polymer with a repeat unit n .

Entry	Pd-PEPPSI-IPr^b (mol%)	Yield (%) ^c	M_n^d (Da)	M_w^e (Da)	$\bar{D}^f$
1	0.5	7.4	8446	14698	1.74
2	1.0	8.1	7004	12360	1.77
3	2.0	50.3	6483	8806	1.36
4	5.0	61.0	5536	7267	1.31

^aReaction conditions: **5** (0.1 mmol), $t\text{BuLi}$ (0.12 mmol, 1.7 M in pentane), the reaction was performed at a final concentration of 0.1 M of **5**. ^b Pd-PEPPSI-IPr , [1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene](3-chloropyridyl)palladium(II) dichloride. ^cYield was determined after purification by soxhlet extraction with CH_3OH , acetone and CHCl_3 . ^d M_n , number average molecular weight. ^e M_w , weight average molecular weight. ^f $\bar{D}$, dispersity. calculated by M_w/M_n .

Upon selection of 5 mol% as the catalyst loading, our attention turned to the optimization of the concentration of the reactant required (Table 4.2). It turned out that a decrease of the concentration of the reactant improved the yield (Table 4.2, entry 1-4) and 0.02 M of the reactant concentration gave the highest yield and quite low $\bar{D}$ as well (Table 4.2, entry 4).

Table 4.2: Optimization of the concentration of the reactant for the t BuLi-mediated polymerization^a

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Entry	Concentration (M)	Yield (%) ^b	Mn ^c (Da)	Mw ^d (Da)	$\bar{D}$ ^e
1	0.5	40.5	8884	18005	2.03
2	0.1	61.0	5536	7267	1.31
3	0.05	67.4	5627	7533	1.34
4	0.02	80.0	5320	7062	1.33

^aReaction conditions: **5** (0.1 mmol), t BuLi (0.12 mmol, 1.7 M in pentane), Pd-PEPPSI-IPr (0.005 mmol, 5 mol%) ^bYield was determined after purification by soxhlet extraction with CH_3OH , acetone and CHCl_3 .

^cMn, number average molecular weight. ^dMw, weight average molecular weight. ^e $\bar{D}$, dispersity. calculated by Mw/Mn.

Subsequently, several other catalysts commonly used for the direct cross-coupling of organolithium compounds were evaluated for the polymerization on hand (Table 4.3), and Pd-PEPPSI-IPr showed to be optimal (Table 4.3, entry 1) when taking both the yield and $\bar{D}$ into consideration (Table 4.3, entry 1-5).

The yield of the polymerization was surprisingly sensitive to amount of t BuLi used. Carrying out the polymerization with 2.0 equivalent of t BuLi led to relatively good yield, the highest molecular weight and the lowest $\bar{D}$ (Table 4.4, entry 4), whereas 1.2 equivalent of t BuLi gave the lowest molecular weight although with the highest yield (Table 4.4, entry 1).

With above optimization, we established a green and atom-economical polymerization methodology for the synthesis of π -conjugated polymers. The organolithium reagent was directly used, producing much less waste than using organotin or organoboron reagents. Furthermore, the conditions for the polymerization was extremely mild without heating and time needed to complete the polymerization was very short. It definitely provides an attractive alternative polymerization methodol-

Table 4.3: Defining the optimal catalyst for the ^tBuLi-mediated polymerization^a

Reaction scheme: Monomer **5** (2,2'-bis(bromophenyl)-5,5'-bibenzothiophene with R groups) reacts with ^tBuLi (1.2 eq.) and [Cat.] (5 mol%) in Toluene (0.02 M) at R.T. for 1 h to form a polymer with repeat units of the monomer.

Entry	[Cat.]	Yield (%) ^b	Mn ^c (Da)	Mw ^d (Da)	Đ ^e
1	Pd-PEPPSI-IPr ^f	80.0	5320	7062	1.33
2	Pd-PEPPSI-IPent ^f	40.7	2548	3646	1.43
3	NiPPh ₃ Cl ₂ IPr ^f	54.4	10449	16138	1.54
4	NiCl ₂ (dppp) ^f	39.1	6581	10649	1.62
5	NiCl ₂ (depe) ^f	46.4	5608	9283	1.66

^aReaction conditions: **5** (0.1 mmol), ^tBuLi (0.12 mmol, 1.7 M in pentane), catalyst (0.005 mmol, 5 mol%), the reaction was performed at a final concentration of 0.02 M of **5**. ^bYield was determined after purification by soxhlet extraction with CH₃OH, acetone and CHCl₃. ^cMn, number average molecular weight. ^dMw, weight average molecular weight. ^eĐ, dispersity. calculated by Mw/Mn.

^fPd-PEPPSI-IPr, [1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene](3-chloropyridyl)palladium(II) dichloride; Pd-PEPPSI-IPent, [1,3-bis(2,6-di-3-pentylphenyl)imidazol-2-ylidene](3-chloropyridyl)palladium(II) dichloride; NiPPh₃Cl₂IPr, [1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]triphenylphosphine nickel(II) dichloride; NiCl₂(dppp), [1,3-bis(diphenylphosphino)propane]dichloronickel(II); NiCl₂(depe), [1,2-bis(diethylphosphino)ethane]dichloronickel(II)

ogy to people for the synthesis of π -conjugated polymers.

4.3. Conclusion

It has been shown that 5,5''-dibromo-3,3''-didodecyl-2,2':5',2''-terthiophene undergoes ^tBuLi-mediated polymerization in the presence of palladium catalyst with high molecular weight and low dispersity. This is a new and significant contribution to the field of transition-metal catalyzed cross-coupling polymerization. With this new methodology, toxic organometallic reagents are not needed any more. Because of the use of organolithium reagents, the polymerization becomes atom-economical. Furthermore, more monomers can potentially be applied in this polymerization methodology for the synthesis of π -conjugated polymers. However, poor functional group compatibility and relatively narrow monomer scope limit further and broader applications of this polymerization methodology.

Table 4.4: Optimization of the stoichiometry of the lithium reagent for the t BuLi-mediated polymerization^a

Entry	eq. of t BuLi	Yield (%) ^b	Mn ^c (Da)	Mw ^d (Da)	$\bar{D}^e$
1	1.2	80.0	5320	7062	1.33
2	1.4	52.8	7031	9313	1.32
3	1.8	29.1	6428	10304	1.60
4	2.0	70.5	15401	19586	1.27

^aReaction conditions: **5** (0.1 mmol), t BuLi (1.7 M in pentane), Pd-PEPPSI-IPr (0.005 mmol, 5 mol%), the reaction was performed at a final concentration of 0.02 M of **5**. ^bYield was determined after purification by soxhlet extraction with CH₃OH, acetone and CHCl₃. ^cMn, number average molecular weight. ^dMw, weight average molecular weight. ^e $\bar{D}$, dispersity. calculated by Mw/Mn.

4.4. Experimental Section

4.4.1. General experimental details

All reactions were performed using oven-dried glassware and dry solvents under N₂ atmosphere unless otherwise specified. Et₂O, toluene, *n*-pentane, DCM and *n*-hexane were taken from an MBraun solvent purification system (SPS-800). All other reagents were purchased from Sigma-Aldrich, TCI Europe, Strem Chemicals or Acros Organics and were used without further purification unless noted otherwise. ¹H-NMR, ¹³C-NMR and were recorded on a Varian AMX400 (400 and 100.6, respectively). Chemical shift values are reported in ppm with the solvent resonance as the internal standard. Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = double doublet, dq = double quartet, qd = quarter doublet, m = multiplet), coupling constants (Hz), and integration. GPC measurements were done on a Spectra Physics AS 1000 series machine equipped with a Viskotek H-502 viscometer and a Shodex RI-71 refractive index detector. The columns (PLGel 5 μ mixed-C) (Polymer Laboratories) were calibrated using narrow disperse polystyrene standards (Polymer Laboratories). Samples were made in THF at concentration of 1.6 mg/ml. Flash chromatography: Merck silica gel type 9385 230-400 mesh. TLC: Merck silica gel 60, 0.25 mm. Compounds were

visualized by UV, Seebachs reagent (phosphomolybdic acid, 25 g, cerium sulfate, 7.5 g, H₂O, 500 mL, H₂SO₄, 25 mL) and potassium permanganate staining.

4.4.2. Synthesis of the starting materials

3-dodecylthiophene (1): To a 250 mL three necked round-bottom flask equipped with a cool condenser, dropping funnel and stirring egg were added 4.89 g (30 mmol) of 3-bromothiophene and 0.20 g (0.36 mmol) of Ni(dppp)Cl₂ in 30 mL Et₂O at room temperature under N₂. A solution of 36 mmol of dodecylmagnesium bromide (1.0 M in dry Et₂O) was added dropwise to the reaction mixture through dropping funnel. After the addition, the reaction mixture was stirring under reflux overnight. Then the reaction was quenched with 5 mL of 1N HCl, poured into 120 mL of H₂O and extracted with Et₂O (3 × 50 mL). The combined organic layer was washed with H₂O (120 mL), brine (120 mL) and dried over MgSO₄. After filtration and removal of the solvent under vacuum, the resulting residue was purified via Kugelrohr distillation to give 7.47 g of compound **1**, 91.1%. ¹H-NMR (400 MHz, CDCl₃) δ 7.24 (dd, *J* = 5.0, 3.0 Hz, 1H), 6.95 - 6.92 (m, 2H), 2.63 (t, *J* = 7.6 Hz, 2H), 1.66 - 1.58 (m, 2H), 1.31 - 1.26 (m, 18H), 0.89 (t, *J* = 6.8 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 143.4, 128.4, 125.2, 119.9, 32.1, 30.7, 30.4, 29.84, 29.82, 29.81, 29.76, 29.6, 29.52, 29.51, 22.9, 14.3.[28]

2-bromo-3-dodecylthiophene (2): To a 100 mL round-bottom flask was added 7.57 g (30 mmol) of **1** in a solution of CHCl₃ (30 mL) and CH₃COOH (30 mL). 5.34 g (30 mmol) of *N*-Bromosuccinimide was added in portions to the reaction mixture over a period of 70 min under ice bath. After the addition, the reaction mixture was continued to stir under ice bath for 1 h and reacted at room temperature overnight. Then the reaction mixture was poured into 100 mL of H₂O and extracted with CHCl₃ (3 × 70 mL). The combined organic layer was washed with H₂O (2 × 70 mL), 1N NaOH (110 mL), brine (110 mL) and dried over MgSO₄. After filtration and removal of the solvent under vacuum, the resulting residue was purified via Kugelrohr distillation to give 9.03 g of compound **2**, yield 90.8%. ¹H-NMR (400 MHz, CDCl₃) δ 7.18 (d, *J* = 5.6 Hz, 1H), 6.79 (d, *J* = 5.6 Hz, 1H), 2.56 (t, *J* = 7.8 Hz, 2H), 1.61 - 1.54 (m, 2H), 1.34 - 1.26 (m, 18H), 0.88 (t, *J* = 6.8 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 142.1, 128.4, 125.3, 108.9, 32.1, 29.89, 29.83, 29.80, 29.73, 29.57, 29.54, 29.52, 29.4, 22.9, 14.3.[29]

2,5-bis(tributylstannyl)thiophene (3): To a 250 mL three necked round-bottom flask equipped with a cool condenser, dropping funnel and stirring egg were added 1.68 g (20 mmol) of thiophene and 4.65 g (40 mmol) of TMEDA in 40 mL

n-hexane under N₂. A solution of 40 mmol of *n*-BuLi (1.6 M in hexanes) was added dropwise to the reaction mixture through dropping funnel under ice bath. After the addition, the reaction mixture was stirring under reflux for 45 min. A solution of 13.02 g (40 mmol) of tributylchlorostannane was added dropwise via dropping funnel after cooling down the reaction mixture to 0 °C. After the addition, the reaction was continued to stir at room temperature overnight. Then the reaction was quenched with saturated NH₄Cl solution (60 mL), extracted with Et₂O (3 × 60 mL). The combined organic layer was washed with brine (2 × 50 mL) and dried over MgSO₄. After filtration and removal of the solvent under vacuum, 13.2 g of crude product **3** was obtained, directly used for next step without further purification.[35]

3,3''-didodecyl-2,2':5',2''-terthiophene (4): To a 250 mL three necked round-bottom flask equipped with a cool condenser and stirring egg were added 3.31 g (10 mmol) of **2**, 3.97 g (6 mmol) of **3** and 208 mg (0.18 mmol, 3 mol%) of Pd(PPh₃)₄ in a solution of 150 mL toluene and 50 mL DMF. The reaction mixture was then sparged with N₂ for 15 min. After this, the reaction mixture was heated to 110 °C and continued to stir for 16 h. The reaction mixture was poured into ice after cooling down to room temperature, extracted with CHCl₃ (4 × 80 mL). The combined organic layer was washed with 1 N HCl (2 × 110 mL), brine (1 × 160 mL) and dried over MgSO₄. After filtration and removal of the solvent under vacuum, the resulting residue was purified via flash silica column chromatography using *n*-hexane as eluent to give 1.90 g of compound **4**, yield 65.1%. ¹H NMR (400 MHz, CDCl₃) δ 7.17 (d, *J* = 5.2 Hz, 2H), 7.05 (s, 2H), 6.94 (d, *J* = 5.2 Hz, 2H), 2.78 (t, *J* = 7.8 Hz, 4H), 1.69 – 1.61 (m, 4H), 1.41 – 1.25 (m, 36H), 0.88 (t, *J* = 6.8 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 139.9, 136.2, 130.6, 130.2, 126.2, 123.9, 32.1, 30.9, 29.85, 29.83, 29.81, 29.78, 29.73, 29.65, 29.5, 29.4, 22.8, 14.3.[36]

5,5''-dibromo-3,3''-didodecyl-2,2':5',2''-terthiophene (5): To a 100 mL round-bottom flask was added 1.67 g (2.9 mmol) of **4** in a solution of CHCl₃ (6 mL) and CH₃COOH (6 mL). 1.02 g (5.8 mmol) of *N*-Bromosuccinimide was added in portions to the reaction mixture over a period of 20 min under ice bath. After the addition, the reaction mixture was continued to stir under ice bath for 1 h and reacted at room temperature overnight. Then the reaction mixture was poured into 50 mL of H₂O and extracted with CHCl₃ (3 × 25 mL). The combined organic layer was washed with H₂O (2 × 30 mL), 1N NaOH (30 mL), brine (30 mL) and dried over MgSO₄. After filtration and removal of the solvent under vacuum, the resulting residue was purified by flash silica column chromatography using *n*-hexane as eluent and recrystallized from *n*-hexane/isopropanol (v/v = 3:1) to give 1.75 g of

compound **5**, yield 81.2%. ^1H NMR (400 MHz, CDCl_3) δ 6.98 (s, 2H), 6.90 (s, 2H), 2.7 (t, $J = 7.8$ Hz, 4H), 1.64 – 1.56 (m, 4H), 1.38 – 1.25 (m, 36H), 0.88 (t, $J = 6.6$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 140.7, 135.3, 132.9, 131.8, 126.6, 110.8, 32.1, 30.7, 29.85, 29.82, 29.81, 29.7, 29.58, 29.52, 29.4, 29.2, 22.9, 14.3.[36]

3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (6): A 250 mL three necked round-bottom flask equipped with a cool condenser, dropping funnel and stirring egg were added with 2.30 g (100 mmol) of Na and 20 mg (0.12 mmol) of FeCl_3 in a solution of 70 mL tert-amyl alcohol. Then the mixture was heated to reflux and cooled to 90 °C until the dissolution of Na. 5.02 g (46 mmol) of thiophene-2-carbonitrile was subsequently added to the reaction solution. Afterwards, 4.05 g (20 mmol) of diisopropyl succinate was added dropwise in 0.5 h. Next the reaction solution was heated to 110 °C and kept at this temperature for 16 h. Then a solution of $\text{CH}_3\text{OH}/\text{H}_2\text{O}/\text{CH}_3\text{COOH}$ (25 mL/25 mL/25 mL) was added and the reaction solution was refluxed for 20 min, while undergoing hot filtration of the reaction solution. The resulting filter was washed with a hot solution of $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ ($v/v = 2/1$, 4×60 mL) and dried under vacuum, to give 3.93 g of compound **6**, yield 65.3%. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 11.24 (s, 2H), 8.22 (d, $J = 4.0$ Hz, 2H), 7.97 (d, $J = 4.8$ Hz, 2H), 7.32 – 7.30 (m, 2H).[37]

2,5-bis(2-hexyldecyl)-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]-pyrrole-1,4-dione (7): To a 250 mL round-bottom flask equipped with a cool condenser were added 3.60 g (12 mmol) of **6**, 10.99 g (36 mmol) of 7-(bromomethyl)pentadecane, 4.98 g (36 mmol) of K_2CO_3 and 0.32 g (0.12 mmol) of 18-crown-6 in a solution of 70 mL DMF. After the addition, the reaction solution was heated to 120 °C for overnight. The reaction solution was poured into a solution of 500 mL Et_2O after cooling down to room temperature, washed with H_2O (2×250 mL) and brine (200 mL), and dried over MgSO_4 . After filtration and removal of the solvent under vacuum, the resulting residue was purified by flash silica column chromatography using n-pentane/DCM as eluent and recrystallized from EtOH to give 4.20 g of compound **7**, yield 46.7%. ^1H NMR (400 MHz, CDCl_3) δ 8.87 (dd, $J = 4.0, 0.8$ Hz, 2H), 7.62 (dd, $J = 5.2, 0.8$ Hz, 2H), 7.27 – 7.25 (m, 2H), 4.01 (d, $J = 7.6$ Hz, 4H), 1.93 – 1.87 (m, 2H), 1.33 – 1.20 (m, 48H), 0.87 – 0.82 (m, 12H).[38]

3,6-bis(5-lithium-thiophen-2-yl)-2,5-bis(2-hexyldecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (8): A solution of **7** (0.22 g, 0.3 mmol) in anhydrous THF (3 mL) was cooled down to -78 °C under N_2 , and then dropwise added with freshly lithium diisopropyl amide (LDA, 1.0 M in THF/hexanes, 0.69 mL, 0.69 mmol). After stirring at -78 °C for 1 h, the reaction mixture was allowed to warm

up to room temperature and further stirred for 1 h. Then tetramethylethylenediamine (TMEDA, 34.9 mg, 0.3 mmol) was added to stabilize the lithium reagent solution. And the solution was used for the test of polymerization without further purification.[31]

3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-hexyldecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (9): To a 100 mL round-bottom flask was added 1.50 g (2 mmol) of **7** in a solution of 40 mL CHCl₃. After the addition, the reaction solution was cooled to 0 °C under ice bath for 20 min. 0.78 g (4.4 mmol) of *N*-Bromosuccinimide was then added in portions to the reaction solution over a period of 0.5 h at 0 °C. The reaction was continued to be stirred at 0 °C for 0.5 h. The reaction solution was then washed with H₂O (3 × 100 mL) and dried over Na₂SO₄. After filtration and removal of the solvent under vacuum, the resulting residue was purified by dispersion in CH₃OH/EtOAc (v/v = 10:1) to give 1.27 g of compound **8**, yield 70.1%. ¹H NMR (400 MHz, CDCl₃) δ 8.61 (d, *J* = 4.4 Hz, 2H), 7.21 (d, *J* = 4.0 Hz, 2H), 3.92 (d, *J* = 8.0 Hz, 4H), 1.91 -1.84 (m, 2H), 1.33 – 1.22 (m, 48H), 0.90 - 0.83 (m, 12H).[39]

4.4.3. General Procedure for the ^tBuLi-mediated polymerization

To a 20 mL schlenk flask were added 73.9 mg (0.1 mmol) of **5** and catalyst in a solution of toluene under N₂. After the addition, the solution was sparged with N₂ for three times. The ^tBuLi solution (1.7 M in pentane) subsequently was added dropwise by syringe to the reaction solution. Then the solution was continued to be stirred at room temperature for 1 h and precipitated by pouring slowly into 50 mL of CH₃OH afterwards. To facilitate the precipitation, 2 mL of 1N HCl was then added. The resulting slurry was filtered by hydrophilic filter membranes and purified by soxhlet extraction with CH₃OH, acetone and CHCl₃. The resulting polymer was analyzed via GPC measurement.

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5

Factors affecting stability of polymer:fullerene solar cells

Abstract: *Semiconductor polymers are essential for the advancement of polymer solar cell technology. The last decade saw the conception of myriad new donor polymers, among which benzodithiophene-co-thienothiophene (BDT-TT) polymers are attractive due to their relatively high power conversion efficiency in bulk heterojunction solar cells. In this work, we conduct a systematic UV-degradation study on a set of PBDDTT-TT polymers:fullerene solar cells. Most importantly, it shows clearly the relationship between the polymer chemical structure and the UV-stability of the solar cells. We find that solar cells of polymers with alkoxy side chains are more stable (<20% loss in PCE) than those with alkylthienyl side chains (48% loss in PCE) over the period of study. With these results, we further examine the effect of UV-light on the stability of other two polymers, namely PBDDTTT-E and PBDDTTT-ET, processed with or without additives. Through combined experimental techniques, the effects of both the polymer chemical structure and additives 1,8-diiodooctane (DIO), chloronaphthalene (CN) and 1,8-octanedithiol (ODT) on the UV-stability*

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of the solar cells are explored. While DIO acts as photo-acid and leads to accelerated degradation of the solar cells, CN does not. Acidity is known to be detrimental to the efficiency and stability of organic solar cells. Finally, the mechanisms behind the effect of DIO are explained, paving the way for the design of new, efficient as well as stable materials and additives.

5.1. Introduction

Over the past few decades, polymer solar cells have received attention in the scientific community due to their potential, though debatable, of becoming cheaper alternatives to the existing solar cell technologies. This notion was mainly driven by the fact that these devices are easily solution-processed,[1] giving the possibility for eventual large scale fabrication (of both small and large area devices) and flexible solar cell technologies. Efforts to boost this technology were mostly limited to the improvement of device efficiency, while relatively little has been done on the device stability and lifetime.[2–7] Device degradation is a complex mechanism, as many factors play key but different roles in the process. Poly(3-hexylthiophene), P3HT, one of the workhorse polymers has extensively been studied and was found to be relatively stable under thermal stress, continuous illumination and in ambient conditions,[8, 9] as will be experimentally shown later in this study. However, P3HT solar cells have low efficiency.[10] Thus, new materials that would yield highly efficient as well as stable devices are needed. In this regard, a decade ago, myriad polymers including the benzodithiophene (BDT) novel polymers were structurally engineered.[11–20] The series of benzodithiophene-co-thienothiophene (BDT-TT) polymers were subsequently synthesized of which among the alkoxy-BDT (1D) polymers, PTB7 quickly became the workhorse material.[21] Subsequently, the alkylthienyl (2D) polymers of the family were engineered giving rise to improvement in the efficiency of their devices. The provision of these novel materials, combined with device architecture and processing techniques yielded power conversion efficiencies (PCEs) above 10% for single junction polymer fullerene cells.[16],[22],[23] A typical example is the combined use of additives (e.g. diiodooctane, DIO or octanedithiol, ODT) and the change in interfacial layers and electrodes in the use of inverted structure.[24–29] These strategies were combined recently to produce a power conversion efficiency (PCE) of 17.3%.[30] These multijunction organic photovoltaic (OPV) devices utilized DIO as an additive as well as PTB7-Th, a BDT-TT polymer.

However, stability studies[2],[5],[6],[23],[31–33] of these materials and their devices are limited, and more importantly the mechanism behind the degradation is still only partially understood and needs more attention to be generalized to all polymer solar cells. Recently, it has been demonstrated that in the case of photo-oxidative degradation, nickel chelates can be used as antioxidant to suppress the photo-induced oxidation, and thus improving the stability.[6] It is also shown that additives, such as DIO, have conflicting effects on device performance, i.e. even

though DIO aids in the improvement of device efficiency, it is an agent of accelerated degradation in the devices.[34–36] The reason behind this conflicting effect is not well understood, difficult to explain, and thus not fully clarified in the literature. While a school of thought has it that DIO becomes an inherent part of the deposited film, tightly bound within upon film formation, that it cannot be fully removed from the film;[37–39] others have it that it is possible to remove DIO by vacuum and/or thermal annealing and washing with methanol. [7],[40],[41]

This paper aims to show the relation between the degradation of polymer:fullerene solar cells and the chemical structure of the polymers, to identify why DIO is not good for device stability irrespective of its positive effect on efficiency, and to explain the mechanism behind these effects for BDT-TT polymers that can be extrapolated. These are PTB7 (hereafter R-O₁), PBDTTT-C (hereafter R-O₂), PBDTTT-E (hereafter E), 1D polymers and their 2D polymer counterparts PTB7-Th (hereafter R-T₁), PBDTTT-C-T (hereafter R-T₂) PBDTTT-E-T (hereafter ET) with similar molecular weight and dispersity as shown in Figure 5.1. The only difference between these materials is in the side chain pendant group, with the former having alkoxy side chains (ether groups) on the BDT unit while the latter has alkylthienyl side chains (thiophene groups). In this work, we study the effect of their chemical structure on their photostability within the bulk heterojunction active layer of the solar cells processed with or without DIO (or CN), in an inert atmosphere. We take a particular look at the possible effect of the UV part of the solar spectrum on the stability of the devices, since the effects of other degradation agents have either been widely studied, as in the case of heat (thermal degradation) or can be carefully and easily avoided by encapsulation, in the case of oxygen (O₂) and moisture (H₂O). Our investigation focuses on the difference in polymer chemical structure and on the effect of DIO (or CN) on PCE and the photostability of conventional solar cells under continuous illumination. The results show that 2D polymers cells processed with or without DIO degrade faster and thus, are less stable compared to 1D polymer cells. This clearly shows that the alkylthienyl side chain polymer is more prone to degradation than the alkoxy ones under ultraviolet (UV) light. FTIR measurements were also studied on both the pristine polymers and blends with [70]PCBM films to have a deep understanding of the observed degradation in the solar cells and its pathway. Finally, we moved a step further to explain why DIO is so detrimental to the device stability and the mechanisms behind these observed trends for both polymers (E and ET) using combined results from current-voltage (*J-V*) characteristics, NMR, and FTIR measurements. Our goal is to understand the

Figure 5.1: Chemical structure of donor polymers used in the blend active layer

underlying chemistry of the DIO-induced degradation mechanism, and to use this understanding to find better radical scavengers or antioxidants that do not undo the benefit of the additives, as these additives that solve some of the laboratory-scale efficiency issues exacerbate oxidative/photo-induced damage. We found that DIO likely acts as a phot-acid in the active layer of the solar cell, generating HI under illumination as compared to ODT. Acidity is known to be detrimental to the efficiency and stability of organic solar cells and HI is a very strong acid (3pKa units more acidic than HCl). And even the acidity of PEDOT:PSS which could be a problem for the underlying electrodes, typically ITO or FTO[42–44] can have deleterious effects on the active layer. In this case, the formation of HI inside the active layer upon

UV-exposure is detrimental to the photo-stability of the devices.

5.2. Results and Discussion

5.2.1. Performance of Devices processed without additives: Initial Power Conversion Efficiency

Comparative efficiency studies were carried out as a control on all four polymers (R-O₁, R-O₂, R-T₁ and R-T₂) as shown in Figure 5.1a, b, d and e each time devices were fabricated in order to check reproducibility and to achieve the purpose of the work in a reliable way. The main experiments were conducted on conventional structure devices without additives and fabricated under the same conditions to ensure there were no differences in processing and environmental conditions. The active layers are blends of either R-O or R-T polymers of two classes of BDT-TT polymers, shown in Figure 5.1a, b, d and e, with [70] PCBM dissolved in 1,2-dichlorobenzene (oDCB). As expected, the polymer solar cells of polymers with the R-T side chains outperformed those with R-O groups. The best cell based on PTB7 (R-O₁) had a PCE of 5.10% with a short circuit current (J_{SC}) of 11.12 mA cm⁻², an open circuit voltage (V_{OC}) of 769 mV and a field factor (FF) of 59.6%. The overall best-performing cell was PTB7-Th (R-T₁) which exhibited a PCE of 9.64% with improved J_{SC} of 17.09 mA cm⁻², V_{OC} of 811 mV and FF of 69.6%. A similar trend was observed for polymer solar cells of PBDTTT-C (R-O₂) and PBDTTT-C-T (R-T₂), with PCEs of 4.17% and 5.82% respectively. The better photovoltaic performance of the R-T devices is attributed to their slightly lower HOMO (see Figure 5.2a especially for R-T₁); to their slightly broadened absorption band, with the onset slightly red-shifted (Figure 5.2b and c), eventually reflected in increase of J_{SC} (Figure 5.3a); and

Figure 5.2: (a) HOMO-LUMO levels; (b,c) Absorption spectra of R-T devices with onset Red-shifted compared to R-O devices.

to their improved charged carriers mobility, explained by better surface morphology

of blend. Detailed parameters of the best-performing solar cells are shown in Figure 5.3a while Figure 5.3b gives the PCE spread for all four polymer solar cells.

Figure 5.3: (a) Current-voltage curves of PSCs of polymers blended with [70]PCBM; (b) Efficiency of PSCs (with the brown points representing the maximum and minimum values (outside the boxes), and the mean values within the boxes). Device thickness: R-O₁~100 nm, R-T₁~100 nm, R-O₂~130 nm, and R-T₂~110 nm.

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5.2.2. Stability of devices processed without additives

The stability tests were conducted in a glovebox on each device (kept at room temperature 295 K by active cooling) in an inert environment (with <0.1 ppm H₂O and <0.1 ppm O₂) under continuous simulated sunlight for 2 hours. The spectrum (black line) of the lamp used is shown in Figure 5.21A (black line).[45] All shown results are for the best-performing cells, and all mentioned devices were fabricated under the same conditions to ensure differences in the UV-degradation pathway are not due to processing. Reports in this paper are based on the best-performing devices. Figure 5.4a shows the decay/degradation pathway of the R-O based devices compared to R-T ones. A decay in PCE within the limit of ~10% of its initial PCE was observed for the R-O₁ device over 2 hours continuous illumination, while the R-T₁ device decayed over the same period by ~35%. This observation seems rather surprising as alkoxy side chains are known to negatively impact polymer stability.[46] That is not the case here for UV-stability. Even under thermal stability it is not entirely clear if that is the case in view of our observation (figure not shown here). Similarly the R-O₂ device recorded a ~16% decay of its initial value compared to R-T₂ with ~48% decay. Details of the decay rate of other parameters of the polymer solar cells of both groups are shown in Figure 5.4b–d. Here, clearly, while V_{OC} decreased, J_{SC} remained almost constant for all blends. The FF, however,

Figure 5.4: (a) Normalized PCE degradation over time of R-O (red) compared to R-T (blue) polymer devices; (b–d) Evolution of V_{OC} , FF and J_{SC} over time.

decreased for R-T devices, but remained almost constant for R-O devices. To further examine the extent of degradation in both type of devices, in terms of stability, their lifetime, T_{80} , was determined. T_{80} is the time at which a device degrades by 20% from its initial PCE irrespective of the testing conditions.[47] The lifetime of the R-T₁ device was found to be <15 min while that of R-T₂ device was <20 min. For the R-O devices, we could only assume a minimum possible lifetime of 2 hours since the devices did not degrade to 80% of their PCE over the duration of the measurements.

To determine if the observed degradation in the devices could be due to photo-bleaching, absorption spectra of the blends were taken before and after 2 hours exposure to light. As can be observed in Figure 5.5a, both the polymer and [70]PCBM absorbs from UV (300–425 nm), so if any significant change is observed in any of the devices compared to the others, it could be attributed to that particular polymer. The spectra of all components looked similar to the one depicted in Figure 5.5a, with notable differences in the polymer and blend spectra. As shown in Figure 5.5b-d the interesting observation, however, was that there was no apparent

change in spectra before and after exposure. Hence, the observed UV-degradation cannot be attributed to photobleaching.

Figure 5.5: Absorption spectra of (a) films of R-T₁ polymer-of [70]PCBM-of blend with [70]PCBM, and of exposed (red) and unexposed (blue) blend films of (b) R-O₁ polymer (c) R-O₂ polymer (d) R-T₁ polymer and (e) R-T₂ polymer.

Additionally, despite being a very good hole transporting layer (HTL), PEDOT:PSS has been found to be unfavourable for device stability, thus researchers have tried to replace it with metal oxides either in conventional or in inverted structure for improved device stability.[43],[48–51] It is believed that the acidic nature of PEDOT:PSS means it could react more with the R-T polymers in the blends and therefore could explain the accelerated degradation of these types of devices. To confirm this hypothesis, conventional devices were fabricated on one hand without the PEDOT:PSS layer (with the structure ITO/Blend/LiF/Al) and on the other hand with a pH-neutral PEDOT:PSS layer (with the structure ITO/pH-neutral PEDOT:PSS/Blend/LiF/Al). Furthermore, there were also concerns about Li diffusion into the active layer of the device and therefore could be the major factor in the degradation observed. To check this effect, we made devices with the following structure ITO/PEDOT:PSS/Blend/Ca/Al. All three types of devices were illuminated under the same conditions as the original ones. To our surprise, as stated earlier, again in these three cases similar trends were observed as depicted in Figure 5.6: R-T devices degraded faster than R-O devices. Also, AFM images of as cast and exposed blend films showed no notable differences in features. Figure 5.7 shows

the case of PTB7:[70]PCBM blend films. Thus, the degradation cannot be at-

Figure 5.6: Current-Voltage characteristics PCE degradation curves: of devices (just with ITO) without PEDOT:PSS (a) R-O₁ and R-T₁ and (b) R-O₂ and R-T₂; of devices with pH-neutral PEDOT:PSS (c) R-O₁ and R-T₁ and (d) R-O₂ and R-T₂; and of devices with (e) Ca/Al as top electrodes.

Figure 5.7: Two films of PTB7:[70]PCBM spin-coated on glass under the same conditions (a) as cast (1 micron and 200 nm) and (b) after 2 hours UV-exposure (1 micron and 200 nm).

tributed to morphology change or pronounced phase separation upon illumination. We therefore attributed the rapid decay in the R-T devices to the alkylthienyl side chain decomposition products or free radical species that could form from the rapid and pronounced photochemical reactions of the alkylthienyl side chains activated by the UV-light exposure. These species could form big decomposition products

and subsequently act as impurities or deep traps which could hamper the stability of the R-T devices more than the R-O free radical species do to the R-O devices. To further investigate the formation of the decomposition products which we ascribed to be the cause of the observed degradation, an ^1H -NMR study was conducted on dissolved BDT-monomers, $M_{\text{R-O}}$ and $M_{\text{R-T}}$, shown in Figure 5.8. The ^1H -NMR were carried out in an inert environment using air-tight/sealed NMR tubes with solutions prepared in a glovebox. The results shown in Figure 5.9 and Figure

Figure 5.8: Molecular structures of monomers

Figure 5.9: Normalized integrated relative peaks to solvent (CDCl_3) of R-O (red curve) and R-T (blue curve) monomer solutions in sealed NMR tubes vs. UV-exposure time in an inert atmosphere (a) backbone characteristic peaks and (b) side chains characteristic peaks.

5.10 confirm our hypothesis. There was a rapid decline (as shown in Figure 5.10b,

Figure 5.14, Figure 5.15 and Figure 5.16) in the integrated intensity of the peaks

Figure 5.10: ^1H NMR spectra of (a) R-O and (b) R-T monomer solutions recorded in an inert environment using sealed NMR tubes under irradiation with 315–400 nm light at ten-minute intervals from bottom-to-top starting from the initial spectrum.

corresponding to the monomers relative to the solvent (CDCl_3) peak, of the R-T monomer solution, compared to the R-O monomer solution (Figure 5.10a, Figure 5.11, Figure 5.12 and Figure 5.13). While both monomer solutions degraded upon UV-exposure, the rate of degradation of R-T was faster, especially as shown in Figure 5.9b, than that of R-O. A typical example is the disappearance of the R-T proton peak at 1.5 ppm just after 10 min exposure, see Figure 5.14. The ^1H -NMR spectrum of the R-O clearly showed the formation of new peaks (highlighted in purple circles) with decreasing intensities of the initial peaks (red circles). These new peaks have the same multiplicity of the monomer, but are shifted down-field, indicating the possible formation of a quinone moiety, present in the solution, upon cleavage of the alkoxy side chains. In the R-T spectrum, however, almost no new

Figure 5.11: ^1H NMR spectra (initial and after exposure to a shuttered UV flood light in steps of 10 mins for 100 mins) of monomer solutions of R-O

peaks were observed. This does not mean, there were no decomposition products. A careful study of the exposed R-T monomer solution spectrum, showed clearly that there was cleavage of the alkyl side chains and possibly of the thiophene rings which could form decomposition products, rather insoluble, and therefore, not detected by ^1H -NMR. Evidently, R-T degraded faster than R-O, which confirms our hypothesis for the trends observed in the degradation of the devices. The photodegradation of polymer solar cells has been recently attributed by some solely to effects triggered by charge collection layers and interfaces[52] and by others to hot carriers breaking C-H bonds at the donor/acceptor interface.[53] The latter claim required energies 44 eV, but we showed here that the monomers themselves are unstable to UV irradiation, which certainly does not involve homolytic cleavage of C-H bonds. If hot carriers were breaking apart C-H bonds, then almost no polymer would be stable, but that is not the case. The observed trend, however, in these four full devices reiterates the role played by the active layer composition.

In order to elucidate the combined effects of the presence or the absence of the fluorine (F) atom and the extra oxygen (O) atom on the TT-unit moieties in the molecular structure of the polymers on the stability of the solar cells, we examined

the degradation pathways in the R-O and R-T devices themselves and compared them to each other. For example, as mentioned above and shown in Figure 5.1a, b, d and e, the structures of the R-O polymers are identical including the side chains on the BDT-units except for the presence of F atom and an extra O atom on the side chain of the TT-unit in R-O₁ compared to R-O₂. The same relation holds between R-T₁ and R-T₂. The best-performing cells revealed that R-O₁ devices were a bit more stable, with ~10% decay over 2 hours light exposure, than R-O₂ ones which recorded ~16% decay. As shown in Figure 5.4a, a similar observation was made about R-T₁, with ~35% decay and R-T₂, with ~48% decay. These observed differences (indicated in olive arrows) were so minimal, compared to differences between an R-O device and an R-T one (indicated in brown and black arrows), that it cannot be inferred with total certainty/confidence what role the presence or the absence of F and O atoms might be playing in the degradation pathway. The effect of fluorination alone on device performance has already been reported to be more complicated than just the changing of energy level as it affects polymer:

Figure 5.13: ¹H NMR spectra of monomer R-O with relative integrated peaks (>7.3 ppm and between 0.5 and 2.25 ppm as used in Figure 5.9a, b) to solvent (CDCl₃)

Figure 5.14: ¹H NMR spectra (initial and after exposure to a shuttered UV flood light in steps of 10 mins for 100 mins) of monomer solutions of R-T

Figure 5.15: ¹H NMR spectra of monomer R-T with relative integrated peaks (P1 ~ 1st peak to P10 ~ 10th peak) to solvent (CDCl₃)

fullerene compatibility.[54]

5.2.3. Performance of Devices Processed with and without Additives: Initial Power Conversion Efficiency

Figure 5.17 reveals the general performance of the solar cells under study, notably the PCE in A and photo-degradation in B, C and D. The *J-V* characteristics in Figure 5.17A, together with their parameters as displayed in Table 5.1, show a better performance for ET over E with 24%, 6%, and 32% increase in short circuit current (J_{sc}), open circuit voltage (V_{oc}), and PCE respectively when one transits from the E cell to the ET cell. This improvement can certainly be explained by combined effects of many factors. ET has a slightly lower band gap (Figure 5.18C), resulting in a slightly broader absorption band with an onset slightly red shifted compared to E as shown in Figure 5.18F and translated into an increase in J_{sc} . Compared to E, ET has an improved charge carrier mobility with μ_h in the order of $19 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ as against $8.5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for E as obtained by the space charge current limited measurements. ET blend films have an ideality factor (n) of 1.43 compared to that of E blend films which is 1.67 as shown in Table 5.1, suggesting

Figure 5.16: ^1H NMR spectra of monomer R-T with relative integrated peaks (>7.3 ppm and between 0.5 and 2.25 ppm as used in Figure 5.9a, b) to solvent (CDCl_3)

Table 5.1: Device parameters of cells: P3HT blended with [60]PCBM in CB and the rest blended with [70]PCBM in oDCB. The average values for the cells are obtained for at least twenty devices processed from oDCB and for ten devices processed from oDCB:DIO. The thickness of devices is around 100 nm.

Polymer/Solvents	L (nm)	J_{sc} (A.m^{-2})	V_{oc} (V)	FF (%)	PCE (%)	PCE_{avg} (%)	η_{lvo}	η_{avg}
P3HT/CB	-	94.6	0.568	64.1	3.4	3.2 ± 0.3	-	-
PBDTTT-E/oDCB	100	102.3	0.686	55.4	3.9	3.6 ± 0.2	1.67	1.73 ± 0.08
PBDTTT-E/oDCB:DIO	100	131.0	0.646	68.0	5.8	5.0 ± 0.5	1.43	1.47 ± 0.04
PBDTTT-ET/oDCB	100	127.3	0.727	55.3	5.1	4.3 ± 0.4	1.43	1.49 ± 0.06
PBDTTT-ET/oDCB:DIO	100	133.9	0.702	61.9	5.8	5.7 ± 0.1	1.34	1.40 ± 0.06

L (Thickness), avg (average), η (ideality factor), and lvo (lowest value obtained). The errors are standard deviations.

fewer traps in ET blend films over E as reflected by a slightly more homogeneous film morphology for ET in Figure 5.19B. The addition of DIO during device processing notably increases J_{sc} and FF, and thus, generally improves the efficiencies of the device as shown in Table 5.1. In general, there was 28%, 23%, 48% increase in J_{sc} , FF and PCE respectively for the E solar cell while there was 5%, 12%, 14% increase in J_{sc} , FF and PCE for the ET one. This improvement in efficiency upon

Figure 5.17: Performance of the cells with (open symbols) and without (full symbols) DIO under simulated 1 sun illumination using (un)filtered lamp: (A) J - V characteristic curves of all cells under study; Evolution of PCE of P3HT:[60]PCBM, E:[70]PCBM and ET:[70]PCBM cells normalized to their initial values under (B,D) unfiltered lamp and (C) filtered lamp.

addition of DIO, as observed in previous report[20], is attributed to a number of factors including a better miscibility of the polymer:fullerene phases in the blend layer as shown in Figure 5.19C,D and Figure 5.20 C,D with a slight improvement of carrier mobilities. This allows for more homogeneous morphology, efficient charge separation and extraction, resulting into more current (J_{sc}) and an increase in FF. This improvement in efficiency is also reminiscent of the drop in n_i from 1.67 to 1.43 for E cells and from 1.43 to 1.34 for ET cells in Table 5.1, suggesting reduction in trap assisted recombination in the devices processed with DIO.

5.2.4. Performance of Devices with and without additives: Stability and Lifetime

UV-Degradation of Conventional E and ET Polymer Solar Cells

Solar cells of E and ET were fabricated under the same conditions. The devices, kept at room temperature by active cooling, were characterized in an inert atmosphere

Figure 5.18: Devices and Optical properties. (A) Device count vs. PCE for E:[70]PCBM and ET:[70]PCBM solar cells; UV-Vis absorption spectra of (B,C) BDT-monomers and polymers (D,E) fullerene, polymers and blends (F) the two blends showing the red-shifted onset of E, ET and (G,H) the two blends before and after UV-exposure.

in a glovebox, with both O_2 and H_2O levels kept below 0.1 ppm. The cells were continuously exposed, under open circuit condition, to both UV-filtered and unfiltered solar simulator lamp (with their spectra shown in Figure 5.21A) for two hours while the J - V characteristics were measured at a constant interval of time over the duration of the experiment. The light source is a SolarConstant 1200 Steuernagel metal halide lamp calibrated to 1 sun intensity and corrected for spectral mismatch with the AM1.5G spectrum using a Si reference cell. The obtained results clearly showed that the observed degradation is due to the UV part of the light.

Figure 5.17C shows the photostability behaviour of the two polymer cells with filtered UV-light, exhibiting clearly a very good level of stability comparable to that of P3HT full light exposed cell shown in Figure 5.17B. In contrast, under unfiltered lamp illumination, both cells showed different trends in their UV-degradation behaviour. For the E polymer there is a gradual decline in the initial PCE which is relatively slow over the period of the experiment. However, for the ET polymer the PCE decay is relatively fast in the first 20 minutes subsequently followed by a much slower and stabilized decline in PCE as depicted in Figure 5.17B. The observed photoinduced degradation started from the side chains in the first few minutes due to the cleavage of the side chains.[32] Upon cleavage, the residual side chains formed decomposition products in the active layers of both cells with the thiophene groups

Figure 5.19: Height profiles of spin-coated films without vacuum treatment before and after solar simulator lamp exposure (2 hrs) with a scan size of 5 μm . For each section, top half shows the morphology of the film before/after UV exposure, bottom half shows the 3D topography of the film before/after UV exposure. (A,B) Films E:[70]PCBM and ET:[70]PCBM without DIO (C,D) Films of E:[70]PCBM and ET:[70]PCBM with DIO.

less stable than the ether groups. This effect could be possibly due to the fact that the alkylthienyl BDT polymers are prone to absorb more in the UV region of the spectrum than alkoxy BDT polymers (Figure 5.18C,D and E), especially, in the wavelength range of 250–310 nm as shown by the absorption spectra of the BDT-monomers in solution in Figure 5.18B. Over the exposure time, E exhibited a decay of 18% from its initial PCE while ET recorded 36% PCE degradation from its initial value. The device parameters shown in Figure 5.21B revealed that ET suffered the most loss in J_{sc} and FF while E suffered the most loss in J_{sc} . The photostability lifetime (T_{80}) of the devices were determined to be < 30 minutes for ET and a minimum of two hours for E. This confirms that E is more stable than ET. However, under the same conditions as shown in Figure 5.17B, considering the 3% decay recorded by P3HT:[60]PCBM (1:1 in CB) solar cell from its initial PCE of 3.4%, both polymer solar cells can be considered unstable.

To further comprehend the mechanisms behind the degradation of the polymer solar cells, variations in nano-morphological structures before and after exposure,

Figure 5.20: Height profiles of spin-coated films without vacuum treatment before and after solar simulator lamp exposure (2 hrs) with a scan size of 1 μm . For each section, top half shows the morphology of the film before/after UV exposure, bottom half shows the 3D topography of the film before/after UV exposure. (A,B) Films E:[70]PCBM and ET:[70]PCBM without DIO (C,D) Films of E:[70]PCBM and ET:[70]PCBM with DIO.

and variations in absorption spectra of polymer blends before and after exposure were studied through AFM, UV-Vis & FTIR spectroscopy and *J-V* characteristics measurements respectively. Morphological change such as phase separation or change in absorbance upon illumination such as photobleaching could be the factors contributing to the observed degradation.

Figure 5.18B,D and E shows the absorption spectra of the BDT-monomers and those of the E polymer, the fullerene derivative, and their blend respectively. Both polymer and [70]PCBM clearly absorb in the UV range of 250–425 nm. Thus, one would assume that any change in the spectrum of the blend films upon UV-exposure could be due mostly to the difference in the polymer structures. As shown in Figure 5.18G and H, both blend films did not register any change in spectra before and after exposure, eliminating photobleaching as a plausible cause for the degradation, within the time limit of the experiment. The same conclusion was arrived at for morphological changes as seen in Figure 5.19 and Figure 5.20. The profiles of as cast (before) and UV-exposed (after) blend films show basically no change in

Figure 5.21: (A) Spectrum of lamp used during the (degradation) experiment.[45] (B) Evolution of J_{sc} , V_{oc} and FF of E:[70]PCBM and ET:[70]PCBM cells without DIO under unfiltered lamp normalized to their initial values. Performance under continuous simulated solar illumination of the cells with (Full symbols) and without DIO (Empty symbols): evolution of (C) J_{sc} , (D) V_{oc} and (E) FF of E:[70]PCBM and ET:[70]PCBM cells.

structure for both polymers. This implies that though morphological changes cannot be entirely discarded, phase separation upon light exposure could not be the reason behind the differences in the observed photodegradation of E and ET polymer solar cells.

Figure 5.22 and Figure 5.23-5.25 shows the FTIR absorption profiles for drop cast films from solution of [70]PCBM, both polymers, and both blends of comparable thickness before and after UV-exposure. The characteristic peaks of the absorption bands of the films were identified and assigned in Table 5.2. The peaks of the aliphatic side chains of the BDT-unit and the carbonyl group in the ester moiety for both pristine polymer films were clearly observed between $2750\text{--}3000\text{ cm}^{-1}$ and 1714 cm^{-1} respectively while peaks characteristic of the thiophene rings are centered around 943 cm^{-1} and 1540 cm^{-1} . From the spectra of the polymer films in Figure 5.22 it is clear that the aliphatic side chains CH_2 and CH_2/CH_3 around $2750\text{--}3000\text{ cm}^{-1}$ suffer the most reduction in intensity with the peaks of the ET side chains recording the higher reduction in intensity in Figure 5.22B. In addition,

while all other peaks remained almost constant for the E polymer in Figure 5.22A, there were noticeable reductions in some peaks of the ET polymer, as shown in Figure 5.22B, notably at 1714 cm^{-1} characteristic of carbonyl group and at the CH_2 bending 1460 cm^{-1} . This observation affirms our explanation that the degradation

Figure 5.22: FTIR absorption spectra of unexposed and exposed (2 hours, 4 hours and 6 hours) films of pristine polymer films with (open symbols) and without (full symbols) DIO: E polymer (A) without DIO and (C) with DIO; ET polymer (B) without DIO and (D) with DIO.

Figure 5.23: Full FTIR absorption spectra of unexposed and exposed (2 hours, 4 hours and 6 hours) films of pristine and blend materials without DIO: (A) E polymer and (B) ET polymer.

process is retarded in the E polymer cell compared to the ET polymer cell. This

stabilized behavior of the E polymer could be due to the observed formation of benzoquinone[32] as shown in Figure 5.22A with a broad shoulder peak centered around 1640 cm^{-1} next to the ester carbonyl peak, as confirmed by recently published reports[55],[56]. This possibly could be an explanation for the reduction of almost all other peaks in the ET system compared to the E system as also suggested by the PCE decay in Figure 5.17B. This finding reiterates that the degradation is very dependent on the polymer chemical structure. The decomposition compounds from ET upon cleavage of the side chains are more volatile and destabilize their blend, and ultimately, their solar cell performance more than those of the E polymer. One would expect that if the exposure time were to be extended, the aliphatic chains peaks of ET would be the first to totally disappear.

Figure 5.24: (Full) FTIR absorption spectra of unexposed and exposed (2 hours, 4 hours and 6 hours) films of pristine and blend materials without DIO: (A) E:[70]PCBM blend, (B) ET:[70]PCBM blend, (C) [70]PCBM, and (D) ET:[70]PCBM blend.

A look at [70]PCBM spectrum in Figure 5.24C also revealed that PCBM went under degradation. Decrease in intensity of the absorbance in the same aliphatic and CH_2 bending regions upon illumination were observed with an increase at the $\text{C}=\text{O}$ stretching region while an initial increase followed by a significant decrease was recorded in the $\text{C}=\text{C}$ stretching region.

Together, in blend films, as shown in Figure 5.24A,B the spectra clearly demon-

Figure 5.25: Full FTIR absorption spectra of unexposed and exposed (2 hours, 4 hours and 6 hours) films of pristine and blend materials with DIO. (A) E:[70]PCBM blend, (B) ET:[70]PCBM blend, and (C) [70]PCBM.

Table 5.2: FTIR Absorption band assignments for [70]PCBM, E and E:[70]PCBM, ET and ET:[70]PCBM films.

Assignments	Pristine E (σ/cm^{-1})	Pristine ET (σ/cm^{-1})	[70]PCBM (σ/cm^{-1})
CH ₃ Symmetric Bending	1365	1378	1329
CH ₂ Bending	1460	1460	1456 & 1430
(Thieno) thiophene ring/band	943	943	-
C=C stretching	1500-1565	1514-1570	1480-1584
Carbonyl Group (C=O stretching)	1714	1714	1737
Aliphatic (hydrogen) bands	2750-3000	2750-3000	2800-3100
CH ₂ Symmetric Stretching	2867	2859	-
CH ₂ Asymmetric Stretching	2930	2925	-
CH ₂ Asymmetric Stretching	2956	2959	-
CH Stretching	3080	3074	-
Hydroxy (-OH) Groups	3100-3500	3100-3500	-
Carboxylic -OH	-	3210*	-
Alcoholic -OH	-	3405	-

* Observed only in the presence of DIO

strated that E:[70]PCBM is more stable than ET:[70]PCBM. The spectra of the blends showed more peaks, characteristics of both polymer and fullerene, than those of the individual polymer films. There was in general a continuous decrease in signals of the aliphatic side chains and a sharp decrease in the peaks of the CH₂ bending in the presence of [70]PCBM upon illumination, which was more pronounced for ET blend. In effect, two peaks can now be clearly seen in the CH₂

bending region namely at 1456 cm^{-1} characteristic of the polymers and 1430 cm^{-1} characteristic of the fullerene. Two peaks were also observed in the C=O region, one at 1714 cm^{-1} characteristic of the polymers and one at 1737 cm^{-1} characteristics of the fullerene. Upon illumination, while these peaks ostensibly remain constant for E:[70]PCBM films they revealed gradual increase for the ET:[70]PCBM films. This is an indication of the presence of probable additional ester or carboxylic acid groups, formed from decomposition products of the ET blend films. There was an appearance of a new peak at 1573 cm^{-1} in both blend films at the initial stage, just next to the C=C stretch as can be clearly seen in the E blend film. While this new peak completely disappeared upon illumination, there was a significant initial increase in the C=C stretch and appeared to be stabilized, a characteristic behaviour of the polymers as shown in their spectra between $1500 - 1570\text{ cm}^{-1}$ in Figure 5.22A,B. This drastic change in the thienothiophene signal is more pronounced for the ET blend than the E blend (quite stabilized through benzoquinone formation). This could mean that the thiophene backbone rings/units were experiencing changes, possibly introduced by the decomposition products. Clearly, it is evident that the ET:[70]PCBM films are less stable than the E:[70]PCBM ones.

Effect of Diiodooctane on Stability and Lifetime of Conventional E and ET Polymer Solar Cells

DIO has an opposing effect on the performance of the devices. First, a positive effect on morphology, that is a homogeneous miscibility of the polymer:fullerene blend irrespective of the polymer as shown in Figure 5.19C and D, resulting in smaller n as compared to devices without DIO, and ultimately on PCE as clearly shown in Figure 5.17A (open symbols) and Table 5.1. Next, a negative effect on device stability, that is an accelerated UV-degradation upon illumination as seen in Figure 5.17D. To have a better grasp of this negative effect, we conducted the same experiments on devices with DIO as in the case of devices without DIO. It emerged that DIO has a pronounced destabilization effect, coupled with the already discussed polymer chemical structure effect on the device stability. For example, in Figure 5.17D it can be seen that the E polymer cell with DIO had a 60% decay in PCE (as opposed to 18%) while that of ET recorded 74% (as opposed to 36%), meaning while E remained more stable than ET, in this case, both had experienced pronounced degradation compared to the devices without DIO. Consequently, the E polymer cell with DIO had a T_{80} of 20 minutes while that of ET had a T_{80} of < 10 minutes.

To further visualize the effect of DIO in the films under UV, FTIR measurements

were performed on drop cast films of polymers, fullerene and blends from solution with DIO. The spectra showed drastic changes in general upon illumination. For the DIO doped fullerene films in Figure 5.25C, there was a continuous decrease in peaks at 1430 cm^{-1} and between $2800\text{--}3000\text{ cm}^{-1}$ with the disappearance of the shoulder peak at 1456 cm^{-1} and an initial increase with a subsequent decrease at the C=C stretching and at 1737 cm^{-1} . In the case of the polymer films with DIO in Figure 5.22C and D, first, while the peaks at the C=C and C=O stretching ($1500\text{--}1570\text{ cm}^{-1}$ and 1714 cm^{-1}) remained almost unchanged for E, a rise in these peaks was observed for ET films with DIO in contrast to ET films without DIO, leading to the appearance, at later stages of the illumination, of a carboxylic -OH peak at 3250 cm^{-1} . Next, there was a massive decrease (compared to films without DIO) in the peaks at the CH_2 bending and at the aliphatic bands which was continuous for ET films but got stabilized and remained afterwards constant for E films. This is clear evidence that UV and DIO react more detrimentally with the ET polymer than the E polymer.

Finally for the blend films with DIO in Figure 5.25A and B, there was a huge increase in all peaks of the fresh unexposed films except at the C=C stretching which appeared almost to be totally quenched in the presence of DIO in the fresh state, but reappeared under illumination. One would say that DIO has altered the spectra. Upon illumination, there was a big reduction in intensity of all peaks due to the combined effects of UV and DIO reactions on polymer and fullerene except for the peaks at 1714 cm^{-1} and 1737 cm^{-1} of the E blend which increased and stabilized at later stages. The substantial decrease, observed in the peaks, was continuous for ET blends but stabilized for the E blends at longer times of exposure. In short, the FTIR data also point to the fact that upon illumination DIO is decomposed to fragments, possibly iodine radicals, that contribute to the accelerated degradation by intrinsically interacting with (the fullerene, the polymers and) the blend materials without overriding the effect of the polymer chemical structure. Similar trends and varied degree of induced degradation effects have been observed for most additives, whether halogenated⁷,^{[34],[35],[57]} such as diiododecane, diiodohexane, diiodopentane, etc... or not^{[24],[38],[39],[55],[58]} such as octanedithiol, butanedithiol, phenylnaphthalene, chloronaphthalene, etc...

The Role of DIO in the Degradation Explained

To pinpoint the exact role of DIO in the degradation process, we set out to study the DIO effect in details to understand the mechanism. There is a possibility that DIO might have significantly altered the nanostructure morphology of the blend

films of E:[70]PCBM and ET:[70]PCBM active layers under the influence of the illumination, explaining the observed pronounced degradation as opposed to the postulated iodine radicals theory; changes that were not really observable under AFM. If that were to be the case, then any light source illumination of their solar cells should cause them to degrade differently. Previously it was found that 1-chloronaphtalene (CN) participates the photo-oxidation (through photobleaching) of BDT-TT polymer:[70]PCBM blend films.[55] To check if CN also accelerates the photodegradation of the solar cells in our experiments, CN ($\geq 85\%$ technical grade with boiling point of $260\text{ }^{\circ}\text{C}$) was used as an alternative to DIO.

Solar cells were fabricated from blend solutions containing 0 and 3vol-% of DIO or CN and characterized under the same conditions as described above with H_2O and O_2 levels lower than 0.1 ppm in a glovebox. The J - V parameters of these cells are displayed in Table 5.3. First all cells were continuously illuminated for 2 hours with unfiltered lamp. Next, solar cells with DIO were then illuminated continuously with filtered lamp for 2 hours under the same conditions as for devices without DIO.

Table 5.3: Device parameters of solar cells processed from oDCB, oDCB:CN and from oDCB:DIO.

Polymer/Solvents	L (nm)	J_{sc} (A.m^{-2})	V_{oc} (V)	FF (%)	PCE (%)
PBDTTT-E/oDCB	100	97	0.671	56.7	3.7
PBDTTT-E/oDCB:CN	100	87	0.660	56.4	3.2
PBDTTT-E/oDCB:DIO	100	118	0.611	62.7	4.5
PBDTTT-ET/oDCB	100	115	0.717	56.3	4.7
PBDTTT-ET/oDCB:CN	100	103	0.740	56.3	4.3
PBDTTT-ET/oDCB:DIO	100	113	0.688	63.2	4.9

Figure 5.26 reveals that ET based solar cells (as well as E based cells in Figure 5.27) with CN and the solar cells without DIO show the same level of stability and in some cases a slightly better stability was observed for solar cells with CN. Only the solar cells with DIO recorded accelerated PCE decay over time. All J - V parameters show the same stability trends as can be seen in the figures. The fact that CN does not further degrade at all the cells (or slightly improve their stability) is offset by the observation of the opposite effect on PCE; CN decreased the PCE of the cells as seen in Table 5.3. To confirm the validity of the DIO effect on all PBDT-TT polymers, PTB7, PTB7-Th, PBDTTT-C, and PBDTTT-CT were also used and similar conflicting trends of improved efficiency but accelerated photodegradation in the presence of UV-light is observed and their PCE decays are shown in Figure 5.28.

Figure 5.26: Performance of ET based cells under continuous simulated solar illumination with no additive (blue, full symbol), with CN (purple) and with DIO (blue, empty symbol): PCE (A), J_{sc} (B), V_{oc} (C) and FF (D).

Figure 5.29A shows the combined results of devices with DIO under continuous illumination with UV-filtered or unfiltered light, leading to the conclusion that all the devices do not degrade under UV-filtered light. First, these data reinforced the fact that the UV part of the light was responsible for the degradation. Next, not only did it reveal that UV affects differently the chemical structure of the polymers but also that it certainly reacted with the DIO molecules, through radical reaction by cleavage of carbon-iodine bonds (breaking them into pieces: iodine, iodo-octane or octane radicals). Thus, the formation of iodine radical species, a possible pathway of DIO reaction with UV as shown in Figure 5.30, in its neutral state I_2 or ionized states (I^- and I_3^-), could intrinsically crosslink with the polymer chemical structure, dope the film[37], and cause pronounced detrimental reaction upon continuous UV exposure. Clearly, DIO as a high boiling point additive could not completely be removed under high vacuum (10^{-8} Torr). Annealing at high temperatures could be desirable for removal of residual DIO, however, the blend of BDT-TT polymers with fullerene tend to reduce in performance at high temperatures, especially, the film morphology tends to deteriorate. They already possess a certain level of crystallinity, otherwise normally achieved with high annealing tem-

Figure 5.27: Performance of E based cells under continuous simulated solar illumination with no additive (red, full symbol), with CN (purple) and with DIO (red, empty symbol): PCE (A), J_{sc} (B), V_{oc} (C) and FF (D)

Figure 5.28: PCE performance of other PBDD-TT polymer-based cells over time under continuous simulated solar illumination without DIO (full symbol) and with DIO (empty symbol).

perature. This explains why the cells under study were not annealed. Therefore, it is convincing to argue that some residual DIO remained in the active layers, and

Figure 5.29: Performance of the cells with DIO, under continuous simulated solar illumination with filtered (diamond) and unfiltered (circle) lamp and $^1\text{H-NMR}$ integrated relative peaks to CDCl_3 of BDT monomer solutions: (A) Evolution of PCE of E:[70]PCBM and ET:[70]PCBM cells normalized to their initial values; and (B) Backbone peaks evolution of E and ET BDT-monomers with DIO normalized to the highest values.

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Figure 5.30: Reaction pathways of DIO upon UV-radiation

upon UV-exposure, its effect is coupled with the chemical structure effect, resulting in selective dissolution of the polymer residues and [70]PCBM. This dissolution, in turn, may cause a chain reaction, starting with increase donor/acceptor aggrega-

tion, then decline in connectivity of donor/acceptor web-like percolation and finally suppressing the volume of charge carriers to be mined from the donor/acceptor active layers. This is consistent with the huge losses recorded in the mobilities of the exposed DIO films and the loss recorded in PV parameters shown in Figure 5.21C,D and E with ET recording the highest loss in μ and J_{sc} . To explain this assertion, we first made a dilute solution of DIO-only and ODT-only (2.1 mL) with $CDCl_3$. Second, we also made dilute solutions (2 mL in volume) of the BDT monomers (as shown in Figure 5.31), with (0.1 mL DIO to the volume) or without of DIO, at very low

Figure 5.31: Chemical structure of (A) E BDT-monomer and (B) ET BDT-monomer used for 1H -NMR and absorption spectra.

concentrations. These solutions were prepared into sealed/air-tight NMR tubes in a glovebox, under cleanroom environment. Then, 1H -NMR spectra (of the samples sealed against air during measurement) were taken before (original solution) and after UV exposure at intervals of 10 minutes for 2 hours and displayed in Figure 5.32 showing the evolution of the backbone peaks of the monomers and the evolution of all other peaks for the mixture of monomers and additives and the additives-only in Figures 5.33-5.36. The results from the NMR data plotted here in Figure 5.29B as relative integrated peaks over time were consistent with the FTIR data. The analysis of the peaks of the backbone and the side chains revealed that the E-monomer is more stable than ET-monomer. Upon UV-exposure in the presence of DIO, there was an initial rise in peaks followed by subsequent decrease in time. The decrease,

Figure 5.32: ^1H -NMR spectra of monomer solutions showing the backbone peaks recorded in an inert environment using sealed NMR tubes under irradiation with 315-400 nm light at ten minutes intervals from bottom-to-top starting from the initial spectrum labeled as: E BDT-monomer (A) without DIO and (B) with DIO; ET BDT-monomer (C) without DIO and (D) with DIO.

also observed for the backbone, points to our earlier statement that the side chains upon cleavage react with the backbone, causing it to undergo slow degradation. This decrease in peaks however, started to stabilize for the E-monomer over time while it was almost continuous with a slow rate for the ET-monomer. This observation, indeed, is clear evidence that DIO may have reacted with the polymers under UV. This reaction is undesirable for device stability in both polymer cells and even more, very detrimental to the alkylthienyl substituted polymers. Upon selection of specific area with chemical shifts between 4.8 and 6.0 ppm of the ^1H -NMR spectra of both monomer solutions in the presence of DIO, and upon UV-exposure, Figure 5.37A,B revealed the appearance of new peaks after 10 mins illumination that grew in intensity over time. These peaks were originally absent from the ^1H -NMR spectra of the monomer solutions without DIO. Vinyl protons are typically found in this ppm-range, suggesting the formation of alkenes during the degradation pro-

Figure 5.33: Integrated ^1H -NMR spectra of E-monomer solutions with DIO recorded in an inert environment using sealed NMR tubes under irradiation with 315–400 nm light at ten minutes intervals showing only the initial spectrum and spectra after 10, 60 and 120 mins.

cess in both monomer solutions. Peaks centered around 5.8 ppm belong to the proton on the 2nd or 7th carbon (H_c) of the alkene radical left after UV-radiation of DIO while peaks centered around 5.0 and 4.9 ppm belong respectively to the 2 protons (H_a and H_b) on the 1st or 8th carbon. In the aliphatic region, with chemical shifts between 0.8 and 1.1 ppm, we observed the formation of new peaks with chemical shift around 0.87 ppm after UV-illumination as shown in Figure 5.37C,D. These peaks only appeared when the solutions were exposed to UV light. From these data, we can formulate two hypotheses: either DIO reacts directly with the monomers/polymers upon UV-exposure or DIO decomposes into (radical species or other compounds which stay in) the film, in the case of the devices, altering the donor/acceptor domains and indirectly impacting the stability. These alterations could in turn be sources of additional electron and hole traps leading to the observed faster degradation. To clarify this point of view, we conducted ^1H -NMR study on DIO-only and ODT-only solutions which resulted in the observation of the same peaks for the DIO-only solution, again only following UV-exposure, pointing

Figure 5.34: Integrated ^1H -NMR spectra of ET-monomer solutions with DIO recorded in an inert environment using sealed NMR tubes under irradiation with 315–400 nm light at ten minutes intervals showing only the initial spectrum and spectra after 10, 60 and 120 mins.

to our second hypothesis. However, we did not see these peaks for the ODT-only solution. The fact that peaks only appear for the DIO-only solution in the olefinic and aliphatic regions of the spectra suggests that DIO undergoes homolytic C-I bond cleavage followed by hydrogen elimination to form HI and alkene as shown in Figure 5.38D,E and/or followed by hydrogen abstraction. The HI, iodine and carbon-centered radicals are sufficiently reactive to react directly with saturated carbon backbone of DIO. H- abstraction[7] has been previously speculated, though without experimental evidence, and thus being ascribed as the precursor to the phenomenon of photo-oxidative degradation of polymers in the presence of DIO when exposed to both air and light. We have shown that indeed this is partly the case isolating the molecules from oxygen in an inert atmosphere. The key finding here is that when used in the active layer of the solar cell and under illumination, DIO is a photo-acid. And this is shown for the first time using a straightforward technique as ^1H -NMR. The HI formation under the sunlight kills the cells over time. Nothing could be concluded for the peaks of the side chains as they were covered

Figure 5.35: Integrated ^1H -NMR spectra of DIO-only solution recorded in an inert environment using sealed NMR tubes under irradiation with 315–400 nm light at ten minutes intervals showing only the initial spectrum and spectra after 10, 60 and 120 mins.

by signals from the presence of the DIO, and thus, could not be easily integrated as shown in Figures 5.33–5.35. This drastic increase can be explained by the fact that DIO has a higher concentration, roughly $2 \text{ mg}\cdot\text{mL}^{-1}$ and was used as received. The ODT-only solution spectra revealed no changes in spectra in terms of the numbers, chemical shifts and ratio of peaks as shown in Figure 5.36. Only the peak around 7.3 ppm disappeared after UV exposure, signaling an acceleration in the kinetics of deuterium exchange of the solvent with the thiol groups. These observations would explain why DIO solar cells degrade much faster in general than the ODT based and also suggest different degradation mechanisms for the additives. Finally, based on the outcome from the NMR spectra leading to these observations, two pathways of degradation schemes were identified from DIO's reaction (shown in Figure 5.38) and could be used to explain the degradation reactions occurring in the active layers: $\text{H}\cdot$ abstraction induced degradation and $\text{H}\cdot$ elimination induced degradation. Figure 5.38A shows that upon UV illumination, DIO first goes through homolytic cleavage to produce a primary alkyl radical and iodine radical. Because

Figure 5.36: Integrated ^1H -NMR spectra of ODT-only solution recorded in an inert environment using sealed NMR tubes under irradiation with 315–400 nm light at ten minutes intervals showing only the initial spectrum and spectra after 10, 60 and 120 mins.

of the high reactivity of the primary alkyl radical, it readily abstracts hydrogen from the E-monomer, which gives iodoctane with terminal methyl group (which appears around 0.87 ppm) and a relatively stable tertiary alkyl radical, followed by the homolytic cleavage of the C-O bond to form more stable oxygen radical and alkene. The occurrence of a homolytic cleavage of the other C-O bond and rearrangement of the radical leads to the formation of a stable quinone moiety in Figure 5.38B along with a primary alkyl radical, propagating further decomposition. Thus, in the presence of DIO, there are two competing/cumulative routes to quinone formation: one due to DIO reaction with the polymer and the second due to a direct UV-reaction[32] with the polymer. This process explains why DIO accelerates the degradation process in E-monomer and thus the E-polymer solar cells. In the case of the ET-monomer as shown in Figure 5.38C, a secondary alkyl radical which is stabilized by the thiophene instead of a third alkyl radical is produced by the hydrogen abstraction reaction. Although this radical is relatively stable, dimerization and hydrogen elimination can still occur due to the reactivity of the radical, leading to

the production of insoluble compounds not observable from the ^1H -NMR spectra. This reaction mechanism also strongly supports the fact that DIO indeed speeds up the degradation of ET-monomer and thus, ET-polymer solar cells. Finally, and

Figure 5.37: Selected peaks of ^1H -NMR spectra of monomer solutions with DIO recorded in an inert environment using sealed NMR tubes under irradiation with 315-400 nm light at ten minutes intervals from bottom-to-top starting from the initial spectrum showing signals (only under illumination): peaks between 4.8 and 6.0 ppm in (A) E BDT- monomer, (B) ET BDT- monomer; and 0.8 and 1.1 ppm in (C) E BDT- monomer, (D) ET BDT- monomer. Peaks centered around 5.8 ppm belong to the vinylic proton at the 2 (or 7) position (H_c) of the alkene radical left after UV-radiation of DIO while peaks centered around 5.0 and 4.9 ppm belong respectively to the terminal vinylic protons (H_a and H_b) - see Figure 5.38E.

as shown in Figure 5.38D, hydrogen elimination of DIO itself also occurs, forming HI which is a strong acid, and competing simultaneously with the other pathways. HI is highly reactive and would definitely kill the cells. The formation of HI leaves alkene radicals in the system which we proved by the ^1H -NMR with the splitting pattern of the proton on the 2nd or 7th carbon shown in Figure 5.38E. The observation is fully supported by the MestReNova prediction of the ^1H -NMR prediction of the protons of the same alkene chain as depicted in Figure 5.39. It should be noted that in general, the same photochemistry is probably active, over a long period of

time, in some other additives. Alkane dithiols,[58] for example, are contaminated

Figure 5.38: Possible degradation pathway after decomposition of DIO under UV light: (A) Decomposition of DIO under UV light; DIO decomposition induced degradation pathways: Hydrogen abstraction in (B) E BDT- monomer, (C) ET BDTmonomer and Hydrogen elimination in (D) DIO with the formation of carbon-centered iodide radicals and in (E) DIO with the formation of HI, an acid supported by the $^1\text{H-NMR}$ splitting pattern. Shown here, H_c is the vinylic proton at the 2 (or 7) position (H_c) of the alkene radical present in solution.

with disulfides that are difficult to remove completely, form readily upon exposure to ambient conditions and cleave homolytically in the presence of UV light.

Figure 5.39: MestReNova prediction of the ^1H -NMR spectra of alkene radical left in solution after UV-radiation of DIO very conformed to experimental results in Figure 5.37 and 5.38E.

5.3. Conclusion

One of the aim of the present research was to examine the role played by the chemical structure of BDT-TT polymers in the UV stability of polymer:fullerene solar cells. Under exposure to light in an inert atmosphere, the alkylthienyl (R-T) solar cells degrade faster than the alkoxy (R-O) ones. In summary, the experiments confirmed that the observed degradation in the solar cells, upon exposure to light, is neither due to photobleaching, nor is the accelerated degradation of the R-T devices compared to the R-O ones due to the acidity of the PEDOT:PSS layer, nor is it due to Li diffusion into the active layer. This led us to ascribe the enhanced degradation of the former cells to their chemical structures, especially the alkylthienyl side chains. Moreover, ^1H -NMR studies revealed a faster degradation mechanism for R-T BDT-TT polymers solar cells based on the monomer solution study. These findings enhance

our understanding of the role played by the chemical structure of BDT-TT polymers in the stability of polymer:fullerene solar cells.

Moreover, we have furnished evidence that reveals that BDT-TT polymers are intrinsically unstable in the presence of UV-light illumination if compared to the known fairly stable P3HT. We have shown that in general, polymers with alkoxy groups (E) on the BDT-unit are more stable than those with alkylthienyl groups (ET) when exposed continuously to full solar spectrum. Thus, UV reacts more negatively with the BDT substituted alkylthienyl group polymers, creating radical species that accelerate the degradation mechanism during the first step of their degradation pathway compared to that of the alkoxy group polymers. These observations have been supported by FTIR, ^1H -NMR measurements and UV absorption profiles of the monomer solutions.

In brief, these findings corroborate the proposition that polymer chemical structure plays a crucial role in the photostability of polymer-fullerene solar cells. These data suggest that stable organic solar cells can be achieved if more studies are done in this direction. Although it cannot be clearly said if F and O atoms are good agents for stability, this study seems to suggest so. However, more investigation on other polymers presenting the same characteristics may be needed before it is possible to draw a clear conclusion. At this stage, it is evident that alkoxy side chains polymers are better performers in general than the alkylthienyl ones of same backbone. These results combined with the above suggested studies would pave the way for new materials that yield efficient as well as stable organic solar cells.

We have also confirmed that the addition of DIO precipitates the UV-degradation and thus, negatively affects the photostability, reducing the lifetime of the cells, on the one hand from more than 2 hours to 20 minutes for the E polymer cells and on the other hand from 30 minutes to less than 10 minutes for the ET polymer cells. However, it does not alter/tweak the influence of the polymer chemical structure; thus, the photostability of BDT-TT polymers solar cells is strongly linked to the polymer structure. We moved a step further to explain the mechanism behind the observed precipitation in degradation of the cells caused by the combined effect of the addition of the DIO and UV-exposure; and henceforth propose schemes of these mechanisms, supported by experimental evidence, for the differences observed for both types of polymers.

All this information lead to three simple conclusions:

- BDT-TT polymers are unstable and their chemical structure is a key factor in the performances of their polymer solar cells, thus, in our case, BDT-TT poly-

mers with alkoxy side chains are more photostable than those with alkylthienyl side chains.

- The TT-units moieties had similar but little effect on the degradation of the polymers.
- DIO and other (mostly halogenated) additives become photo-acids and are inimical to device stability as it is really difficult to completely remove their residues from the film with 100 % certainty.

These findings inform us of ways to achieve efficient but stable materials and additives.

5.4. Experimental

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5.4.1. Materials

All polymers and [70]PCBM were purchased from Solarmer Energy Inc. and Solenne BV respectively, while P3HT and all used solvents were acquired from Sigma-Aldrich Co. LLB. All materials commercially purchased were used as received without further purification

5.4.2. Solution Processing

For the polymer solar cells: i) blend of P3HT polymer with [60]PCBM (in a ratio of 1:1 with a total concentration of 20 mg.ml⁻¹) were dissolved in anhydrous chlorobenzene (CB) and ii) blends of BDT polymers with [70]PCBM (in a ratio of 1:1.5 with a total concentration of 25 mg.⁻¹) were dissolved in anhydrous 1,2-dichlorobenzene (oDCB) with or without DIO. When DIO was added, it was in a volume ratio of 97:3 for oDCB:DIO. The solutions were mostly dissolved overnight by stirring on a hot plate at 60 °C.

5.4.3. Device & Film Fabrication

All solutions and devices were prepared in a cleanroom environment. All samples or devices were prepared on glass or ITO-coated glass substrates. Glass or pre-patterned ITO glass substrates were cleaned respectively in soap, deionized water, then in acetone and isopropanol with ultrasonic bath for at least 10 minutes each and spin-dried. Next, the substrates were annealed in an oven at 140 °C for 10 minutes and then treated in UV-Ozone for 20 minutes. The dissolved materials were used to either fabricate conventional solar cells or films on glass. For polymer

solar cells, the blend solutions were spin coated at 800 rpm for 5 s and spin dried for 120 s atop PEDOT:PSS (VP AI4083, H.C. Starck) layer (50 nm, and dried in oven at 140 °C for 10 minutes), previously spin coated in ambient conditions on the prepatterned ITO glass substrate. The films were left in vacuum overnight and the devices were finished by thermal evaporation at $<10^{-8}$ Torr of LiF (1 nm) and Al (100 nm) with the following structure ITO/PEDOT:PSS/Blend with or without DIO/LiF/Al. The P3HT solar cells were annealed at 150 °C for 30 minutes. The thickness of the active layers of the solar cells is around 100 nm. Finally, films of pristine polymers, of [70]PCBM and of blends were made either by spin-coating on glass substrates for AFM and UV-Vis absorption measurements or by drop casting on KBr crystals for FTIR measurements.

5.4.4. Characterization

Current–voltage (J – V) characterization

For PCE, the J – V curves were measured on unencapsulated polymer solar cells in the dark in the glovebox and under simulated AM1.5G white light illumination (Steuernaugel SolarConstant 1200 metal halide lamp), by means of a computer-controlled Keithley 2400 source meter, in an inert atmosphere (with <0.1 ppm H_2O and <0.1 ppm O_2). The intensity of the light was calibrated using a mono-silicon reference cell for one sunlight intensity of 1000 W m^{-2} and corrected for spectral mismatch.[59] All devices were measured at room temperature $\sim 295 \text{ K}$ by a controlled N_2 gas flow by means of a liquid N_2 bath.

For the UV-degradation measurement, the cells were continuously exposed to light, in inert atmosphere (with <0.1 ppm H_2O and <0.1 ppm O_2) for a period of 2 hours while being kept at $\sim 295 \text{ K}$ by actively cooling the samples. The J – V sweeps were obtained both under dark and illumination for the polymer solar cells. The collected data are presented and discussed under results and discussion.

UV-Vis Absorption

For this measurement [70]PCBM, pristine polymer and blend (polymer:[70]PCBM) solutions were spin-coated into films on glass and measured before and after 2 hours light exposure. The spectra of the films were obtained against a glass reference spectrum using a UV-VIS-NIR spectrometer (UV-3600) with tungsten-iodide (WI) monochromatic light source scanning within a 300–900 nm range. Diluted solutions of the BDT monomers in CDCl_3 at very low concentration were prepared in an inert atmosphere in a glovebox in sealed cuvettes (0.7ml in volume) for the

absorption measurements. Absorption measurements were performed similarly to that of the films in a UV-3600 Shimadzu UV-Vis-NIR spectrometer against a cuvette of CDCl_3 as a reference.

^1H -NMR probed UV-degradation

Diluted solutions of the BDT monomers in CDCl_3 at very low concentration were also prepared in an inert atmosphere in a glovebox, namely, two times 2.1 ml (in 95.2:4.8 v/v ratio of CDCl_3 :DIO) and 2 ml without DIO in air-tight/sealed NMR tubes for the NMR measurements. To complete the NMR measurements, 2.1 ml diluted solutions of DIO-only and ODT-only in CDCl_3 (95.2:4.8 v/v ratio of CDCl_3 :DIO/ODT) were prepared under the same condition. The fresh solutions were then transferred from the glovebox into the NMR set-up, a computer-controlled Varian AMX 400 (400 MHz), where ^1H -NMR spectra were obtained and recorded. Next, the solutions were exposed to UV light (IntelliRay, Uvitron 600W, shuttered UV floodlight, at 50% power) in steps of 10 minutes for 2 hours. ^1H -NMR spectra were measured and recorded after each 10 minute exposure to UV. Chemical shift values are reported in ppm with the solvent resonance as the internal standard.

FTIR Measurement

The measurements were performed on both as the cast and exposed films against KBr crystal as a reference with a Shimadzu IR-Tracer-100 FTIR spectrometer in transmittance mode from 400 to 4000 cm^{-1} .

AFM measurement

Exposed and as-cast blend films of BDT polymer:[70]PCBM on glass were investigated for morphological differences in ScanAsyst mode on a Bruker Multimode 8 microscope (Model number: MMAFM-2) with ScanAsyst-Air probes (spring constant: 0.4 N/m , resonant frequency: 70 kHz , nominal tip radius: 2 nm). All samples were scanned at $5\text{ }\mu\text{m}$, $1\text{ }\mu\text{m}$, and 500 nm at a scan rate of 0.8 Hz and a resolution of 640 samples per line. Both height and peak force error were collected for analysis during the scan. We used NanoScope Analysis (provided by Bruker) for data analysis and converting 2D morphology into the 3D structure for better interpretation.

5.4.5. Synthesis of BDT-monomers

All reactions were performed using oven-dried glassware and dry solvents unless otherwise specified. THF was taken from an MBraun solvent purification system (SPS-800). All other reagents were purchased from Sigma-Aldrich, TCI Europe, or

Acros Organics and were used without further purification unless noted otherwise. ^1H -NMR spectra were recorded on a Varian AMX600 (400MHz). Chemical shift values are reported in ppm with the solvent resonance as the internal standard. Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = double doublet, dq = double quartet, qd = quarter doublet, m = multiplet, br = broad), coupling constants (Hz), and integration. Flash chromatography: Merck silica gel type 9385 230–400 mesh. TLC: Merck silica gel 60, 0.25 mm. Compounds were visualised by UV.

Synthetic Procedures of $\text{M}_{\text{R-O}}/\text{M}_{\text{E}}$

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Benzo[1,2-b:4,5-b']dithiophene-4,8-dione (1) was synthesized according to previously reported methods.^[60]

4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene (2): (1) (0.22 g, 1.0 mmol), Zn powder (0.16 g, 2.5 mmol), and H_2O (6 mL) were put into a 25 mL flask, then NaOH (0.6 g, 15.0 mmol) was added into the mixture. After the mixture was stirred and refluxed for 1 h, 1-bromioisooctane (0.58 g, 3.0 mmol) and a catalytic amount of tetrabutylammonium bromide (TBAB) (0.06 g, 0.2 mmol) were added into the flask. The reactant was refluxed for 8 h and then was poured into cold water (50 mL) and extracted by Et_2O (3×50 mL). The organic layer was dried over anhydrous MgSO_4 . After the solvent had been removed, the crude product was purified by column chromatography using *n*-hexane/DCM (v/v = 8:2) as eluent. Compound 2 (0.28 g, yield 62%) was obtained as a pale yellow oil. ^1H -NMR (400 MHz, CDCl_3) δ 7.48 (d, J = 5.2 Hz, 2H), 7.37 (d, J = 5.6 Hz, 2H), 4.18 (d, J = 5.6 Hz, 4H), 1.85–1.75 (m, 2H), 1.73–1.49 (br, 8H), 1.46–1.37 (br, 8H), 1.01 (t, J = 7.4 Hz, 6H), 0.94 (t, J = 7.2 Hz, 6H).

Synthetic Procedures of $\text{M}_{\text{R-T}}/\text{M}_{\text{ET}}$

2-(2-ethylhexyl)thiophene (3) was synthesized according to previously reported methods. ^[61]

4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (4): 3.0 mL of *n*-BuLi (4.8 mmol, 1.6 M) was added dropwise to the solution of (3) (0.79 g, 4.0 mmol) in 12 mL of anhydrous THF at $-30\text{ }^{\circ}\text{C}$ under N_2 . The mixture was heated up to $50\text{ }^{\circ}\text{C}$ for 2 h. Then the solvent was cooled in ice-water bath, subsequently, (1) (0.22 g, 1.0 mmol) was added in one portion, and the mixture was heated at $50\text{ }^{\circ}\text{C}$ for another 2 h. After cooling the mixture down to room temperature, a mixture of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (1.81 g, 8.0 mmol) in 5 mL of aqueous HCl (10%) was added, and the mixture was stirred overnight. The reaction mixture was poured into cold water (50 mL) and extracted by Et_2O ($3 \times 50\text{ mL}$). The combined organic layer was washed with H_2O and brine, dried with MgSO_4 , filtered, concentrated via rotary evaporation. Further purification was carried out by column chromatography on silica gel eluting with petroleum ether to obtain pure compound 4 as a yellow liquid (0.44 g, 77%). $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 7.65 (d, $J = 6.0\text{ Hz}$, 2H), 7.46 (d, $J = 5.6\text{ Hz}$, 2H), 7.30 (d, $J = 3.2\text{ Hz}$, 2H), 6.89 (d, $J = 3.2\text{ Hz}$, 2H), 2.86 (d, $J = 6.8\text{ Hz}$, 4H), 1.72–1.65 (m, 2H), 1.47–1.26 (br, 16H), 0.97–0.89 (m, 12H).

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Summary

This research content of this thesis is mainly focused on π -conjugated polymers, including synthesis of π -conjugated polymers and study of their performance when applied in organic photovoltaic devices. In Chapter 2, a nickel-catalyzed disubstitution of 1,6-dichlorohexa-2,4-diyne reaction methodology for the synthesis of diaryl- or dialkenyl-substituted ene-yne-enes was developed. This is a new and significant contribution to the field of transition metal-catalyzed allylic and propargylic substitution reactions in which the mechanism is considerably more complex and involves extensive rearrangements of the intermediate nickel species. Although these ene-yne-ene compounds are unstable, they might function as building blocks for π -conjugated polymers because of the double-triple-double carbon bond π -conjugation unit, making them definitely worthwhile to pursue.

In Chapter 3, the mechanism of bis(pinacolato)diboron (BiPi)-mediated polymerization methodology for the synthesis of thiophene-based, π -conjugated co-polymers was investigated through analysis of the polymerization process from the molecular weight change over the monomer conversion. Based on the molecular weight and dispersity trend over the polymerization process, we proposed the BiPi polymerization methodology proceeded in a step-growth mechanism. With understanding the mechanism better, it gives people more information to design controlled polymerization methodologies.

Chapter 4 describes a t BuLi-mediated polymerization methodology with palladium catalyst for the synthesis of thiophene-based π -conjugated polymers with high molecular weight and low dispersity. Although poor functional group tolerance and relatively narrow monomer scope limit further and broader applications of this polymerization methodology, this is still a new and significant contribution to the field of transition-metal catalyzed cross-coupling polymerization, without the need of toxic organometallic reagents and atom-economical advantage because of the use of organolithium reagents.

In Chapter 5, a systematic UV-degradation study on the stability of set of PBDTTTT polymers:fullerene solar cells was performed. The relationship between the polymer chemical structure and the UV-stability of the solar cells was revealed evidently

via the study. It shows that solar cells of polymers with alkoxy side chains are more stable than those with alkylthienyl side chains. Through combined physical and chemical experimental techniques, the effects of both the polymer chemical structure and additives [1,8-diiodooctane (DIO), chloronaphthalene (CN) and 1,8-octanedithiol (ODT) on the UV-stability of the solar cells are further investigated. It is found out that DIO acts as photo-acid and results in accelerated degradation of the solar cells while CN does not. The mechanisms behind the effect of DIO are explained as well, paving the way for the design of new, efficient as well as stable materials and additives.

Samenvatting

Deze onderzoeksinhoud van dit proefschrift is voornamelijk gericht op π -geconjugeerde polymeren, inclusief synthese van π -econjugeerde polymeren en studie van hun prestaties wanneer toegepast in organische fotonische apparaten. In hoofdstuk 2 beschrijft een nikkel-gekatalyseerde disubstituut van 1,6-dichloorhexa-2,4-diyne reactiemethodologie voor de synthese van diaryl- of dialkenyl-gesubstitueerde een-yne-ene werd ontwikkeld. Dit is een nieuw en belangrijk kan geen bijdrage leveren aan het gebied van overgangsmetaal gekatalyseerd allylisch en propargylisch substitutiereacties waarbij het mechanisme aanzienlijk complexer is en omvat uitgebreide herschikkingen van de tussenliggende nikkelsoort. Hoewel deze een-yne-ene verbindingen zijn instabiel, ze kunnen als bouwstenen fungeren voor π -econjugeerde polymeren vanwege de dubbele-drievoudige-dubbele koolstofbinding π -ervoegingseenheid, waardoor ze zeker de moeite waard zijn om na te streven. In Hoofdstuk 3 het mechanisme van bis (pinacolato) diboron (BiPi)-gemedieerde polymerisatiemethodiek voor de synthese van op thiofeen gebaseerde, π -econjugeerde co-polymeren werd onderzocht door analyse van het polymerisatieproces uit de moleculaire gewichtsverandering ten opzichte van de monomeeromzetting. Gebaseerd op het molecuulgewicht en dispersiteitstrend over het polymerisatieproces, hebben we de BiPi-polymerisatie methodologie voorgesteld in een stap-groei mechanisme. Met begrip voor de mechanisme beter, het geeft mensen meer informatie om gecontroleerde polymerisatie te ontwerpen methodieken. Hoofdstuk 4 beschrijft een $t\text{BuLi}$ -gemedieerde polymerisatie methode met palladium katalysator voor de synthese van op thiofeen-gebaseerde π -econjugeerde polymeren met een hoge molecuulgewicht en lage dispersiteit. Hoewel slechte functionele groepstolerantie en een relatief smalle reikwijdte van monomeren beperken verdere en bredere toepassingen hiervan polymerisatiemethode, dit is nog steeds een nieuwe en belangrijke bijdrage aan de veld van overgangsmetaal gekatalyseerde kruis-koppelingen polymerisatie, zonder de noodzaak van giftige organometallische reagentia en atoom-economisch voordeel vanwege de gebruik van organolithium reagentia. In hoofdstuk 5, een systematisch UV-degradatieonderzoek naar de stabiliteit van de set PBDTTT polymeren: fullereen zonnecellen werden uitgevoerd.

De relatie tussen het polymer chemische structuur en de UV-stabiliteit van de zonnecellen werd duidelijk onthuld via de studie. Het laat zien dat zonnecellen van polymeren met alkoxy zijketens zijn stabielere dan die met alkylthienyl zijketens. Door fysiek gecombineerd en chemische experimentele technieken, de effecten van zowel de chemische polymer structuur en additieven 1,8-diiodooctaan (DIO), chlooraфтаleen (CN) en 1,8-octaandithiol (ODT) op de UV-stabiliteit van de zonnecellen wordt verder onderzocht. Het is gebleken dat DIO werkt als fotozuur en resulteert in een versnelde afbraak van de zonnecellen, terwijl CN dat niet doet. De mechanismen achter het effect van DIO zijn ook uitgelegd, de weg vrijgemaakt voor het ontwerpen van nieuwe, efficiënte en stabiele materialen en additieven.

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