Preparation and characterization of nucleobase-functionalized poly(phenylenevinylene)

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ABSTRACT

Conjugated polymers (CPs) are unique among organic materials due to their diverse electrical and optical properties. Whereas most polymers are excellent insulators, conducting and semiconducting CPs have found use in several domains of electronics as active circuit components. Their use, however, is limited in part by their relatively disordered microstructure compared to other electronic materials, and the impact this has on their properties.

Although polymers are usually microscopically disordered materials, DNA nanotechnology has emerged as a means of creating well-defined structures on remarkably small scales using purely polymeric systems. This fine morphology control is enabled by the great strength and specificity of the base-pairing interactions that take place between / moieties pendant to the main polymer chain. Despite being created by evolution in biological systems, these interactions have been harnessed in entirely artificial contexts as a means of controlling the spatial position of not just DNA strands, but also various functional materials.

Inspired by the successes of structural DNA nanotechnology, the synthesis of a nucleobase-functionalized conjugated polymer (NB-CP) has been investigated. Poly(phenylenevinylene) can be used in the production of a wide array of electronic devices, and has been extensively studied. As such, it provided an excellent model system with which to explore the nucleobase-driven control of interactions between

CPs. We conducted a thorough review of the diverse synthetic approaches that have been applied to the preparation of PPV, and palladium-catalyzed polymerizations were identified as promising methods of preparing the material. The Stille, Mizoroki-Heck, and Suzuki couplings were explored. Using the Stille reaction, achieving sufficiently large molecular weights proved challenging. Mizoroki-Heck polycondensation under optimized conditions overcame this problem; however, the resulting material was found to contain structural defects due to poor regioselectivity. A new monomer was therefore prepared, and it was found that that the Suzuki coupling could produce low-defect PPV with a degree of polymerization greater than 30. This method was then used to prepare both adenine- and thymine-substituted PPV, which were found to have higher photoluminescence quantum yield than the parent PPV.

RESUMÉ

Les polymères conjugués (PC) sont uniques parmi les matériaux organiques grâce à leur propriétés électroniques et optique très variées. Alors que la plupart des polymères sont des matériaux isolantes, les CP ont dans plusieurs dispositifs électroniques des rôles actifs. Pourtant, leur utilité est limitée en partie du fait du désordre de leur structure microscopique, et de l'impact que ce dernier porte sur les propriétés électroniques.

Bien que les matériaux polymériques aient l'habitude d'un certain de désordre au niveau de leur structure moléculaire, la nanotechnologie en ADN s'est récemment établie comme une façon de créer des structures bien-définies et incroyablement petites en utilisant uniquement des polymères. Ce contrôle micrometrique provient de la force et spécificité des interaction entre les bases azotées attachées au long de la chaine polymérique de l'ADN. Malgré leur origine biologique, ces interactions peuvent aussi être employées dans des systèmes entièrement abiotiques, pour contrôler l'organisation spatiale non seulement de l'ADN, mais aussi celle des matériaux fonctionnels.

Inspirée par les succès de la nanotechnologie en ADN, la synthèse d'un polymère conjugué portant des bases azotées a été examiné. Le poly(phenylenevinylene) (PPV), qui a été amplement étudié, peut être impliqué dans la production d'une diverse gamme de dispositifs électroniques. En tant que tel, le PPV offre une excellente base à partir de laquelle on peut lancer une exploration de l’assemblée des PC contrôlés par les interactions des bases azotées. Nous avons effectué examen approfondi des diverses façons de préparer le PPV, et les polymerizations catalyzées par le palladium ont été identifiées comme méthodes prometteuses. Les réactions Stille, Mizoroki-Heck, et Suzuki ont été examinés. Utilisant la réaction Stille, la réalisation des poids moléculaires suffisants s’est présenté comme un défi. L’application de la polycondensation Mizoroki-Heck sous des conditions optimisées nous a permis de surmonter ce dernier, mais les polymers qui en résultaient possédaient de nombreux défauts structurels. Un nouveau monomer a été préparé, et nous avons trouvé que la reaction Suzuki pouvait produire le PPV avec peu de défauts en degrée de polymerization supérieur à 30. Nous nous sommes servis de cette méthode pour préparer les PPVs fonctionalizés d’adenine et thymine, et l’on a trouvé que ces derniers possédaient des rendements quantiques de photoluminescence plus élevés que le PPV sans base azotée.

DEDICATION

This work is dedicated to my parents, Marc Blayney and Maria Helly, who have unwaveringly supported me through all of my successes and failures, accomplishments and mistakes.

ACKNOWLEDGMENTS

I must first acknowledge the incredible and unrelenting patience and assistance offered to me by Professor Dmitrii Perepichka throughout the course of my undergraduate and graduate research in his laboratory. Without his trust and support, I would not have had the chance to follow my dreams.

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I dearly thank my family, and all of my friends who supported me through years of, “I think this will be the one that works.” Chances are the one I was talking about didn’t, but I wouldn’t have made it to the one that did without your encouragement.

I offer both gratitude and praise to the many highly talented scientists at McGill, CSACS, and UQAM who have helped me perform and understand the numerous analyses without which my work would amount to little more than the slow production of glowing

orange vials. Particular thanks go to Volodymyr Kriuchkov, who performed the gel permeation chromatography for the fourth chapter. I thank also the staff at the McGill Department of Chemistry, particularly Chantal Marotte, for helping me stay on track. Finally, I thank Estevan ‘falcxne’ Falcone for his album ‘Timbits’, my soundtrack to writing this thesis.

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Chapter 1: Introduction

1.1 Conjugated Polymers

Conjugated Polymers (CPs) form a unique subset of polymeric materials, and although they frequently share many of the useful qualities their more commonly encountered non-conjugated brethren, such as processability, flexibility, and toughness, they are set apart by their unique optical and electrical properties. Doped CPs can be used to prepare highly conductive films and coatings, and show potential for use as molecular wires for nanoscale devices.[1] Meanwhile, undoped CPs are semiconducting, presenting an opportunity for use in a wide range of applications. In perhaps the most obvious application of a semiconducting material, CPs have been used to produce field effect transistors,[2] which allow logic gates to be constructed on flexible substrates. The explosion of scientific interest in CPs, however, occurred after the creation of the first Polymer Light Emitting Diode (PLED).[3] This led to rapid development in the field as new materials were designed to emit a broader range of colours with greater efficiency.[1b] This was complemented by the development of organic photovoltaics, in which CP electron donors, and more recently acceptors too, are at the heart of scalable devices that promise to cheaply harvest light over large areas.[4] For any of these devices to function well, it is not just important to synthesize a material with good optoelectronic properties, but also to ensure it assumes an appropriate morphology in the solid state. It is the morphology of the active layers that determines the ultimate mobility of charges in a polymer transistor, and the quantum efficiency of a photovoltaic device.[5] While significant advances have been made in exerting control through deposition and annealing techniques, and some work has been done to control assembly through molecular design, the goal of reproducible and versatile controlled assembly remains far off.

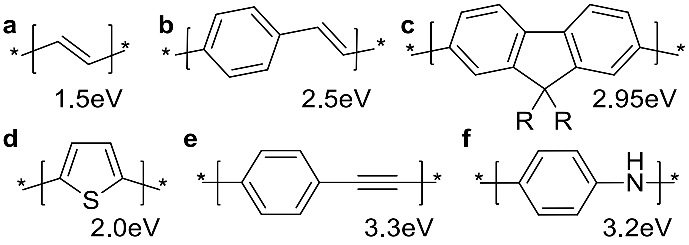

Figure 1.1: Structures and bandgaps of illustrative CPs a) polyacetylene, b) poly(p-phenylene vinylene), c) poly(fluorene), d) poly(3-hexylthiophene), e) poly(p-phenylene ethynylene) f) polyaniline

1.1.1 Properties of CPs

Conjugated polymers are synthetic macromolecules in which the polymer backbone is composed of a continuous chain of sp2 or sp hybridized atoms. This planar backbone gives rise to the eponymous extended conjugation and electron delocalization that are responsible for the unique optical and electronic properties of conjugated polymers. The primary effect of extended conjugation is a reduction in the HOMO-LUMO gap, and the spread of the associated absorbance bands from the UV (>3.1eV) to the visible or even infra-red. As a result, CPs are usually coloured, and often show intense fluorescence. In combination with the significant intermolecular interactions available from such extended molecular orbitals, this reduced band gap also gives rise to semi-conducting materials with moderate to high charge mobilities (>5 cm^2/Vs).[6]

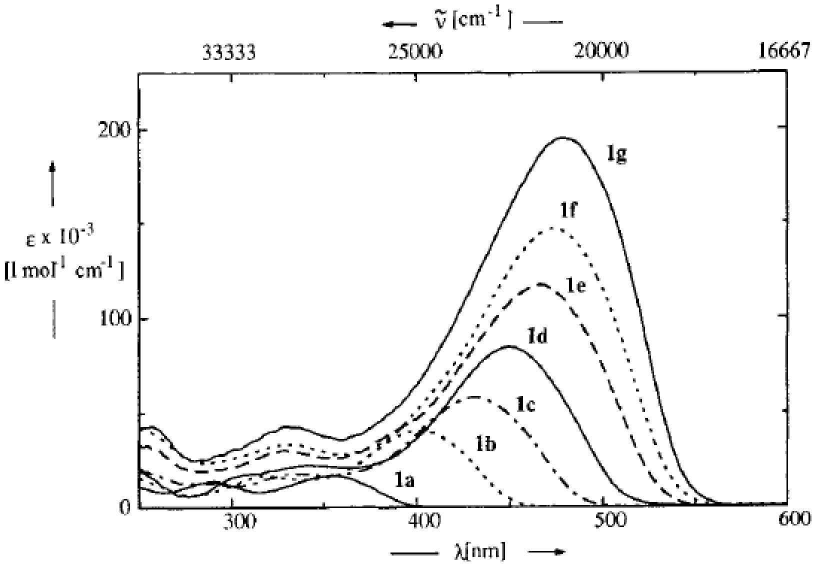

Figure 1.2: Solution-phase absorption of spectra of dialkoxy-oligo(phenylenevinylene). Redshift is observed as the number of repeat units increases from 2 (trace 1a) to 11 (trace 1g). Reproduced with permission from [7] Copyright 1996 Wiley and Sons.

A CP's HOMO and LUMO can be controlled through rational design of the monomer core and pendant functionalities, and this has been used to produce both n- and p-type semiconductors,[8] reduce contact resistance, modulate donor/acceptor properties,[9] and enhance stability.[10] The HOMO-LUMO gap, and corresponding band-gap of the bulk material, can be controlled in the same manner, allowing absorption and emission properties to be tuned for photovoltaic[11] and electroluminescent applications.[12]

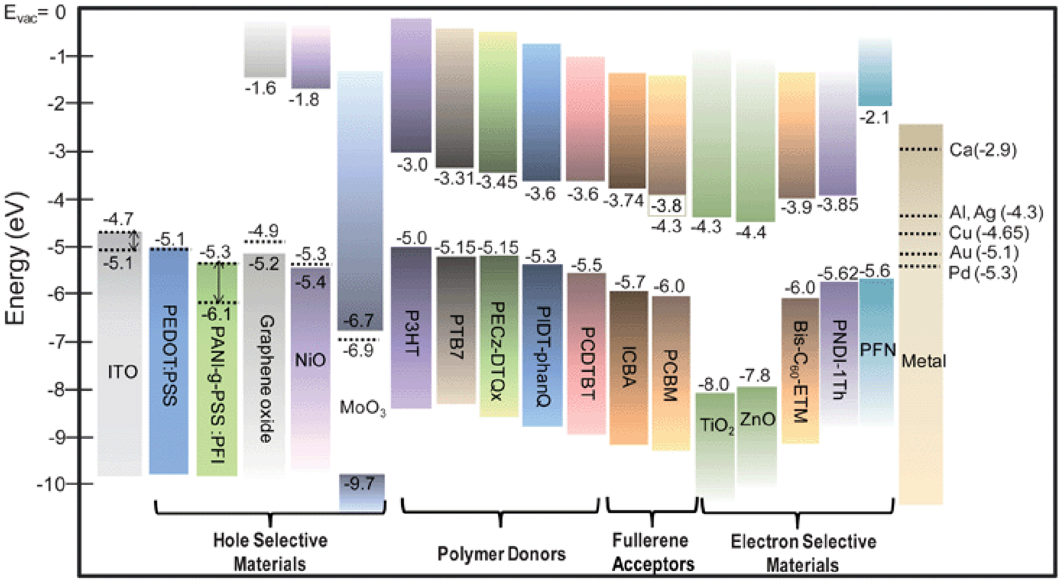

Figure 1.3: HOMO and LUMO levels of various commercially relevant conjugated polymers and related materials.

Reproduced with permission from ref [13]. Copyright RSC 2012.

Even in amorphous, liquid, or solution phases, the limited degrees of freedom available to the mostly planar backbone and narrow range of dihedral angle favoured by conjugation causes most CPs exhibit rod-like behaviour. As a result of this, and their large π-surfaces, most CPs show significant crystallinity and are often completely insoluble unless functionalized with solubilizing chains. These modifications can significantly influence the microscopic packing, as well as the mechanical and electrical properties of the polymer.

1.1.2 Morphology control and CP self-assembly

As noted, a CP's solid-state morphology can significantly influence its material properties. Charge-transport in organic materials requires continuous π-contact. In conjugated small molecules, this leads to high mobility in single-crystals, but far less in amorphous or microcrystalline samples. Polymers do not normally form single crystals, but CPs can support charge transport in semi-crystalline and amorphous phases due to the mobility of charges along individual chains and potential for significant electronic contact offered by large π-surfaces; however, both of these mechanisms can be disrupted if a CP's molecular packing induces conjugation-disrupting distortions, or precludes contact between neighbouring π-systems. Understanding and controlling solid-state processes is thus of utmost importance in the creation of effective transistor and diode devices.

Photovoltaic cells present an even greater challenge. Excitons in organic materials are short-lived, and thus have diffusion lengths much shorter than the thickness necessary to absorb most of the light incident on an organic heterojunction solar cell. As a result, devices must be designed with non-planar interfaces between the donor and acceptor layers, to decrease the distance an exciton must travel before charge-separation can occur. Ideally, this would be accomplished with an ordered interdigitated heterojunction, however, such structures have proven difficult to create. Instead, bulk heterojunctions are used, in which the two components are mixed and annealed to drive segregation into irregular but largely continuous phases, which are kinetically trapped upon cooling.[11] However, these morphologies require extensive optimization during fabrication to ensure optimal domain size, and the stability of such non-equilibrium structures can limit device lifetime. Ordered heterojunctions are expected to be at least

15-20% more efficient, and would be significantly more durable if created using self-assembly rather than kinetic trapping.[14]

π-π interactions, moderated by primarily aliphatic solubilizing groups, are the main driving force controlling the solid-state order of most conjugated polymers.[15] As such, the bulk of the research into controlling the morphology of CP systems via self-assembly, however, has relied on the phase-segregation of block-copolymers with aliphatic and aromatic components. Hydrogen bonds are highly versatile non-covalent interactions, and can achieve great strength and specificity though the rational design of multiple donor-acceptor systems; however, the applications of hydrogen bonding in CP research have largely been limited to the self-assembly of conjugated oligomers through terminal functionalities.[16] The one noteworthy exception to this lies in the continued study of pendant hydrogen-bonding moieties to control the assembly of polymeric electron donor materials with functionalized PCBM acceptors.[17] Little has been done, however, to extend this sort of control to all-CP or CP-oligomer systems.

1.2 DNA Nanotechnology

Unlike most biomacromolecules, the highly specific self-assembly of DNA can be largely described using a single guiding principle. Although there the double-helical form of DNA is stabilized by a combination of hydrophobic, ionic, and π-stacking interactions the specific association between complementary strands, and the lack of significant interaction between non-complementary strands, follows the simple rules of hydrogen bond-driven Watson-Crick base pairing.[18] This allows the interactions of individual DNA molecules, as well as distinct double-helices with single-stranded overhangs, to be predicted with incredible accuracy. The advent of sequence-specific DNA synthesis made it possible to construct and manipulate DNA systems ex-vivo. Combined with the simple heuristic of Watson-Crick base-pairing, this offered an unprecedented opportunity to exercise control over a material at the molecular level, and led to the birth of DNA nanotechnology.[19]

DNA nanotechnology has found diverse uses in both basic and applied research. Discrete two- and three-dimensional structures with features on the sub-ten nanometer length scale have been created with high fidelity, and can be selectively functionalized to encapsulate both organic and inorganic cargo, and modified to tune their properties and assembly, and interactions with biological systems. Extended lattices with similarly small features or addressable units have also been prepared for use as nanoscale scaffolds: in one- and two- dimensions, these structures can template nanoparticles to create plasmonic wires and circuits,[20] while three-dimensional lattices are expected to find use in crystallography.[19, 21] The tendency of DNA systems to maximize base-pairing through strand-exchange can be used to create dynamic systems capable of chemical signal amplification and molecular computation,[22] and the combination of these dynamical properties with directed assembly has enabled the development of molecular-scale devices capable of precise manipulation and movement.[23] The applications of DNA nanotechnology remain a highly active field of research.[24]

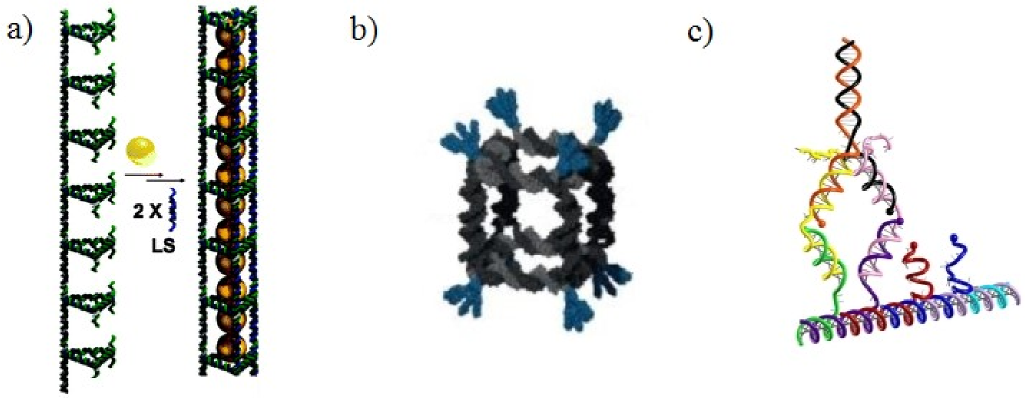

Figure 1.4: Some examples of DNA nanotechnology: a) Gold ladder b) functionalized drug delivery cube d) DNA walker.

Images adapted with permission from: a) ref [20a] Copyright ACS 2010. b) ref [25] Copyright NPG 2013. C) ref [26] Copyright ACS 2004.

1.2.1 Structural DNA Nanotechnology

In biology, higher-dimensional structures are found to form through crossovers between sequence-symmetric DNA helices; however, these are dynamic, and generally unstable with respect to reversion to uncrossed strands. The insight that junctions would be static and stable if formed from asymmetric sequences led to the use of DNA junctions and helices as nodes and connectors in the creation of well-defined supramolecular networks.[19] Moreover, the DNA double-helix has a persistence length of more than 50nm, and behaves like a rigid rod across three helix turns (10nm).[27] This allows the creation of structurally well-defined DNA polyhedra, which can be selectively functionalized at individual vertices using overhanging strands, and opened or closed through strand-exchange. DNA's dimensional stability can be extended over larger distances through the construction of tightly-linked networks;[19, 28] recently, this has even been shown in three dimensions.[21] As DNA is itself largely inert, the utility of such well-defined grids lies in its addressability by complementary sequences, which can be used to selectively organize secondary, DNA-conjugated active elements with great precision. With the advent of DNA origami, in which short stapling segments are used to fold a single long strand into arbitrary shapes on the 100nm scale, it also became possible to create complex non-periodic arrangements with similarly high resolution in a manner likened to using a DNA breadboard.[29]

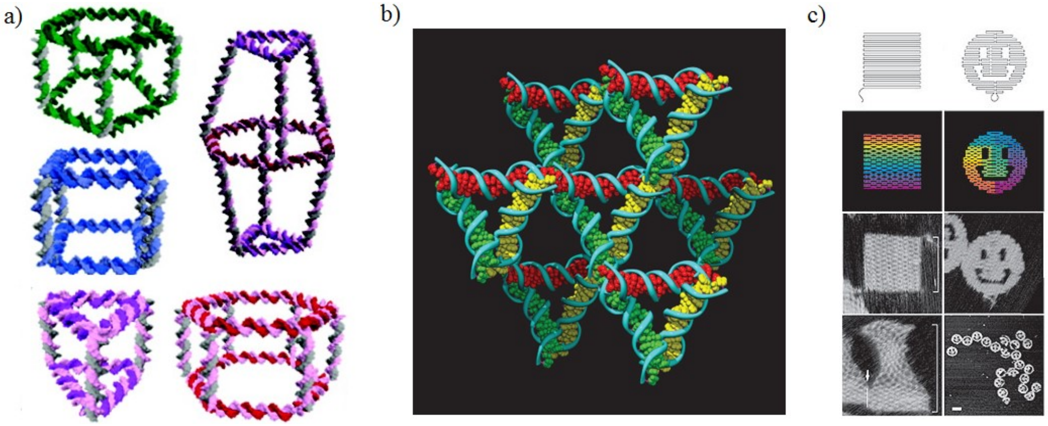

Figure 1.5: State of the art structural DNA nanotechnology a) DNA polyhedra b) Seeman's tensegrity triangle crystal c) DNA origami.

Adapted with permission from a) ref [30] Copyright ACS 2007. b) ref [21] Copyright NPG 2009. c) ref [29] Copyright NPG 2006.

1.2.2 Barriers and Limitations of DNA Nanotechnology

While advances in DNA nanotechnology have highlighted DNA's ability to do much more than store genetic information, DNA's biological origin imposes a number of challenges. Although kinetically stable under physiological conditions, the phosphodiester linkages that make up the backbone of a DNA strand are thermodynamically unstable with respect to hydrolysis, a reaction that can be catalyzed by acid, base, metal ions, and biologically ubiquitous phosophodiesterases. Furthermore, the glycosidic linkages connecting the bases to the backbone are known to undergo spontaneous hydrolysis, a process that is only kept in check by continuous enzymatic repair in biological systems.[31] The basic self-assembly of DNA, although straightforward under physiological conditions, is highly sensitive to ionic strength and solvent conditions that interfere with the precise set of non-base pairing interactions required to stabilize its double helical structure.[32] The preparation of synthetic DNA is also an expensive process that limits scalability in many applications.[33] Finally, although DNA has the advantage of being largely non-toxic and biocompatible, exogenous nucleic acids can trigger an immune response, particularly if they contain unmethylated CpG sequences.[34]

Beyond these challenges, the use of DNA in nanotechnology faces a number of limitations. The helical structure of DNA must be accommodated by ensuring that individual segment lengths represent in integer number of turns, and this imposes a larger fundamental building block length and courser granularity than might be expected for a molecular system.[29] Beyond this, in many applications, DNA is at best an inert scaffold; although useful, this also represents added cost and complexity in the case of materials that could be designed to self-assemble, and adds molecular bulk that can be disadvantageous in optical/electronic applications.

1.3 Nucleobase-Functionalized Synthetic Polymers

Through DNA nanotechnology, nucleobase driven self-assembly has shown itself to be one of the most powerful methods of finely controlling polymer morphology. However, as noted in section 1.2.2, the chemistry of nucleic acids also carries with it a number of limitations that could be remedied through the development of nucleobase-functionalized synthetic polymers with different backbones. In particular, the hydrolytic instability of phosphodiester and glycosidic bonds could be immediately disregarded, while, by design, enzymatic degradation could be avoided and immunogenicity, modulated. Furthermore, these synthetic DNA-analogues could be designed to be less sensitive to solvent and ionic conditions, and to be more easily synthesized in bulk. However, with a vast chemical space to explore and lacking the guidance of billions of years of evolution, the implementation of rationally-designed hydrogen-bonding polymers has progressed more slowly than DNA nanotechnology.[35]

Early work in this field involved the polymerization of modified nucleobases to create nucleobase-functionalized derivatives of simple radical polymers – polyolefins, polyacrylates, and polyacrylamides – as well as grafting nucleobases to functional macromolecules, such as polyethyleneimine and polylysine.[36] It was found that the presence of pendant nucleobase moieties could exert significant influence on the rate or tacticity of the polymerization, and nucleobase-driven aggregation of the resulting materials was illustrated though measurement of the hypochromism induced by stacking of purine and pyrimidine heterocycles during base-pairing between polymers; in most cases, however, knowledge of secondary structure was limited to what could be inferred from circular dichroism changes, stoichiometry, and melting curves.[35b] A noteworthy special case was the development of Peptide Nucleic Acid (PNA), a nucleobase-bearing poly(2-aminoethylglycine) derivative. This polymer has dimensions and periodicity very similar to those of DNA, allowing it to form hybrid double-helices with greater binding affinity than native DNA.[37] Since the turn of the millennium, much of the work in this area has focused on harnessing living polymerization techniques, including ATRP and ROMP, to produce well-defined homopolymers and block-copolymers, and on the development of alternative hydrogen bonding moieties to avoid unfavourable interactions and expand the available 'alphabet ' of complementary pairs.[38] In particular, diamino- and diamido-pyridine and pyrazine function as adenine mimics, forming three hydrogen bonds with thymine while avoiding adenine's self-aggregation and catalyst-complexation.[39] For even stronger intermolecular contacts, a urea-linked modified cytosine moiety was developed to offer self-complementary four-point hydrogen bonding.[40]

The combination of improved recognition moieties with modern polymerization techniques has yielded a variety of materials with useful tertiary structures and aggregation modes. This includes the selective encapsulation of metal complexes in unimolecular micelles,[41] the preparation of molecular-responsive block-copolymer micelles[42] and giant vesicles,[39b] the implementation of highly controlled emulsion microreactor polymerization systems,[43] and the use of NB-polymers as 'mortar' to build ordered NP aggregates[39a, 39d] Self-assembly of monomers along well-defined template strands has also been used to selectively polymerize complementary units, as well as to control or enhance molecular weight.[44]

This field has a long way to go, as sequence-specific interactions have yet to be shown, and even using homopolymers, building blocks for scalable interactions have yet to be developed

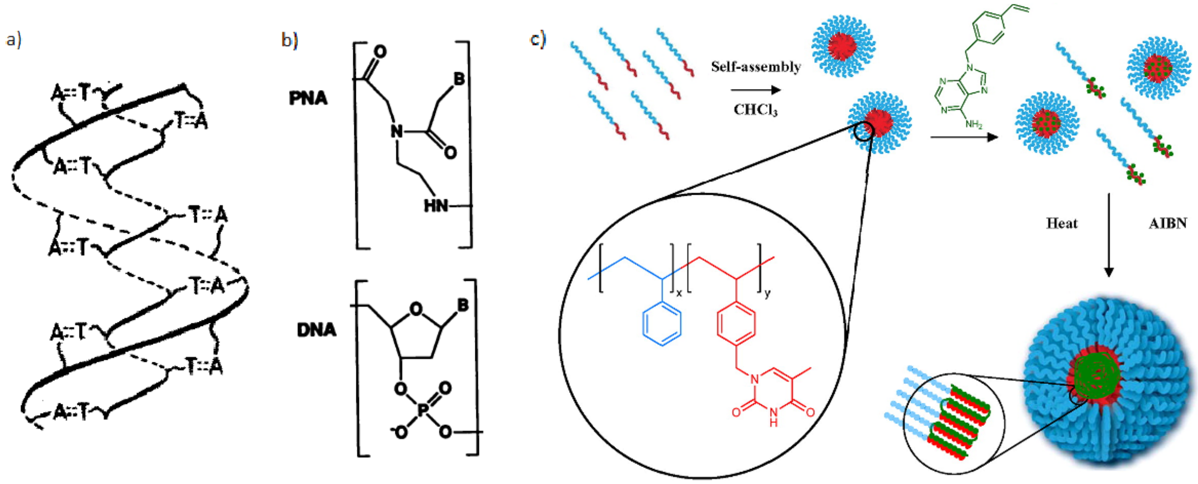

Figure 1.6: Examples of NB-substituted synthetic polymers. a) Proposed helical structure of poly(2-(thymin-1-yl)ethyl methacrylate) (inner) and poly(2-(adenine-9-yl)ethyl methacrylate) outer. b) structures of PNA and DNA c) Polymerization of high MW, low PDI NB-PS

Adapted with permission from a) ref [36] copyright Springer 1981, b) ref [37] Copyright AAAS 1991, c) ref [43] copyright NPG 2012.

1.4 Nucleobase-functionalized conjugated polymers

Although significant work has been done to produce nucleobase-functionalized polymers and characterize their various interactions, far fewer studies have included conjugated polymers, and none have explored their behaviour so systematically. What work has been done with nucleobase-CPs, however, is very encouraging.

In one of the earliest studies on the topic of NB-CPs, Bauerle and co. showed that the electronic properties of thiophene with appended nucleobases or nucleobase analogues can be influenced by the presence of complementary bases.[45] The authors emphasized that this represented the direct modulation of an electrical signal in response to a base-pairing interaction. Tang et al and Xing et al would go on to demonstrate that this and a related adenosine-containing system could act as useful sensors for mercury and copper.[46] Bauerle and co. returned to the topic a decade later to demonstrate that a similar effect could be demonstrated using PEDOT, thus increasing the compatibility of the system with aqueous conditions.[47]

More recent work from Lo and Sleiman demonstrated a number of promising results using NB-functionalized benzene-alkyne copolymers. First, they prepared hydrophilic thymine-functionalized poly(phenylenebutadiynylene), which was found to selectively bind complementary bases and complementary DNA. Substrate binding was associated with enhanced fluorescence and, in the case of DNA binding, changes in secondary structure as observed by circular dichroism.[48] This result illustrated the ability of a NB-

CP to undergo well defined interaction with another NB-polymer. Later, the molecular weight and dispersity of hydrophobic adenine-bearing poly(phenyleneethynylene) were found to be enhanced when the polymer was prepared in the presence of a complementary NB-poly(norbornene) template, a result analogous to those previously seen with non-conjugated polymers.[49]

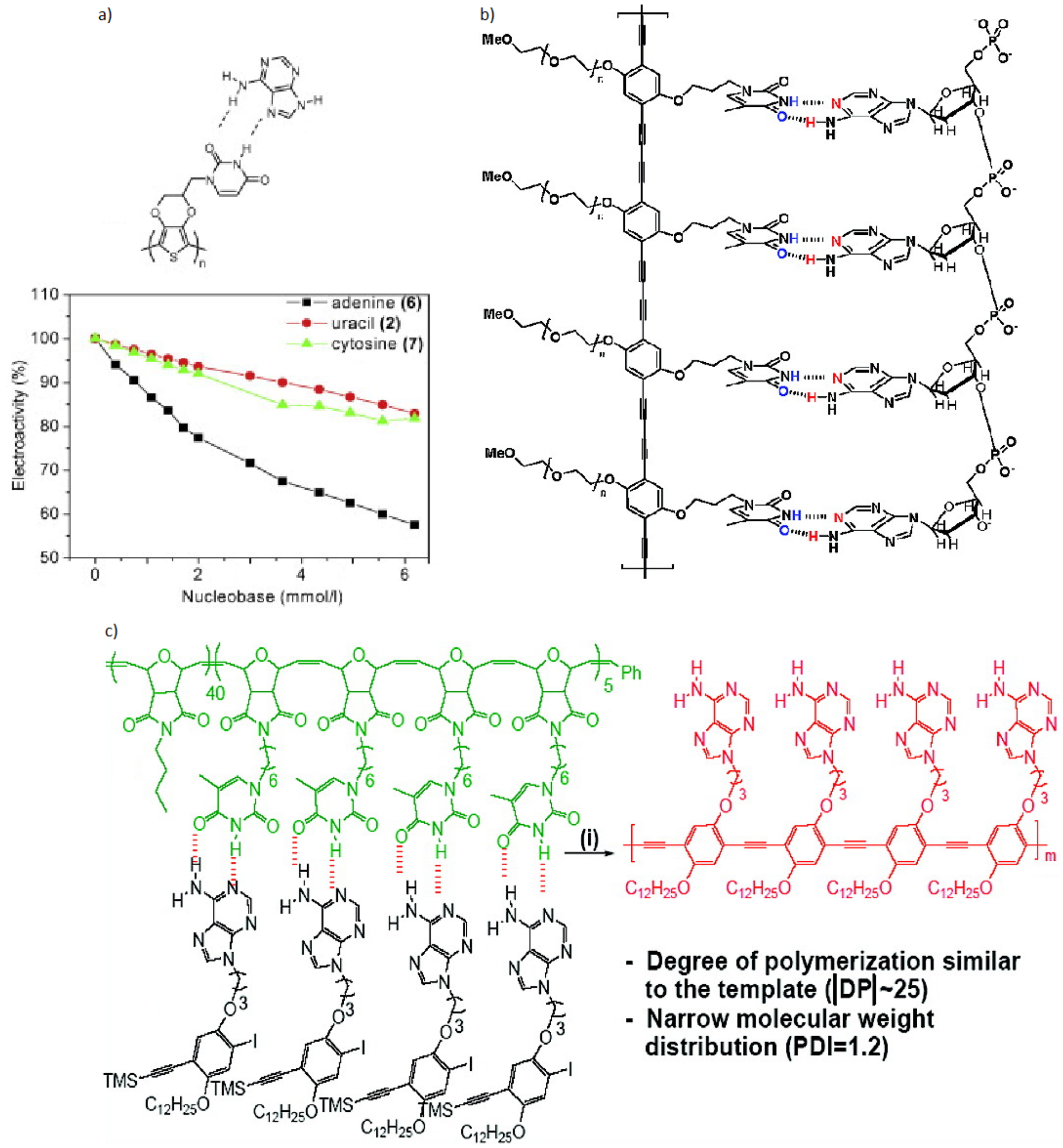

Figure 1.7: Examples of NB-functionalized CPs a) Interaction of NB-PEDOT with complementary base b) Hybridization of NB-poly(phenylenebutadiynylene) with DNA c) Polycondensation of NB-poly(PPE) on a ROMP-derived template.

Adapted with permission from a) ref [47] Copyright Elsevier 2009 b) ref [48] Copyright ACS 2008 c) ref [49] Copyright ACS 2009.

Despite inspiring results from structural DNA nanotechnology, there has not been any work on NB-driven-self-assembly between CPs. The ability to bypass DNA scaffolds and organize functional materials directly in a manner analogous to what is currently being accomplished using structural DNA nanotechnology would be a significant step towards the dream of constructing molecular electronics.[16] Furthermore, the reduced conformational freedom of CP compared to other polymeric materials can be used to reduce the complexity of the systems being developed. As synthetic techniques for preparing CPs continue to improve, this recommends these materials as a test-bed for future studies into nucleobase-driven self-assembly of synthetic macromolecules, and suggests great potential for such techniques in the field of organic electronics.

1.5 Thesis summary

The goal of this work is to describe the preparation of a poly(phenylenevinylene)-based NB-CP. PPV has been extensively studied, and used to construct a great variety of organic electronic devices, and is therefore expected to be an excellent model compound for this study. Furthermore, it is highly symmetric, and can prepared as a densely-functionalized homopolymer or alternating co-polymer. However, preliminary work indicated that standard methods of preparing PPV might not be suitable. Therefore, having described the potential advantages of nucleobase-driven self-assembly as a means of controlling CP morphology and microstructure in this introduction, Chapter 2 of this thesis will review the state of the art of PPV synthesis.[50]

This survey of the literature will identify the relative advantages and disadvantages of the diverse methods of preparing PPV, and which are appropriate for use in the subsequent experimental sections.

Chapter 3 will detail initial attempts to prepare nucleobase-functionalized PPV, and identify the characteristics of the resulting materials that precluded their use in self-assembly studies. Two distinct synthetic methods will be described, and the mechanistic features of these methods that lead to the observed characteristics of the resulting materials will be discussed where possible.

Chapter 4 will then present a novel variation on one of the synthetic methods described in Chapter 2. This method will be shown to produce low-defect, moderate-molecular weight PPV. Its use to prepare NB-functionalized polymers, and the properties of the resulting materials, will be described.

The final chapter will offer a summary and conclusion to the work presented, and identify areas where future work is needed.

Chapter 2: Advances and Challenges in the Synthesis of Poly(p-phenylenevinylene)-Based Polymers

Previous research into nucleobase-functionalized conjugated polymers has focused on using base-pairing to achieve modulation of specific properties, such as conductivity or electrochemical activity or fluorescence, in response to the presence of complementary nucleobases or DNA. The self-assembly of NB-CPs with other synthetic polymers has only been addressed in passing with respect to its impact on the preparation of such materials. As such, the choice of polymers used in past research has focused primarily on modulating a specific property.

In this work, we seek to begin exploring more generally the opportunities presented by pendant hydrogen-bonding moieties to control the self-assembly of CPs. The CP to be studied was therefore selected with an eye towards generality. As described below, PPV offers symmetry and chemical versatility, and is an extensively studied material that can be used to prepare a diverse array of semiconducting devices. It was therefore though to be an ideal candidate to generate results of general utility to the CP research community. However, the most commonly used methods of preparing PPV, the 'precursor methods' (vide infra) are known to produced material containing significant numbers of defects, and of ill-defined molecular weight. As such, other methods of producing the desired nucleobase-functionalized PPV (NB-PPV) had to be investigated.

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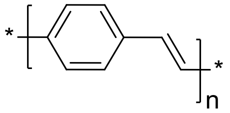
2.1 Introduction

Poly(*p*-phenylene vinylene) (PPV) has a special historical place in polymer electronics: it was the first polymer used to create organic light emitting diodes (OLEDs). The demonstration of yellow-green electroluminescence (EL) in PPV (**1**) films in a simple Al/PPV/indium tin oxide (ITO) diode in 1990[3] transformed the field from an area of purely academic interest to one of great technological promise. A number of major industrial players and new start-ups quickly became involved in research and development of organic light-emitting diodes and other organic electronics technologies. Just a few years later (1995), the first "bulk heterojunction" solar cell was introduced based on a solution-processed blend of poly(2-methoxy-5-(2-ethylhexyloxy)-*p*-phenylene vinylene) (MEH-PPV) and fullerene derivative PCBM.[4a] In 1996, the first (optically pumped) polymer lasers were demonstrated, again using PPV derivatives.[51] Also during the 1990s, the first conjugated polyelectrolytes, based on sulfonated PPV, were developed and found to be remarkably sensitive fluorescent sensors.[52].



PPV, 1

Figure 2.1: Structure of poly(p-phenylene vinylene).

Although it now is giving way to higher-performing, tailor-made materials in most applications, PPV's relative stability, structural simplicity and convenient band-gap – falling in the visible range – made it the material of choice for studies of basic photophysics of conjugated polymers.[53] As such, its popularity among researchers continued to grow well into the 2000's, and the time is now ripe to look back on the synthetic advances made in this field over the past two decades.

Here, we set out to take stock of the major methods used to prepare PPVs and related polymers, and to describe the advantages, disadvantages and unique characteristics of each. This review is by no mean a comprehensive summary of the literature (or recent literature) discussing PPV materials and their analogues. A number of other reviews focusing on various other aspects of PPV synthesis and applications have appeared through the years, and we refer the reader to some of these in

Table 2.1: Previous review articles discussing PPV

Year	Title	Authors	Publication	Ref
1998	Electroluminescent Conjugated Polymers – Seeing Polymers in a New Light	A. Kraft, A. C. Grimsdale, A. B. Holmes	*Angew. Chem. Int. Ed., 37*, 402–428	54
1998	The Chemistry of Electroluminescent Organic Materials	J. L. Segura	*Acta Polym*, *49*, 319–344	55
1998	Design and Synthesis of Polymers for Light-emitting Diodes	A. Greiner	*Polym. Adv. Technol.*, *9*, 371–389	56
2000	The Electroluminescence of Organic Materials	U. Mitschke, P. Bäuerle	*J. Mater. Chem., 10*, 1471–1507	57
2000	Progress in Light-Emitting Polymers	M. T. Bernius, M. Inbasekaran, J. O'Brien, W. Wu	*Adv. Mater., 12*, 1737–1750	58
2000	Semiconducting (Conjugated) Polymers as Materials for Solid-State Lasers	M. D. McGehee, A. J. Heeger	*Adv. Mater., 12*, 1655–1668	59
2002	Processible conjugated polymers: from organic semiconductors to organic metals and superconductors	A. Pron, P. Rannou	*Progr. Polym. Sci. 27*, 135–190	60
2003	Electroluminescent Polymers	L. Akcelrud	*Prog. Polym. Sci,. 28*, 875–962	61

2003	Conjugated Polymers as Molecular Materials: How Chain Conformation and Film Morphology Influence Energy Transfer and Interchain Interactions	B. J. Schwartz	*Annu. Rev. Phys. Chem.*, *54*, 141–172	62
2004	Synthesis of Conjugated Oligomers and Polymers: the Organometallic Way	F. Babudri, G. M. Farinola, F. Naso	*J. Mater. Chem.*, *14*, 11–34	63
2005	Single-Molecule Spectroscopy of Conjugated Polymers	P. F. Barbara, A. J. Gesquiere, S.-J. Park, Y. J. Lee,	*Acc. Chem. Res.*, *38*, 602–610	64
2005	Poly(arylenevinylene)s – Methods of synthesis	M. Grigoras, N. C. Antonoaia,	*Revue Roumanie de Chimie*, *50*, 245–256	65
2006	Transition Metal-Catalyzed Polycondensation and Polyaddition	W. Heitz	in: *Materials Science and Technology,* Wiley	66
2006	The Heck Polycondensation for Functional Polymers	Y. G. Lee, Y. Y. Liang, L. P. Yu	Synlett., *18*, 2879–2893	67
2006	Light Emitting Polymers	D. F. Perepichka, I. F. Perepichka, H. Meng, F. Wudl	In: *Organic Light-emitting Materials and Devices* (Z. Li, M. Hong), CRC Press, Florida, 45–294	68
2006	Poly(para-Phenylene Vinylene)s	N. Vilbrandt, S. Nickel, S. Immel, M. Rehahn, K. Stegmaier, C. Melzer, H. von Seggern	in: *Materials Science and Technology*, Wiley	69
2007	Fluorinated Organic Materials for Electronic and Optoelectronic Applications: the Role of the Fluorine Atom	F. Babudri, G. M. Farinola, F. Naso, R. Ragni	*Chem. Commun.,* 1003–1022	70
2009	Synthesis of Light-Emitting Conjugated Polymers	A. C. Grimsdale, K. Leok Chan, R. E. Martin, P. G. Jokisz, A. B. Holmes	*Chem. Rev., 109*, 897–1091	12
2011	Stille Polycondensation for Synthesis of Functional Materials	B. Carsten, F. He, H. J. Son, T. Xu, L. Yu.	*Chem. Rev., 111*, 1493–1528	71
2012	Synthesis of poly(p-phenylene vinylene) materials via the precursor routes	T. Junkers, J. Vandenbergh, P. Adriaensens, L. Lutsen, D. Vanderzande	*Polym. Chem, 3*, 275–285	72
2013	Poly(2,3-diphenyl-1,4-phenylenevinylene) (DP-PPV) derivatives: Synthesis, properties, and their applications in polymer light-emitting diodes	J.-T. Chen, C.-S. Hsu	*Polymer*, *54*, 4045–4058	73

2.1.1. Properties of PPV

Chemically, PPV can be considered a copolymer combining the repeating building blocks of polyacetylene and poly(*p*-phenylene) (PPP). Accordingly, its properties are intermediate of the former two: it is more chemically stable than polyacetylene (a major limitation of the latter) though not as robust as PPP, and while polyacetylene is black and lustrous – in line with its small 1.4 eV band gap (E_g)[74] – films of unsubstituted PPV **1** are yellow due to an absorption band centered at ~420 nm, Eg = 2.4–2.5 eV)[68].

PPV's chain structure is more flexible than that of other common conjugated polymers, such as PPP, resulting in conformational disorder and the formation of distinct microstructures depending on the stiffness and strength of interaction between the polymer chains and types of defects present.[53a, 62] Thus, the optical properties of PPV are significantly influenced by conformational factors. This is illustrated by PPV's pronounced solvatochromism:[75] chain extension in good solvents leads to a planar 'red phase', while coiling induced by poor solvents creates a 'blue phase' with a significantly reduced conjugation length.[76] By contrast, poly(3-alkylthiophenes) undergo a redshift in the presence of antisolvents during aggregation due to planarization and increased interchain interactions).[77]

In addition, π-π stacking interactions between chains leads to the formation of both H- and J-type aggregates.[78] These solvent-dependent conformational effects in PPV are frozen-in during spin-casting, leading to modulation of device properties.[79] Conformational factors also play an important role in the red-shift of the absorbance band maximum of dialkoxy-PPVs to nearly 500 nm, which results in part from a stiffening of the main chain due to H bonding between the alkoxy substituents and adjacent vinylic hydrogens.[80]

The yellow-green of PPV **1** and orange-red fluorescence of MEH-PPV **3** exhibits vibronically structured emission bands (Figure 2.2). Structural modifications to the polymer have generated materials with emissions spanning the visible spectrum from 420 to 680nm. Solid-state photoluminescence quantum yields up to 82% have been reported, with electroluminescence attaining up to 4% in all-PPV devices.[12]

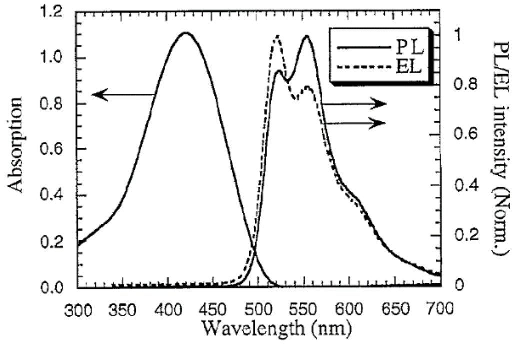


Figure 2.2: Typical absorption, photo- and electroluminescence spectra of 2,5-dialkyl-PPV. Reproduced with permission from ref [81] Copyright Elsevier 1997.

The HOMO and LUMO of PPV are accessible via cyclic voltammetry (Figure 2.3), which reveals reversible oxidation and reductions waves, and an electrochemical gap of 2.4 eV [74] that is in reasonable agreement with the optical band gap of 2.5 eV. Being a relatively good electron donor, PPV and its derivatives can be chemically doped by strong oxidizing agents and strong acids, affording highly conductive *p*-doped materials with conductivity up to ~10^4 S/cm^2[74] (cf. 10^5 S/cm^2 for polyacetylene[82]). In their neutral form, PPV derivatives display moderate charge mobility (μ). Hole mobility of up to 10^{-2} $cm^2V^{-1}s^{-1}$ was observed for electron rich dialkoxy-PPV.[83] Recently, even higher electron (field-effect) mobility of >1 $cm^2V^{-1}s^{-1}$ was demonstrated for electron-deficient planarized PPV derivatives under ambient conditions.[84]

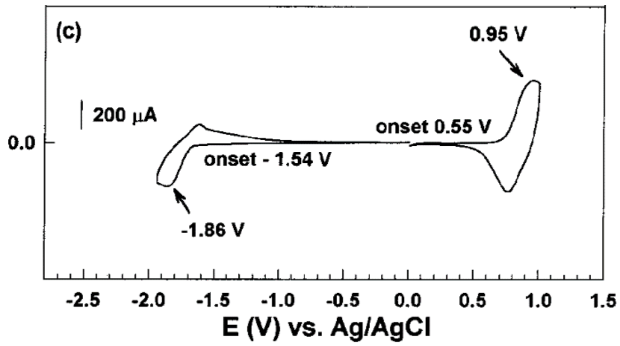


Figure 2.3: Cyclic voltammetry of MEH-PPV.

Reprinted with permission from ref [85] Copyright ACS 2002.

The strong fluorescence, electron-donor character and extended conjugation of PPV make it a very effective sensor material.[86] The loss of luminescence in the presence of analytes is enhanced by the superquenching effect, whereby a single quencher can 'turn off' the emission of an entire polymer chain.[87] This intrinsic signal amplification has been harnessed for the selectivne detection of metal cations, [88] explosives,[89] and biological targets.[90] Furthermore, PPV aggregates ("organic quantum dots") have received recent interest as bright, non-toxic emitters for in-vivo fluorescent labeling.[91]

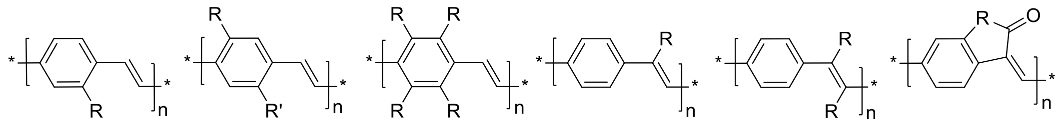
2.2 Synthetic Routes to PPV

As is the case for many other conjugated and non-conjugated polymers, PPV can be successfully prep ared by a variety of different reactions. Although we often assume the same chemical structure for the polymers prepared by different routes, the properties, particularly electronic properties, of the polymeric material can depend dramatically on the polymerization method. It is sometimes underappreciated that synthetic methodology controls electronic device performance and general “usefulness” of a polymer, as strongly as does the structure of its repeating block.

Thus, before discussing progress in the synthesis of PPV-based polymers, we first establish a set of criteria relevant to applications, in terms of which different synthetic protocols should be evaluated.

Both the **molecular weight** – expressed in this text by the number average (M_n) – and the related **polydispersity** (PDI), accessible by a given synthetic method, play significant roles in determining the solubility, crystallinity, processability and optoelectronic properties of a PPV sample.[92] Analytical polystyrene-calibrated gel-permeation chromatography (GPC) is almost universally used to report M_n and PDI. Values determined using this method, although subject to significant systematic error,[93] facilitate comparisons between synthetic methodologies, and will be used throughout this text.

The addition of **functional groups** to PPV (Figure 2.4) is necessary to produce a soluble material. Alkoxy, aryl, or alkyl substituents are generally used to this end, while the incorporation of other functionalities can also be used to produce materials with distinct electronic, spectral, morphological and self-assembly properties.[68] Certain polymerization techniques, however, may not be compatible with the steric, electronic, or chemical effects of diverse substitution.



2 3 4 5 6 7

MEH-PPV: R = OMe,
R' = 2-ethylhexyloxy
MDMO-PPV: R = OMe,
R' = 3,7-dimethyloctyloxy

Figure 2.4: Some substitution patterns of poly(p-phenylene vinylene).

Regiocontrol – control over the precise orientation of adjacent repeat units – is another feature that should be noted when comparing approaches to polymer synthesis. Placing different substituents R and R’ (or just one substituent) on the PPV repeat unit renders it regio-irregular, depending on head-to-head and head-to-tail coupling in the polymer chain. Regioregularity has been long known to produce improved materials properties in other classes of conjugated materials, most notably in poly-3-alkylthiophenes.[94] Although investigators were hindered by its reduced solubility,[95] fully-regioregular MDMO-PPV **3** has been demonstrated to show improved electronic properties, with higher hole-mobility[96] and improved fill-factors in OPV devices.[97]

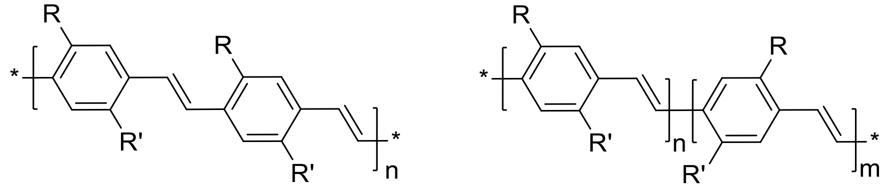


Figure 2.5: Regio-regular (left) and regio-irregular (right) PPV

The type and prevalence of **structural defects** in PPV depend entirely on the method by which the material is produced. These defects, in turn, influence the polymer’s properties. Most notably, non-conjugated defects result in a reduction in the effective conjugation length – ca. 11 repeat units in pristine dialkoxy-PPV[98] – of the material, thereby altering its optoelectronic characteristics. Furthermore, specific defects have been implicated in the formation of cross-links between chains or decreased device lifetimes.

Finally, the properties of PPV compounds can be modulated by **co-polymerization**. While early synthetic protocols were limited to produce nothing more complex than stochastically substituted PPV, newer approaches allow the production of well-defined alternating co-polymers, and the inclusion of diverse co-monomers. Furthermore, improved control over initiation and termination has led to the use of end-functionalized PPV as a macro-initiator for block-copolymer synthesis.[99]

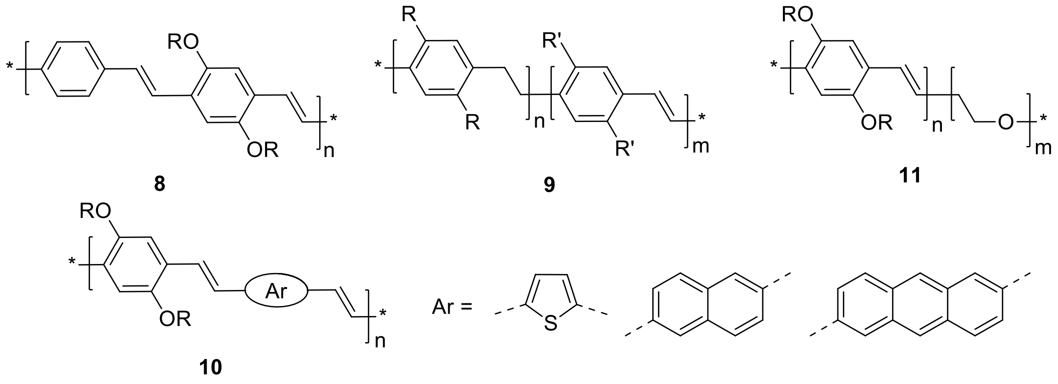
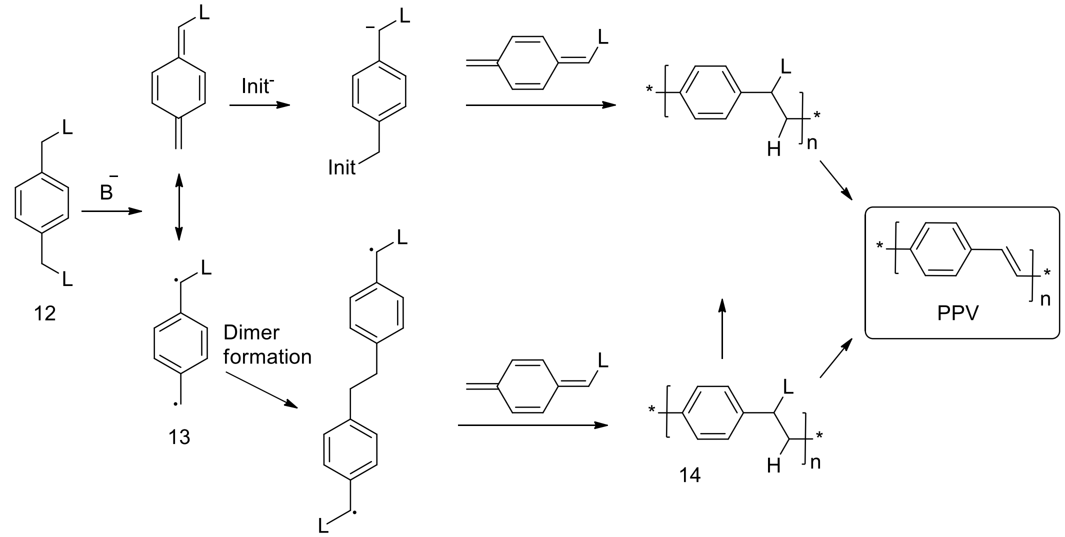


Figure 2.6: Selected PPV copolymers. [100,101,102,103]

2.2.1 Polymerization of *p*-Quinodimethane Intermediates

The earliest methods of preparing high-molecular weight PPV were adapted from existing techniques used to synthesize poly(*para*-xylylene), a non-conjugated polymer used as a barrier material. In the adapted approach, *para*-xylene is functionalized with leaving groups on the α and α' positions to give pre-monomer **12**. Base-driven 1,6-elimination yields an α-substituted quinodimethane **13** which polymerizes to give an α-substituted poly(*para*-xylylene) precursor **14** that can undergo elimination to yield PPV. This topic has recently been reviewed in detail by Junkers et al.,[72] thus only highlights will be presented here. Specific cases will be discussed after a general description of the polymerization.

p-Quinodimethane polymerizations were quickly determined to proceed via chain-growth,[104] however it was long uncertain whether the propagating chain was radical or anionic (Scheme 2.1). It is now established that the two mechanisms compete, and one or the other can be selected by controlling reaction conditions.[105]

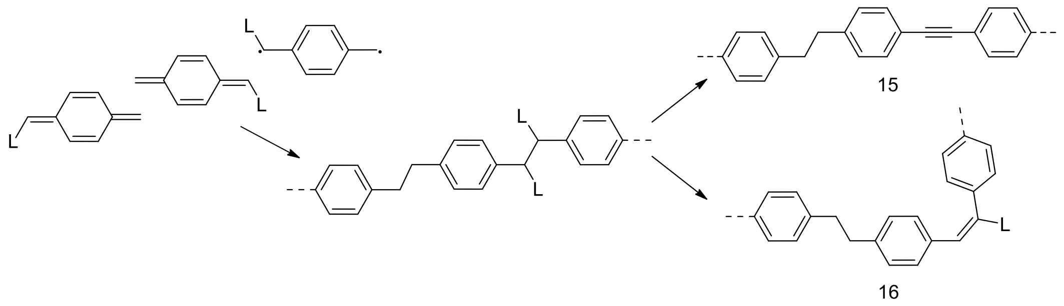


Scheme 2.1: Radical and anionic polymerization of PPV precursors.

Protic solvents block the anionic pathway, leading to radical polymerization. This can easily yield molecular weights in excess of one million Daltons. Such high molecular weights, however, are not necessarily advantageous as they affect the processability of the polymer and even lead to gelation of the reaction mixture. Chain termination groups (growth stoppers) such as benzyl halides and radical scavengers (TEMPO, BHT) have been applied to control gelation by reducing molecular weight, however they also cause a significant reduction in yield.[106] More recently, CBr_4 has been used as a chain transfer agent to control molecular weight and produce bromine-functionalized telechelic PPV derivatives suitable for use as ATRP macro-initiators in synthesis of block copolymers.[107]

Polar aprotic solvents and strong bases favour anionic chain growth. Although, originally recognized as a side-reaction that produced oligomeric material during radical polymerization,[108] recent work has demonstrated that purely anionic polymerization can be initiated by severely hindered bases, such as lithium 1,1,1,3,3,3-hexamethyldisilazide (LiHMDS), and can produce molecular weights in excess of 50 kD.[105] Although the polymerization is not fully living, such conditions still can produce relatively low PDIs (< 1.5).

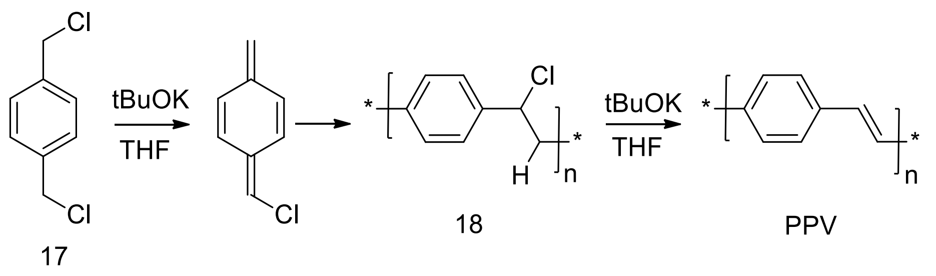
Regioregular head-to-tail coupling of the precusor is necessary to produce high qualtity PPV. Head-to-head and tail-to-tail coupling leads to the formation of conjugation-disrupting tolane-bisbenzyl **15**[109] and reactive substituted vinyl **16**[110] defects (Scheme 2.2). When conditions are chosen to favor radical polymerization, some regioirregularity in the precursor is unavoidable. Regioregularity can be greatly improved by using polarizing substituents to encourage selective deprotonation of one methylene position.[111] Regioregular PPV can also be prepared by anionic polymerizations from asymmetrically substituted α-alkylsulfoxide-α’-chloro-*p*-xylene pre-monomers.[111b, 112]



Scheme 2.2: Tolane-bisbenzyl and chlorovinyl defect formation in PPV following head-to-head and tail-to-tail couplings.

2.2.1.a The Gilch Route

The first quinodimethane polymerization of PPV was developed by Wheelman and Gilch at Union Carbide in 1965,[104] and employs α,α'-dichloro-*p*-xylene **17** as a pre-monomer. Upon treatment with strong base, the pre-monomer undergoes 1,6-elimination of HCl to form an α-chloro-*p*-quinodimethane, which polymerizes radically to produce poly(α-chloro-*p*-xylylene) **18**.[113] In the presence of excess base, the precursor **18** is converted to high-molecular weight PPV **1** by simple E2 elimination (Scheme 2.3). The polymerization proceeds rapidly with fewer defects and lower PDI at reduced temperatures, as low as –78 °C, but subsequent elimination proceeds slowly without heating.[114]



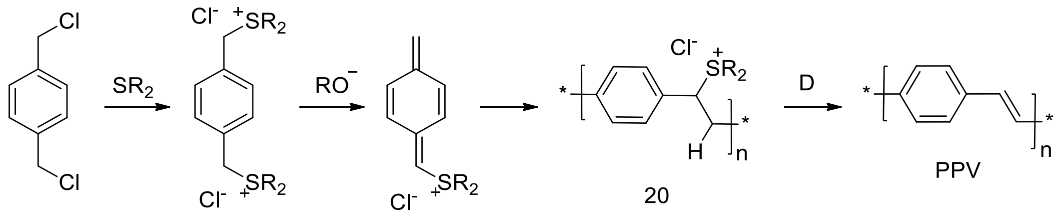
Scheme 2.3: Gilch polymerization to PPV.

The Gilch route provides an economical means of synthesizing very high molecular weight PPV at an industrial scale; however, without solubilizing substituents, the resulting material is completely insoluble and infusible. As such, it is primarily used in the production of soluble polymers such as MEH-PPV and MDMO-PPV (**3**). One "negative phenomenon" in Gilch route, know for a long time, is a gel formation during the polymerization process; the nature of such gelation has been recently discussed by Schwalm and Rehahn.[115]

When only one equivalent of base is used, the saturated – and therefore soluble – chlorine-substituted precursor polymer **18** can be isolated and thermally eliminated to PPV after device fabrication;[104] however, the HCl released during elimination has been found to degrade indium tin oxide (ITO) transparent electrodes, leading to inefficient OLED devices.

2.2.1.b The Wessling Precursor Route

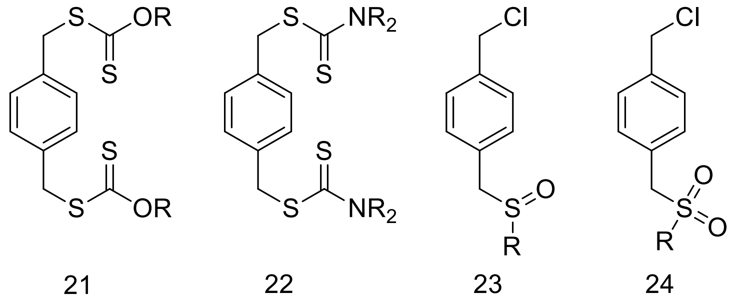
The predominant method of producing an isolable PPV precursor was developed by Wessling and Zimmerman for Dow Chemicals in 1966. It relies on a pre-monomer in which the two chlorine atoms of **17** are substituted by sulfonium groups (**19**). Base-driven polymerization of this compound yields a sulfonium-substituted poly-*p*-xylylene precursor **20** that is soluble in water and alcohols. Heating this precursor drives elimination of hydrogen chloride and dialkylsulfide from the polymer, converting it to PPV (Scheme 2.4)[116] However, the HCl released during this process will degrade ITO substrates, necessitating more complex device design to maintain efficiency.[117] The presence of a strong leaving group on the precursor material also makes it prone to degradation by nucleophilic solvents.



Scheme 2.4: Wessling polymerization to PPV.

2.2.1.c Improved Precursor Methods

Several improvements to the Wessling method were reported using different leaving groups. Xanthate monomers **21** provide a non-ionic route to PPV,[118] allowing the precursor material to be handled in organic solvents and alleviating the degradation of ITO substrates by HCl during elimination. The use of dithiocarbamates **22** in the place of xanthates produces precursor polymers of significantly reduced polydispersity, and enables elimination at temperatures below 100 °C, to afford high molecular weight PPVs (M_w up to 1,000 kDa).[119] High molecular weight (M_w = 113–248 kDa) water-soluble PPVs have also been obtained by this route.[120]

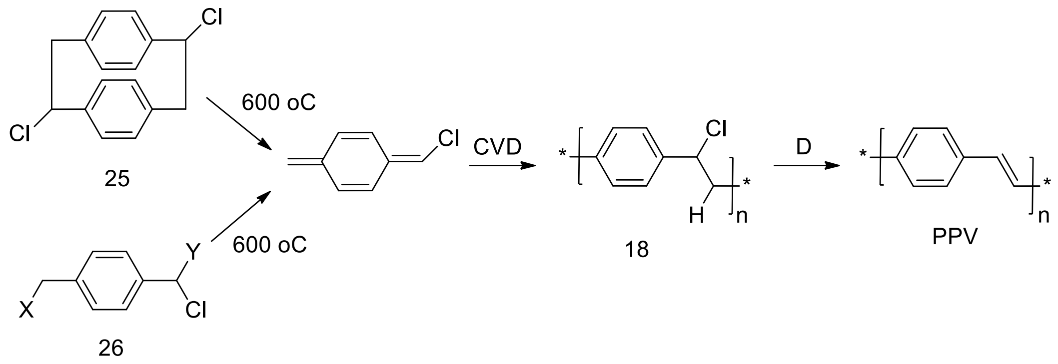


Scheme 2.5: Sulfinyl, sulfonyl, xanthate, and dithiocarbamate pre-monomers.

Substitution of one of the two chlorines of **17** with sulfinyl or sulfonyl group has been used to create polarized pre-monomers **23** and **24**.[121] These compounds undergo selective deprotonation at the sulphur-substituted methyl position, enabling greater control of the subsequent polymerization. Polymerization of these compounds, particularly under anionic conditions, can produce regioregularly substituted PPV that also contains significantly fewer defects from regio-irregular coupling.[111b] More recently, partially living growth of precursors has been demonstrated using sulfinyl-substituted monomers.[122]

2.2.1.d Chemical Vapour Deposition

PPV precursor films can also be formed by chemical vapor deposition (CVD) of substituted *p*-quinodimethanes, which are generated by thermal cracking of a suitable pre-monomer in the gas phase at high temperatures. Despite sharing identical active monomers, these precursor polymers are distinct from their solution-synthesized cousins both in their ability to form highly uniform conformal coatings[123] and in the fact that they are completely infusible and insoluble due to the presence of cross-links between polymer chains.[124]



Scheme 2.6: Chemical vapor deposition of PPV.

PPV by CVD was first demonstrated using 1,9-dichloro[2.2]-paracyclophane **25** in 1991,[125] then using more synthetically accessible α,α'-dichloro-*p*-xylene in 1994 (**26**, X = Cl, Y = H).[126] Later research demonstrated that the use α,α-dihalo-*p*-xylenes produced films containing fewer saturated defects, (**26**, X = H, Y = Cl). Poor device performance, however, remains a problem due to degradation of the ITO substrates by the hydrogen chloride liberated during the process.[127] Recent work has shown that the conjugation length of PPV prepared by CVD depends strongly on the conditions of synthesis (sublimation and pyrolysis temperatures, the substrate used for deposition).[128] Thus, lowering the temperatures of the deposition substrate produces more conjugated materials.[128a]

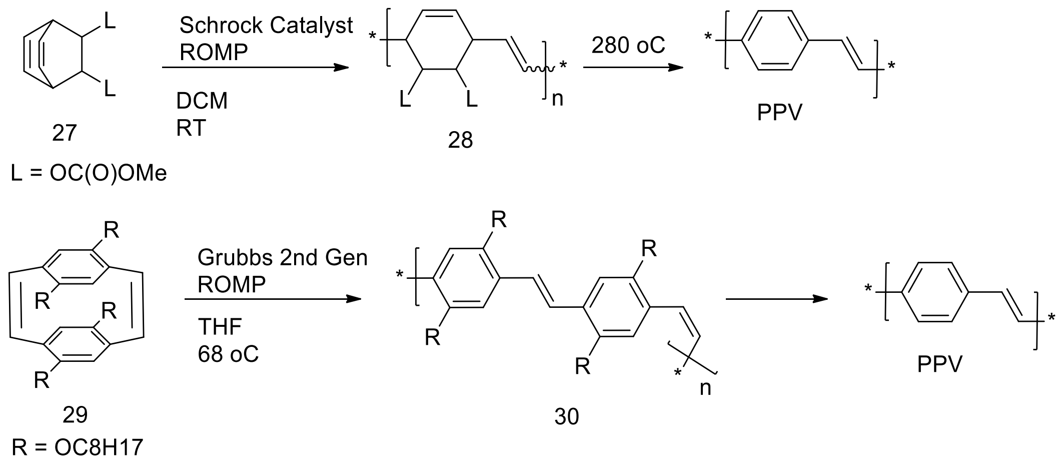
2.2.2 Olefin Metathesis Polymerizations

Metathesis polymerization offered the first *catalytic* method of preparing high molecular weight PPV precursors, and subsequently was adapted to produce PPV directly. Polymers produced by this method are not expected to contain any saturated defects, although the stereochemistry (*cis*/*trans*) of the vinyl bonds is strongly dependent on the catalyst used.

Unlike the *p*-quinodimenthane-based methods (2.1), no strong acids or bases are employed or produced in metathesis polymerization which expands the scope of possible substituents and device compatibility. On the other hand, the reliance of olefin metathesis on transition-metal catalysts, present the challenge of eliminating trace metal contamination from resulting material. In optoelectronic applications, this contamination can negatively affect the device performance and batch-to-batch reproducibility (see 2.2.4).

2.2.2.a Ring-Opening Metathesis Polymerization (ROMP)

ROMP is noteworthy as being the only technique that can produce PPV in a fully living manner. It provides unparalleled control over molecular weight and produces polymers with small polydispersity (< 1.3). This was first demonstrated in 1991 by Grubbs, who prepared the PPV-precursor **28** from substituted bicyclo[2.2.2]octadiene **27** using a Schrock-type catalyst (Scheme 2.7).[129] The elimination of CO_2 and methanol at high temperature aromatizes precursor **28,** producing a fully conjugated PPV. Bazan and co-workers developed an alternate precursor method based on polymerization of silyloxy[2.2]paracyclophene and used it to prepare the first PPV block-copolymer (with norbornene).[130]



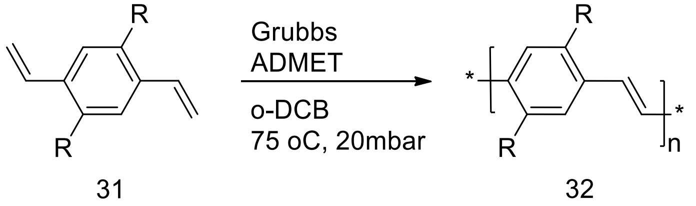
Scheme 2.7: Living ring-opening metathesis polymerization toward PPV.

The first direct synthesis of PPV by ROMP took place in 1992 using paracyclophanediene; however, only insoluble material was produced.[131] Direct, living polymerization producing soluble PPV was demonstrated by Turner in 2006, using tetraalkoxy[2.2]paracyclophanediene **29** and a second-generation Grubbs catalyst (Scheme 2.7).[132] The resulting polymer **30** had a molecular weights of ~7.5–24 kD (by GPC and ^{1}H NMR) and an alternating *cis-trans* structure, which was later shown to be convertible to an all-*trans* structure (within the limit of detection of ^{1}H NMR) by irradiation at 365 nm in THF solution over 36 h.[133] Interestingly, this conversion caused the apparent molecular weight (according to GPC vs. polystyrene standard) of the polymer to increase by a factor of 2.5, which highlights the known dependence of the GPC-derived M_w on the subtle details of the polymer structure. The living nature of ROMP has also been used to prepare block-copolymers of PPV and poly(*m*-phenylene vinylene).[134] It is worth noting that paracyclophanedienes are perhaps the most difficult

PPV monomers to prepare, although improved synthetic approaches continue to be developed.[135]

2.2.2.b Acyclic Diene Metathesis Polycondensation (ADMET)

Acyclic diene metathesis (ADMET) provides a route to high molecular weight, all-*trans* PPVs. It does not require the complicated monomers used in ROMP but cannot achieve the same low polydispersity for high molecular weight material. In this reaction, polycondensation takes place via the extrusion of ethylene gas, which must be removed to drive the reaction forwards. Initially used to produce unsubstituted oligo(*p*-phenylene vinylene),[136] and later all-*trans* oligo(*p*-phenylene vinylene) **32**,[137] improved catalysts and methodologies[138] and the addition of solubilizing groups allowed the production of polymers with molecular weights in excess of 100 kD (Scheme 2.8).[139] This process, however, was not found to be suitable for the production of 2,5-dialkoxy-PPV, potentially due to chelation of the ruthenium catalyst by the reacting vinyl group and *ortho*-oxygen. More recently, iterative ADMET couplings have been used to prepare large well-defined oligomers up to 15 units in length with well-defined termini.[140]



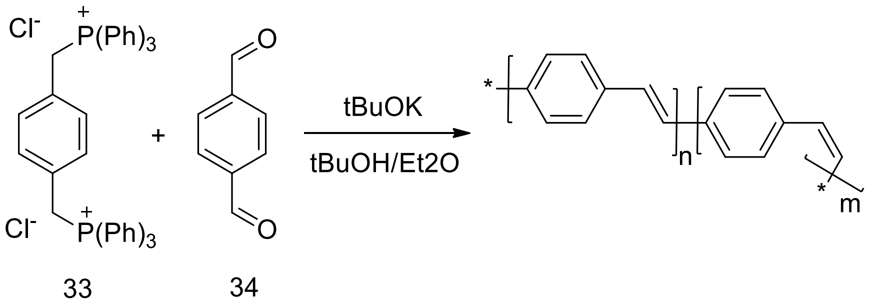
Scheme 2.8: Acyclic diene metathesis polymerization to PPV.

2.2.3 Nucleophilic Condensations

Several methods of producing PPV via classic organic alkene-forming reactions have been described. In contrast to ROMP and the precursor methods discussed above, these reactions produce macromolecules through polycondensation, or step growth polymerization. As such, the polydispersity indicies of these polymers are expected to converge to 2: larger than would be expected for a living reaction, but smaller than for a radical polyaddition. Condensation reactions are frequently performed using complementary bifunctional comonomers (AA/BB polymerizations); in such a case, the attainable molecular weight is highly dependent on the ratio of the two monomers. Where possible, homopolymerization of asymmetric 'AB' monomers can be used to eliminate this hurdle, and to access a regioregular product.

2.2.3.a Wittig-type Polycondensations

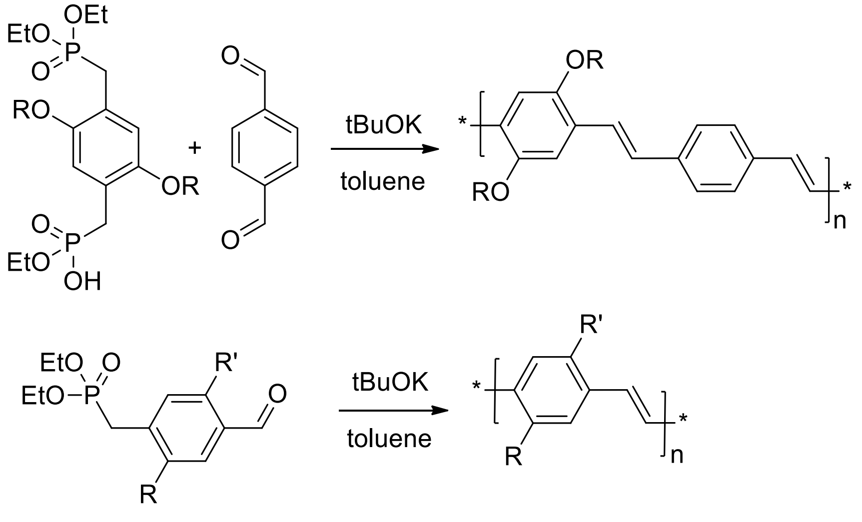
A straightforward method of producing fully conjugated PPV and its derivatives directly, the Wittig polycondensation was used by McDonald and Campbell in 1960 to prepare the very first unsubstituted PPV from α,α'-*p*-xylenediylbis(triphenylphosphonium chloride) **33** and terephthalaldehyde **34** (Scheme 2.9).[141]



Scheme 2.9: Wittig polymerization to PPV.

Although it represents a convenient approach to PPV copolymers with alternating substituents,[142] the Wittig polycondensation produces only low molecular weight materials ($M_n \leq 10$ kD) containing a mixture of *cis*- and *trans*-vinylene units.[143] Also, an attempt to prepare PPV from (*p*-formylbenzyl)triphenylphosphonium chloride by homopolymerization was unsuccessful. Iterative Wittig reactions, however, were used to produce the first series of well-defined *p*-phenylene vinylene oligomers.[144]

As demonstrated by Pfeiffer and Horhold, use of the Wittig-Horner modification not only improved the *trans*-content of the PPV produced, but also increased the attainable molecular weights beyond 10 kD (Scheme 2.10).[145]



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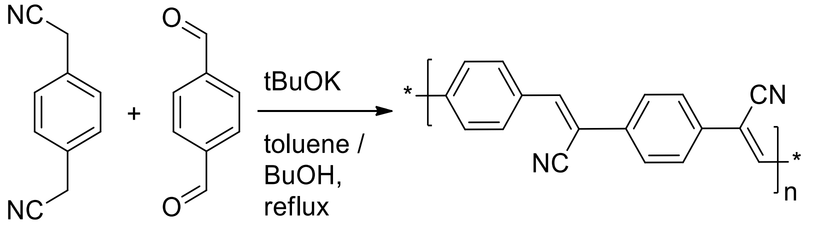
Scheme 2.10: Wittig-Horner polymerization to PPV.

These features, combined with versatility in monomer selection, have led to significant use of the Wittig-Horner method to prepare of a variety of PPV copolymers.[102, 112b, 146] Furthermore, this reaction can be used to perform homopolymerization of tolualdehyde phosphonates **35**.[95] This enabled the first in depth studies of the effect of regioregularity on the properties of a PPV sample.[97] It is also a method of choice in the preparation of well-defined oligo-PV.[7, 95, 147] Recently, this approach has been used to produce monodisperse oligomers up to 12 nm (nineteen units) in length.[148]

2.2.3.b Knoevenagel Polycondensation

A useful reaction to produce electron-deficient PPV, the Knoevenagel polycondensation takes advantage of the active benzylic hydrogens of *p*-xylenes derivatives with strong electron-withdrawing groups on their α-positions. These groups enable condensation with terephthalaldehyde in the presence of strong base to produce PPV. First introduced in 1960 using α,α'-dicyano-*p*-xylene **36** (Scheme 2.11),[149] this procedure can yield polymers with molecular weights on the order of 10 kD. Homopolymerization of asymmetrically substituted α-cyanotolualdehyde can also be performed, and yields a regioregular product.[150] In both cases, synthetic conditions must be carefully tuned to avoid Michael addition of the propagating nucleophile to the cyanovinylene moiety of another polymer chain.[151] Another limitation of this reaction is that it requires strong electron withdrawing substituents on the xylene α-positions to increase the acidity of the methylene hydrogens.

Knoevenagel polymerization of α,α'-dicyano-*p*-xylene **36** with aromatic dialdehyde **37** was also demonstrated using $(Ph_3P)_4RuH_2$ catalyst in the place of base, but, so far, this mild approach has yielded relatively low (7 kDa) molecular weight polymers.[152]



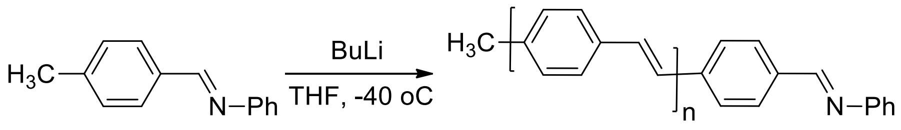
36 37

Scheme 2.11: Knoevenagel polymerization to PPV.

Note that Knoevenagel, as other aldol-like condensations, proceeds via *reversible* addition followed by dehydration, there exists the possibility of developing dynamic polymerization techniques based on this chemistry. While not yet demonstrated, such approach would certainly create exciting new opportunities in the field of conjugated polymers.

2.2.3.c Siegrist Polycondensation

A less known reaction, the Siegrist polycondensation was developed in the early 1990's by Kretzchmann and Meier as a method of producing regioregular all-*trans* PPV.[93] The reaction proceeds via deprotonation of the unsubstituted benzylic methyl group or **38** using a strong base, and its subsequent nucleophilic attack on the imine carbon of another monomer, leading to step-growth polymerization.



38

Scheme 2.12: Siegrist polymerization to PPV.

The benzylic carbanion intermediate is intramolecularly stabilized by the imine group. This leads to progressively reduced reactivity as the polymer chain grows, resulting in low molecular weights (M_n < 5 kD) and unusually narrow polydispersities. Having electron-withdrawing substituents or heteroatoms near this position allow greater molecular weights (~10 kD) to be achieved.[153] Additionally, since the polymerization is halted by falling reactivity rather than a termination reaction, the products have well defined end groups, which have been used to create PPV block-copolymers.[154]

2.2.4 Pd-catalyzed C-C coupling polymerizations

The past few decades have seen an explosion of progress in the field of metal-catalyzed cross couplings that has changed the face of synthetic organic chemistry.[155] The ability of these reactions to create bonds between sp^2 carbons has facilitated the modular construction of new conjugated materials by allowing easily-synthesized halo- and metalloarenes to be mixed-and-matched in the pursuit of new properties. Although less easily prepared, olefin derivatives can also be employed in these reactions, thus creating new avenues for the preparation of vinyl-containing materials.

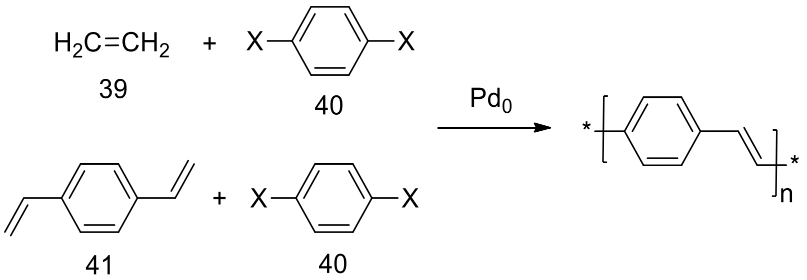
Such polymerizations are generally vulnerable to chain termination through proto-dehalogenation, -deborylation, and -demetallation, although it has been noted that this can be alleviated by stringent drying of materials.[156]

Another side-product of concern in Pd-catalyzed cross-couplings – particularly those of electron-rich arenes – stems from exchange of aryl groups between the metal centre and attached phosphine ligands.[157] Although it has not been studied in PPV specifically, this side-reaction was found to lead to incorporation of phosphine centers in the polymer backbone of related poly(*p*-phenylenes).[158] Minimization of such defects was demonstrated using bulky tri*alkyl*phosphine ligands and less polar solvents.[159]

One more complication comes from the aggregation of soluble metal catalysts to form nanoparticles.[160] Even at low concentrations (< 1%wt) these nanoparticles severely impact the efficiency of light-emitting and photovoltaic devices, and the mobility of field-effect transistors. Standard analytical tools used in organic chemistry – NMR, UV-vis-IR spectrophotometry, elemental analysis – are insensitive to such low levels of impurity, but impedance measurements[161] and X-ray fluorescence[162] can provide sufficient sensitivity. Although palladium nanoparticles persist through conventional purification by precipitation, they can be extracted by stirring the product mixture at room temperature with azothioformamide, which dissolves the metal by complexation, followed by selective precipitation of the polymer.[163] Alternatively, heterogeneous catalysis by graphite-supported palladium (Pd/C) was shown to reduce the contamination by a factor of 100–1000, while also eliminating the above mentioned aryl-exchange with phosphine ligands.[164]

2.2.4.a Mizoroki-Heck Polycondensation

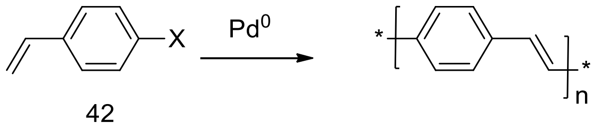
The first of the palladium cross-couplings, the Mizoroki-Heck reaction utilizes unsaturated halides or ‘pseudohalide’ analogues, and olefin C-H activation. Unlike many of the methods described above, this approach requires only mild base, and, although traditionally performed in refluxing DMF, modern catalyst systems allow the reaction to take place at room temperature in diverse solvents, making it one of the mildest routes to PPV. As one of the simplest metal-catalyzed cross-couplings, the Mizoroki-Heck reaction was the first to be applied to PPV synthesis.[165] Co-polymerization of *p*-dihalobenzene derivatives **40** with ethylene **39** (Scheme 2.13), although straightforward, yielded only material of low molecular weight (< 10 kD), likely due to difficulty in achieving 1:1 stoichiometry of the co-monomers while using gaseous ethylene.[165-166] On the other hand, co-polymerization of functionalized *p*-dihalobenzenes **40** with *p*-divinylbenzene **41** can produce polymers with molecular weights in excess of 20 kD.[167] However, the instability of the divinylbenzene monomer **41** to radical autoinitiation (producing cross-linked polystyrene) under the anoxic conditions required by catalytic cross-couplings is a serious problem. Yet, the reaction worked well in synthesis of PV-type block copolymers using divinyl monomer with two *p*-vinylphenyl end frangments are separated by non-conjugated aliphatic linker.[168]



Scheme 2.13: Mizoroki-Heck polymerizations to PPV.

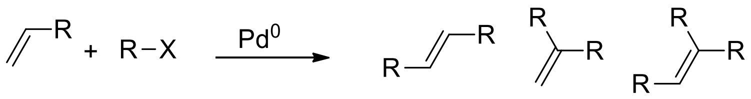
Homopolymerization of asymmetric *p*-halostyrene derivatives **42** has also been used to produce regioregular PPV[169] with molecular weights over 20 kD (Scheme 2.14).[170]

Degree of polymerization has been noted to vary greatly based on the choice of catalyst.[169]


42

Scheme 2.14: Regioregular Mizoroki-Heck polymerization to PPV.

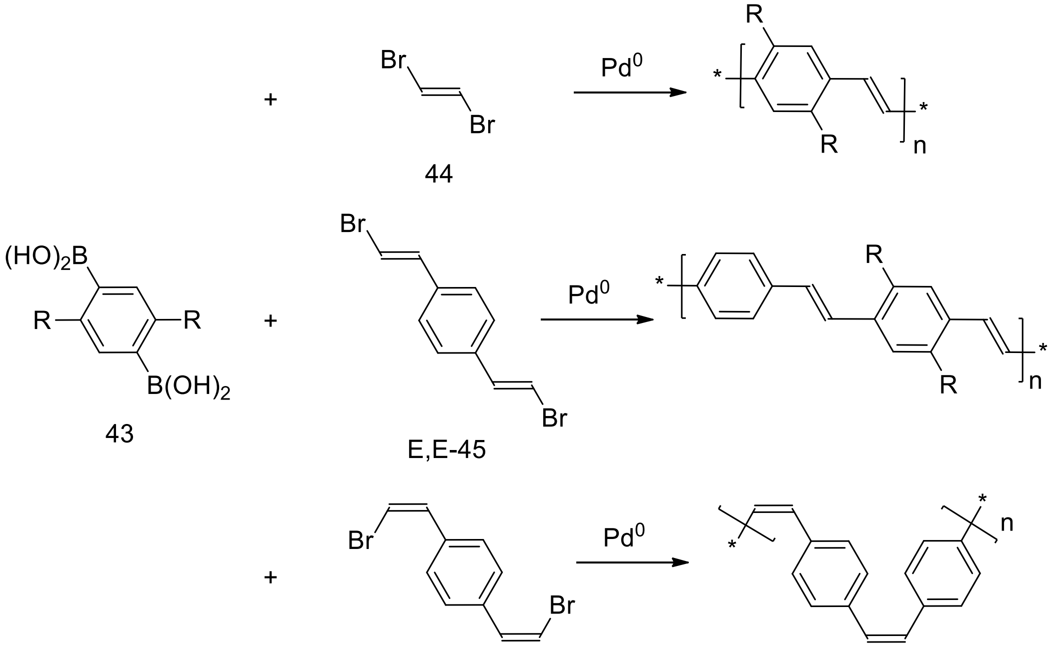
PPV produced by Mizoroki-Heck polycondensation is not expected to contain saturated or *cis*-defects. The reaction is, however, vulnerable to coupling at the styrene α position, leading to the formation of 1,1-ethylenediyl and ethylenetriyl defects (Scheme 2.15). The regiochemistry of addition is highly sensitive to both the electronic and chelating effects of nearby heteroatoms.[171] In particular, α-coupling in PPV is enhanced by the presence of substituents *ortho* to the styrene vinyl group,[172] limiting the applicability of this reaction to the synthesis of 2,5-dialkoxy-PPV derivatives. This shortcoming can be partially mitigated by the use of unsubstituted divinylbenzene as a co-monomer.[167]



Scheme 2.15: Illustration of alpha- and beta-substitution products in Mizoroki-Heck reaction.

2.2.4.b Suzuki Polycondensation

Extensively studied in the context poly(arylene) synthesis,[173] the Suzuki polycondensation has been adapted to prepare PPV by coupling benzenediboronic acids **43** with either *trans*-1,2-dibromoethene **44**[174] or *E,E*-1,4-bis(β-bromovinyl)benzene *E,E*-**45** (Scheme 2.16),[175] with the former combination attaining molecular weights in excess of 10 kD. The Suzuki reaction is distinguished by its high regio- and stereoselectivity, and has been used to benchmark other polymerization approaches.[172] Furthermore, the excellent stereocontrol of the Suzuki reaction allowed producing all-*cis* PPV using *Z,Z*-1,4-bis(β-bromovinyl)benzene *Z,Z*-**45** (Scheme 2.16).[176] The resulting material was found to undergo photoisomerization to the all-*trans* material in solution and as a film, and the associated reduction in solubility was used for photopatterning.



44

43

E,E-45

Z,Z-45

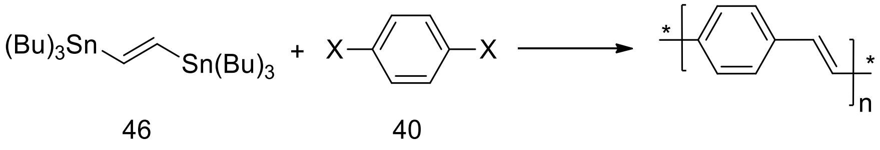
Scheme 2.16: Suzuki polymerization to PPV.

Expected side-reactions include homocouplings, yielding biphenyl or butadienyl defects, as well as the phosphine transfer and termination reactions described above. Recently, it was shown that such defects can be practically eliminated by using strong aqueous bases together with the bulky *t*-Bu$_3$P ligand.[175]

Generally, the widespread use of Suzuki reaction in PPV series appears to be limited by synthetic availability of the monomers (bearing halogen or boronic group at the vinylene moiety). However, the method has found a widespread application in preparation of aryl-rich PPV analogues, such as poly(*p*-biphenylene vinylene) and poly(*p*-terphenylene vinylene),[177] as well as in all-*cis* poly(*m*-phenylene vinylenes).[178]

2.2.4.c Stille Polycondensation

The Stille coupling is distinct from the Mizoroki-Heck and Suzuki reactions in that it does not require basic conditions. This polycondensation can be used to prepare PPV from dihalobenzene derivatives **40** and the commercially available 1,2-bis(tributylstannyl)ethylene **46** (Scheme 2.17), allowing the facile and modular development of novel PPV materials.[179] This simple reaction, however, is not without its drawbacks: homopolymerization of stannylated halostyrenes have not been demonstrated, and the symmetry of the reactive groups prevents regioregular polymerization of asymmetrically functionalized monomers. Furthermore, although trialkyltin groups are generally quite stable and improve the solubility of large aromatic monomers, care must be taken in managing the toxic trialkyltin halides that result from the reaction.



Scheme 2.17: Stille polymerization to PPV.

Despite excellent results with other materials,[180] the molecular weight of PPV prepared by the Stille polycondensation is generally low, (< 10 kD) and strongly dependent on reaction conditions.[180] No in-depth studies have been done to explain the poor results of this reaction, however, significantly larger molecular weights of up to 60 kD have been achieved with some electron deficient monomers.[181] Despite these variable results, the Stille polycondensation has been used by several groups as a convenient method of producing unique PPV materials and their heteroanalogs.[63, 71, 84b, 182]

2.3 Summary and Outlook

Poly(*p*-phenylene vinylene)s, some of the oldest polymers to have shaped the field of organic electronics, remain an important yet not fully understood class of conjugated materials. Combining the structural elements of the most conducting (polyacetylene) and most stable (poly-*p*-phenylene) conjugated polymers, they still present a number of challenges, as well as opportunities, in materials design. Inclusion of the non-aromatic vinylene repeat unit makes PPV distinctly different from most semiconducting polymers, which are almost exclusively formed by transition metal-catalyzed or oxidative coupling of aromatic monomers. Accordingly, a very rich synthetic chemistry for preparing PPV has been devoped over the last ~half-century.

p-Quinodimethane precursor polymerizations have evolved from being merely a method of circumventing insolubility into one that can provide regioregular material in a broad range of molecular weights with controlled chain ends. These polymers, however, inevitably contain some quantity of conformation and conjugation disrupting defects that are known to limit device lifespans. Meanwhile, chemical vapor deposition of similar monomers can produce highly conjugated, cross-linked films of arbitrary thickness, although substrate etching during elimination remains a challenge to be resolved.

Nucleophilic condensations, having their roots in tried-and-true organic synthetic reactions, presented limited room for improvement. The Wittig-Horner polymerization remains a straightforward method of producing fully regioregular PPV, while the Siegrist and Knoevenagel fill distinct synthetic niches in the production of well-defined low molecular weight and electron-deficient PPV, respectively.

Metathesis polymerizations have undergone significant improvement since their first realization, to the point that both ROMP and ADMET methods can be used to prepare all-*trans* polymers with essentially no defects at moderate temperatures and low catalyst loading. Moreover, while both of these processes can be used to obtain very high molecular weight material, the living nature of ROMP allows molecular weight to be fine-tuned, while also providing active chain ends for block-copolymerization. The high fidelity of these synthetic methods presents the opportunity to verify old results, which may in many cases stem from the baseline level of defects that are necessarily present in commercial PPV samples prepared by *p*-quinodimethane polymerizations.

Palladium cross-couplings have undergone extensive development since they were first applied to the preparation of PPV, and this has led to massive improvements in the quality of the polymers that can be produced. These reactions are particularly noteworthy not only for their convenience, but also for their generality, allowing the mild synthesis of not only high-quality PPV, but also a broad array of related copolymers.

Despite the above progress, the synthetic chemistry of PPV is far from being “mission accomplished”. We suspect that the defect concentration and/or the chain length accessible by a particular synthetic procedure are still limiting the performance of a number of reported PPV derivatives and analogues. In particularly, metal-catalyzed metathesis and cross-coupling approaches clearly need further optimization.

It is true that simple substitution of the parent PPV offers only limited possibilities for tailoring the properties required in organic electronic applications (band gap, charge mobility, etc). However, incorporation of vinylene units in more elaborate poly(*p*-arylene vinylenes), together with many modern aromatic building blocks, offers a unique opportunity for materials design. We anticipate that more of such polymers with state-of-art electronic properties will continue to be reported. We hope that the above overview of the synthetic approaches and challenges will help redefining the scope of the modern conjugated polymers field.

Chapter 3: Optimization and Evaluation of the Stille and Mizoroki-Heck Reactions as Means of Producing Functionalized PPV

3.1 Introduction

Detailed study of a material's self-assembly requires that the material in question be structurally well-defined, if meaningful results are to be generated. The structure and properties of poly(phenylenevinylene), as described in Chapter 2, are highly dependent on synthetic method used to prepare it, due primarily to the formation of defects. In the case of nucleobase-functionalized PPV, care must also be taken to identify synthetic methods that are compatible with the various functionalities found on heterocyclic nucleobase moieties, to ensure both that polymerization takes place unimpeded, and that the nucleobases are not transformed during the polymerization.

3.1.1 Characteristics of well-defined PPV

Functionally, a polymer can be distinguished from an oligomer as, "a chain long enough that the addition of one more monomer does not change the properties of the material."[183] As illustrated for 2,5-dialkoxy-PPV in Figure 3.1, the fluorescence maximum of PPV converges to a single value as chain-length increases. This convergence can be described by an exponential function of the reciprocal chain-length, as noted by Meijer et al in 1997.[98] Interestingly, although the absorption maxima of OPV samples undergo similar redshift with increasing size, convergence is not observed in the absorption spectra of higher molecular weight PPV. This may result from differences in the ground- and excited-state dynamics of different-length PPV chains,[184] but it could also be caused by molecular weight dispersity, conjugation-disrupting defects,[110] or the formation of inter-chain absorption bands due to solution-state aggregation.[78] These effects are difficult to distinguish based on the literature, as the bulk of the physical investigation in to the fundamental properties of PPV have been conducted using material prepared via the Gilch method, or of unspecified origin. As such, saturation of the fluorescence red-shift will be used as the primary indicator that a sample has length-independent, polymeric optoelectronic properties.

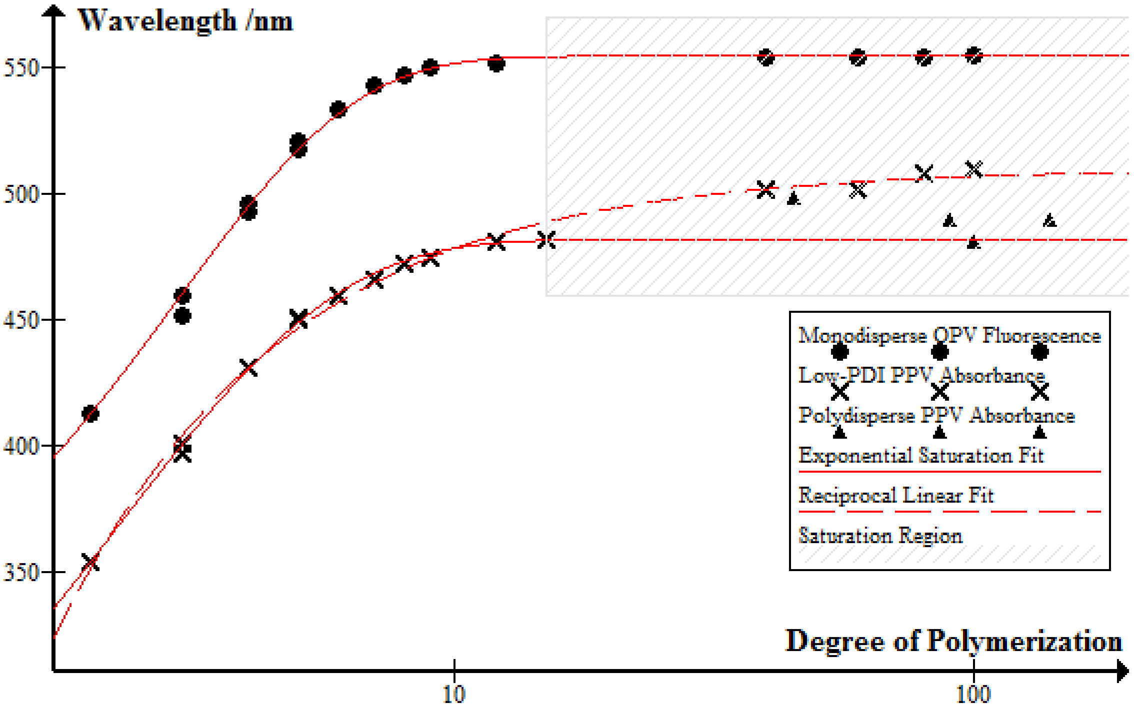


Figure 3.1: Optical transition energies in various 2,5-dialkoxy-PPV samples in good solvents. Data for low DP PPV taken from refs [98] and [147]; data for high-DP PPV taken from ref [133]

The significance of this relationship between optical properties and molecular weight is twofold. First, it allows the conjugation length of a sample to be estimated from its optical properties – a useful feature in light of the limitations of GPC analysis described in the previous chapter. Second, the value at which the emission converges is characteristic of a given substitution pattern and chemical environment, and can thus be treated as a probe of the polymer's electronic structure.

To reduce the inaccuracy inherent in analyzing a rod-like material by GPC with amorphous standards, a calibration curve was constructed using data for dialkoxy-PPV of known molecular weight found in the literature. These data (Figure 3.2) were fitted reasonably by the function

$$MW_{GPC} = aMW^{1/0.6} + bMW \quad (1)$$

where MW represents the true molecular weight of the material as determined by the authors, and MW_{GPC} represents the molecular weight of amorphous standards of equivalent retention time. This equation assumes that the hydrodynamic radius of a rodlike polymer increases approximately linearly with molecular weight. The general shape of the curve is therefore given by the exponent in the first, which is derived from the ratio of the rates of increase of the hydrodynamic radii of rodlike and well-solvated amorphous polymers respectively as a function of chain length.[185] The second term is a parameter added to reflect non-ideal behaviour. Constants were determined by least-squares fitting (a=0.00267, b=0.954).

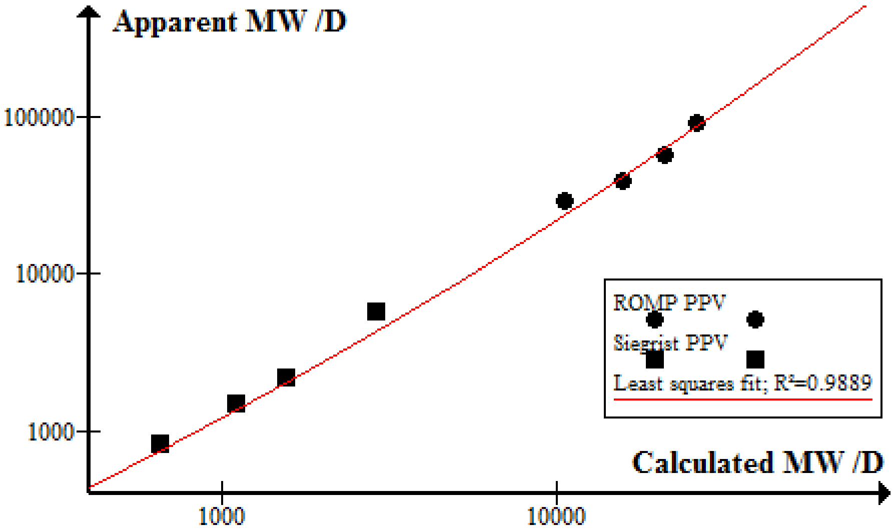


Figure 3.2: Apparent molecular weight observed by GPC vs expected true molecular weight for a series of all-trans dialkoxy-PPVs.

Curve fitted to eq 1 by least squares in Graph, R^2=0.9889. Siegrist PPV data taken from ref [93], ROMP PPV data taken from ref [133].

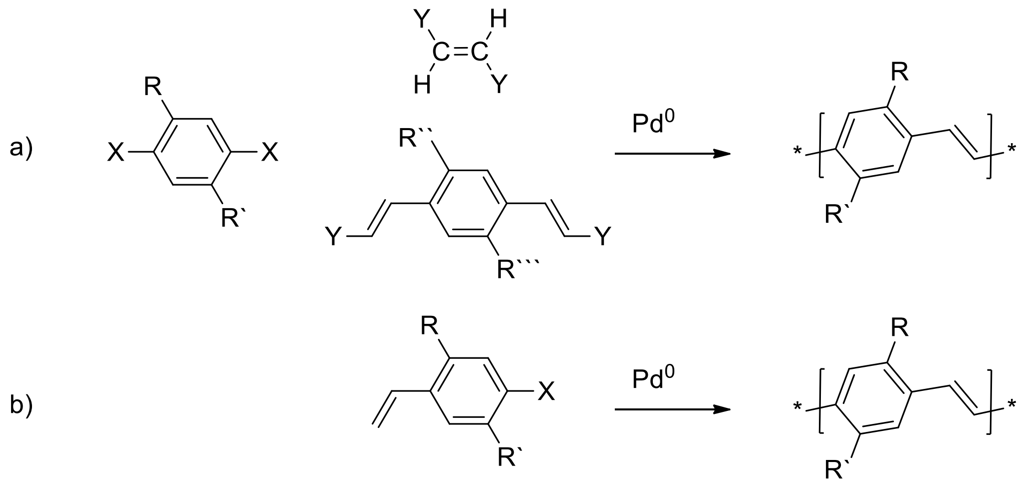
The requirements of mild conditions, low defect levels, and moderate molecular weight collectively point towards metal-catalyzed polymerization as a means of preparing NB-PPV, and as a number of distinctly functionalized monomers will need to be prepared, synthetic accessibility recommends palladium-catalyzed cross-coupling over olefin metathesis.

3.1.2 Palladium Catalyzed Polymerization of Poly(phenylene vinylene)

Palladium catalyzed C-C bond formation has proven to be a great asset to the field of conjugated materials, and is noteworthy not only for its high yields and specificity, but also its tolerance of a broad range of functional groups in the reaction mixture. Discovered by Richard Heck at the turn of the 1980's,[186] this class of reactions takes advantage of the facile generation of organometallic palladium species through the oxidative addition of unsaturated halides to Pd(0) complexes. These complexes can then be used to selectively form new C-C bonds through insertion of olefins, or by the addition of a second Pd-C bonded ligand, followed by reductive elimination. The manner in which the second carbon enters the cycle is what differentiates the various named reactions in this class. An excellent overview of the history and development of palladium catalyzed chemistry is provided by Seechurn et al. in ref [155].

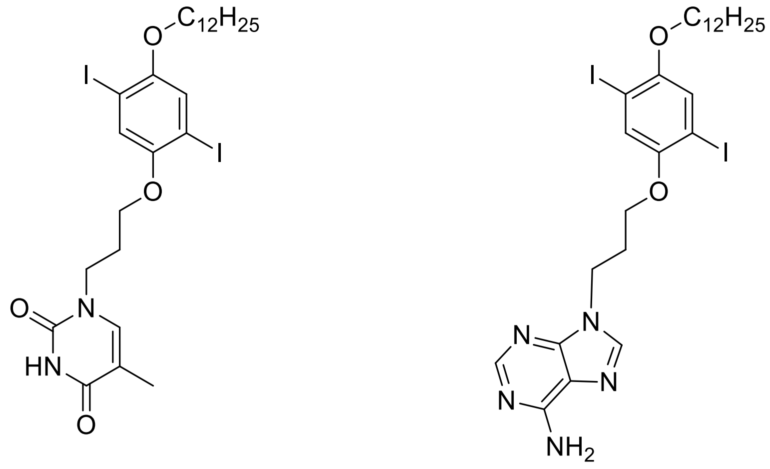
3.1.3 Palladium Catalyzed Polymerization of Poly(phenylene vinylene)

There are two general methods of producing PPV using palladium-catalyzed cross-coupling chemistry. The first is to copolymerize a benzene moiety bearing para-oriented reactive groups with an ethylene or para-divinylbenzene synthon (Scheme 3.1a). The second is to homopolymerize a reactive styrene monomer bearing a para-oriented reactive group. (Scheme 3.1b) This second method offers the opportunity to produce a regioregular polymer when an asymmetric monomer is employed (R┴R`), and avoids the problems of stoichiometry control inherent to copolymerization. However, the first method offers greatly reduced synthetic complexity of the monomers, and allows for the creation of alternating copolymers.



Scheme 3.1: Methods of producing PPV via palladium catalysis

In this study, the copolymerization approach was also favoured by the availability of suitable, nucleobase-functionalized monomers prepared by Dr. P.K. Lo.[49] Nucleobase-monomers compounds 1-dodecyloxy-2,5-diiodo-4-(3-(thymin-1-yl)propoxy)benzene (T-Dd-PhI$_2$) and 1-dodecyloxy-2,5-diiodo-4-(3-(adenin-9-yl)propoxy)benzene (A-Dd-PhI$_2$) were already available (Figure 3.3), and therefore the copolymerization method was chosen.

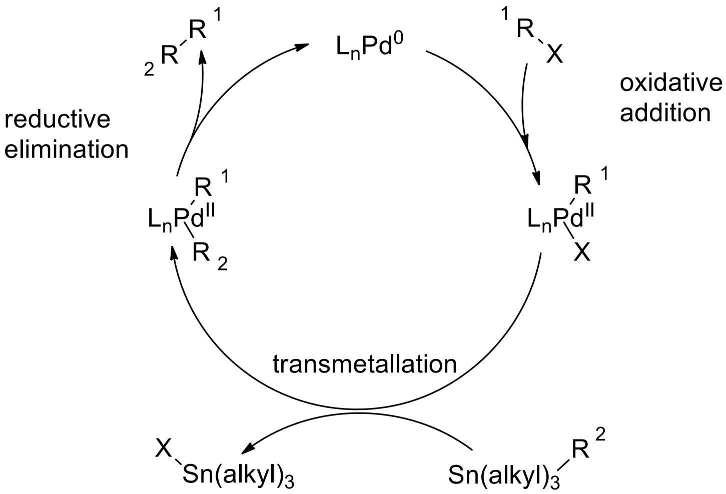


T-Dd-PhI$_2$ **A-Dd-PhI$_2$**

Figure 3.3: Nucleobase-functionalized monomers NB-Dd-PhI2 prepared by Dr. P.K. Lo.

3.1.4 Stille Polymerization

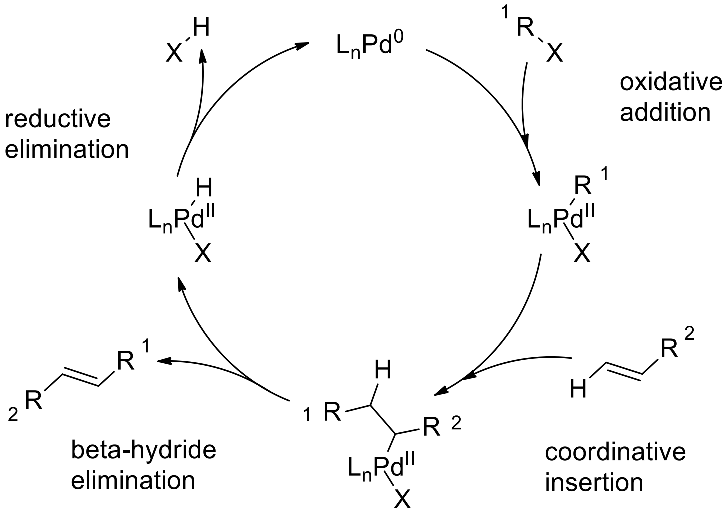
In the Stille reaction, one of the carbon fragments – in this case the olefin component of PPV – must be functionalized with a trialkylstannyl moiety, and enters the catalytic cycle through transmetallation onto the organopalladium(II) intermediate (Scheme 3.2). During transmetallation ethylene moiety exchanges with the halide on the palladium, creating a relatively inert trialkylstannyl halide side product. Compared to other palladium-catalyzed carbon-carbon bond forming reactions, the Stille polycondensation proceeds under neutral conditions and does not generate any acidic side products, although care must be taken as trialkylstannyl halides can be toxic – particularly trimethyltin chloride.



Scheme 3.2: Stille catalytic cycle

3.1.5 Mizoroki-Heck Polymerization

The Mizoroki-Heck reaction is a formal C-H activation that occurs through the insertion of an olefin into a Pd-C bond, followed by beta-hydride elimination to regenerate the now more highly substituted olefin (Figure 3.3). The reaction can occur with very high conversion and, for styrenic olefins, is expected to yield the *trans* product, which recommends it as a potential method of choice for preparing PPV.[186]



Scheme 3.3: Mizoroki-Heck catalytic cycle

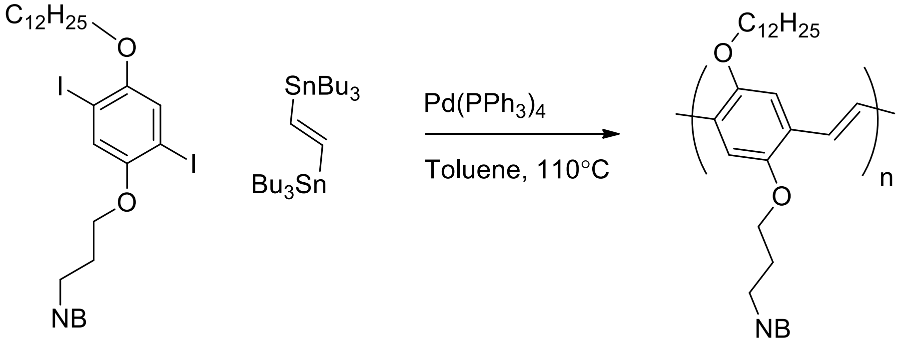
Much like the Suzuki reaction, the Mizoroki-Heck reaction must be performed in the presence of base, to abstract the protons the protons generated by beta-hydride elimination; However, in the case of the Mizoroki-Heck reaction, only mild bases are necessary, due to the acidity of the palladium hydride intermediate.

3.2 Results and Discussion

As noted, A-Dd-PhI$_2$ and T-Dd-PhI$_2$ had been prepared by Dr. P.K. Lo.[49] After purification by chromatography/crystallization, the compound were both pristine white powders and >95% pure by ^{1}H NMR. These materials were used in all polymerizations of NB-PPV.

3.2.1 Stille Polymerization of PPV

The Stille copolymerization was evaluated first due to its simplicity and the commercial availability of the necessary E-bis(tributylstannyl)ethylene. This olefin was polyermized with A-Dd-PhI$_2$ and T-Dd-PhI$_2$ under standard Stille conditions[182] in refluxing toluene with tetrakis(triphenylphosphine)palladium(0) (Scheme 3.4).



Scheme 3.4: Preparation of NB-PPV via Stille copolymerization

A red powder was obtained after precipitation of the reaction mixture in methanol, suggesting that conjugated polymer had formed. A comparison of the absorption and emission spectra of the material with those described above indicated that the product consisted of low molecular weight material, with the absorbance maximum corresponding to that expected for a pentamer. Monitoring of reaction progress by UV-visisble absorption spectroscopy indicated that, in agreement with literature protocols, indicated that the reaction continued to progress over several days; however, analysis also suggested that even extended reaction times would not yield degrees of polymerization greater than ~7 (Figure 3.4). It was unclear whether this was due to catalyst inactivation, chain termination, decomposition, or defects affecting conjugation length.

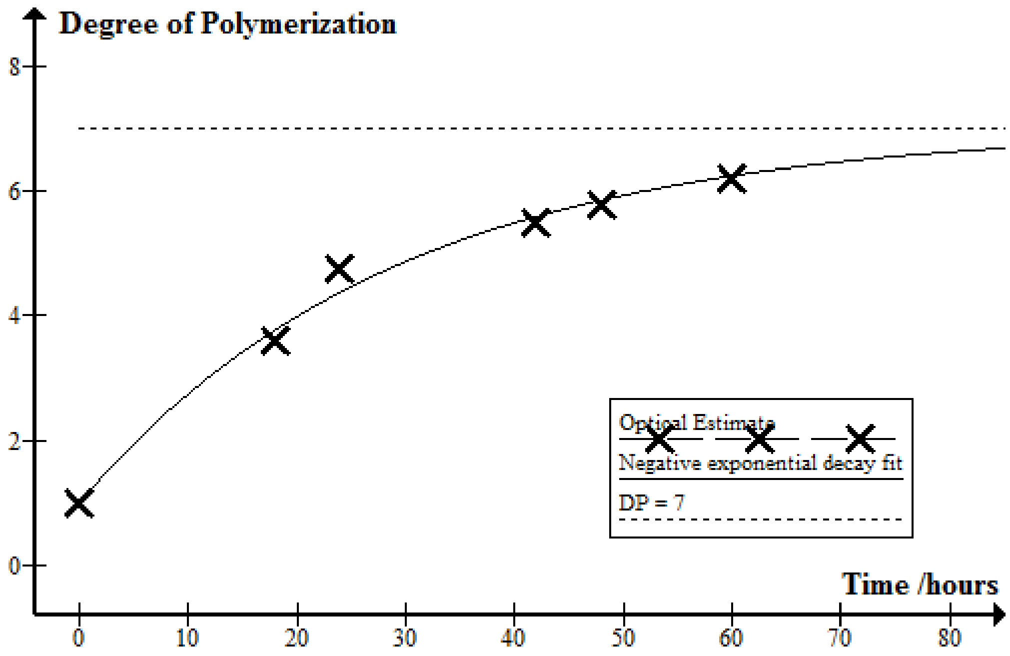
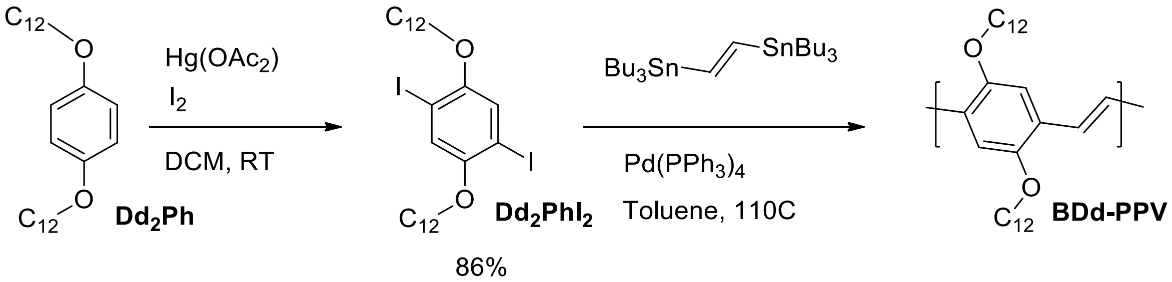


Figure 3.4: Stille polymerization time course results.

Degree of polymerization is estimated from the absorption maximum of the sample using data from Meier et al. presented in . Negative exponential decay curve fitted using lease squares in Graph, R^2=0.9899.

Concerned with the low molecular weight of the product, an analoguous monomer not containing a nucleobase moiety was prepared as a control to optimize the reaction conditions. 1,4-bis(dodecyloxy)benzene Dd_2Ph, synthesized by Dr. Lo,[49] was iodinated to 1,4-diiodo-2,5-bis(dodecyloxy)benzene Dd_2PhI_2 using mercuric acetate and elemental iodine in dichloromethane (DCM), in good yield (86%). This material was copolymerized with E-bis(tributylstannyl)ethylene under the same conditions (Scheme 3.5).



Scheme 3.5: Preparation of BDd-PPV from Dd_2PhI_2

Molecular weights were similarly small for both NB-PPV and BDd-PPV, indicating low conversion of the monomer and intermediate oligomers to polymer. A review of the literature indicated that although the Stille reaction was explored for the production of PPV by Bao et al in 1995, and employed by several groups since then, it has generally been found to produce low-molecular weight polymers in which the degree of polymerization depended strong on the halide (or pseudohalide, *eg*. triflate) used, as well as the solvent and catalyst.[180] More recent work on the Stille reaction, however, has demonstrated that conversion can be greatly increased by the addition of soluble salts of copper and fluoride, and a thorough discussion of this effect is provided by Mee et al..[187] Additionally, work by Babudri et al showed that higher molecular weight PPV is produced when an electron-deficient ethylene moiety is used.[181c]

Different reaction conditions and additives were therefore screened in order to improve the molecular weight of the product. As results had been comparable for both monomers, the dialkoxy monomer Dd_2PhI_2 was used to perform the optimization study. Optical spectroscopy and gel-permeation chromatography in tetrahydrofuran (THF) were used to evaluate the resulting polymers, and the data are presented in Table 3.1.

Toluene, 1,4-dioxane, THF, and DMF were evaluated as reaction solvents. Increased solvent polarity was observed to favour the formation of higher molecular weight PPV, as indicated by increasingly red-shifted optical transitions; however, isolated yields from the DMF reaction were very low, and thus ethereal solvents were preferred. The addition of copper(I) iodide was not found to have and discernable effect on the reaction in dioxane, and the addition of cesium fluoride in fact decreased the degree of polymerization of the product. Finally tri(o-tolyl)phosphine, and triphenylarsine were evaluated as alternative catalyst ligands (to triphenylphosine). Tri(o-tolyl)phosphine was detrimental to both yield and degree of polymerization. The yield was found to improve when triphenylarsine was used, however, the wavelength of the absorption maximum did not increase, indicating that longer conjugated systems were not forming.

Table 3.1: Optimization of reaction conditions for Stille polycondensation (Scheme 3.5)

Entry	*Solvent*	*Catalyst Ligand*	*Additive(s)*	*λmax /nm*	*λpl /nm*	*Mp /kD*	*Yield /%*
AB18	Toluene	PPh3	-	431	518	5	76
AB22	Dioxane	PPh3	-	444	540	-	57
AB23	DMF	PPh3	-	446	545	-	<10
AB24	THF	PPh3	-	465	538	-	66
AB26	Dioxane	PPh3	CuI	444	527	-	25
AB28	Dioxane	PPh3	CuI, CsF	436	511	6.5	78
AB29	DMF	PPh3	-	454	561	6	<10
AB30	DMF	PPh3	CuI,CsF	430	511	6	79

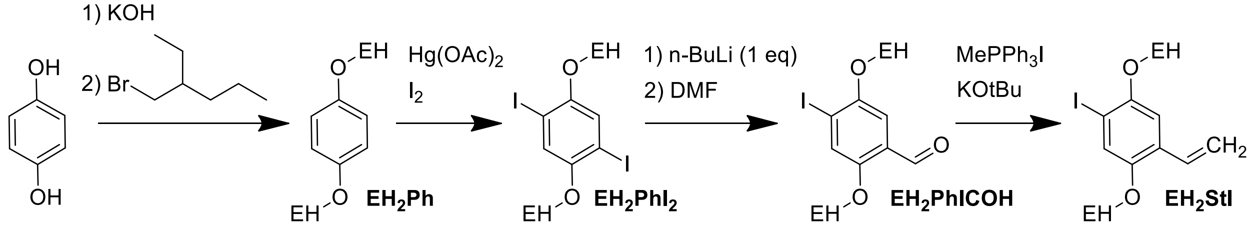
AB32	THF/DMF 2/1	PPh3	-	465	575	7	<10
AB33	THF	PPh3	-	437	534	7	17
AB34	THF	P(o-Tol)3	-	444	522	6.5	93
AB35	THF	AsPh3	-	444	535	7	7
AB36	THF	PPh3	CuI, CsF	428	511	-	79

After this extensive optimization, and despite significant improvements in isolated yield, the optical properties of the best materials produced still fell short of the saturation region of Figure 1. Furthermore, no clear trends could be identified from the assembled data to suggested avenues for further improvement. As such, it was concluded that another method would need to be used to produce material of sufficient quality for self-assembly studies.

3.2.2 Heck-Suzuki Polymerization of PPV

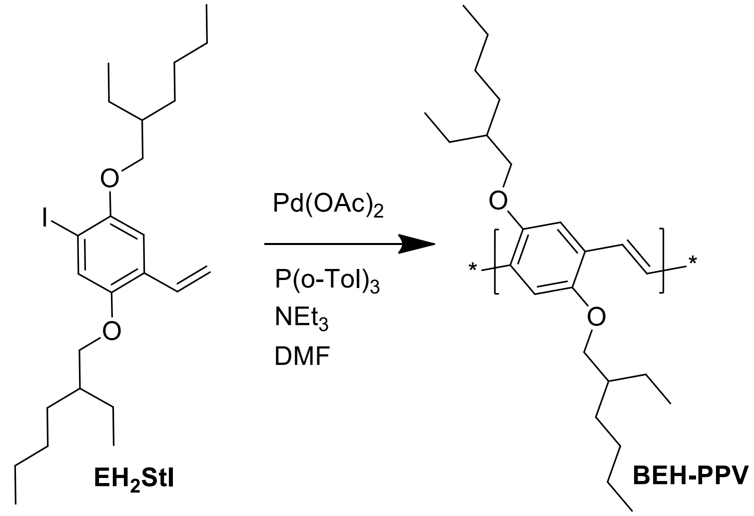
As described in the Chapter 2, the Mizoroki-Heck reaction has been used in a number of ways to produce PPV, with molecular weights in excess of 20kD; however, the chemical structures of the materials prepared are too diverse, and optical data too sparse, to draw strong conclusions about quality of the resulting polymers. The reaction was therefore evaluated using a non-nucleobase monomer to determine if it would produce appropriate polymers for further study. In the interest of simplicity, a homopolymerization strategy employing a para-iodostyrene derivative was attempted first, and to improve the solubility of the resulting polymer, the linear alkyl chains used in the previous section were replaced with branched ones.

1,4-Bis(2-ethylhexyloxy)benzene **5** was prepared by treating hydroquinone with potassium hydroxide, and alkylating with 2-ethylhexyl-1-bromide in refluxing ethanol. The desired product was obtained in 85% yield after purification by solvent extraction. **5** was then converted in 90% yield to 1,4-bis(2-ethylhexyloxy)-2,5-diiodobenzene EH_2PhI_2 by mercuration-iodination.



Scheme 3.6: Preparation of 2,5-di(2-ethylhexyl)-4-iodostyrene

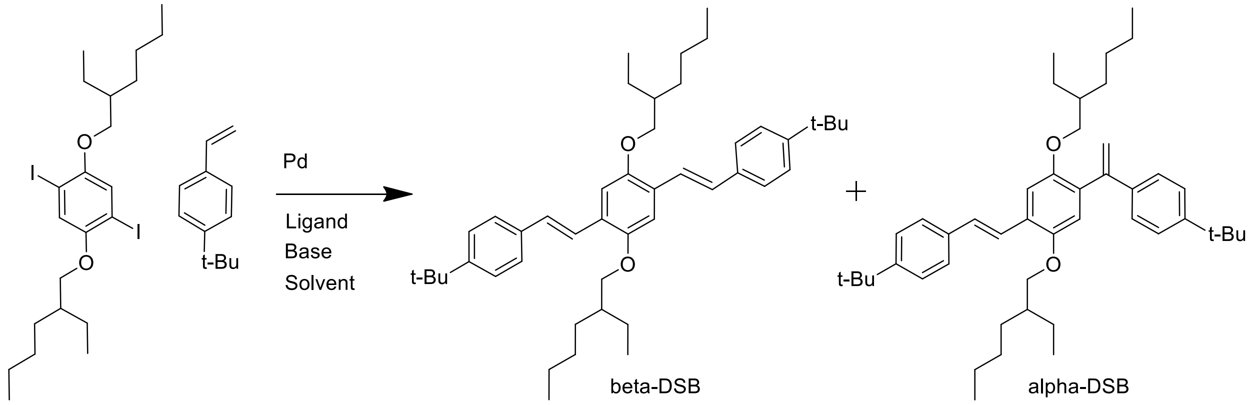
Conversion of the diiodobenzene intermediate to a styrene monomer was accomplished by lithiation-formylation via lithium-halogen exchange followed by a Wittig reaction. EH_2PhI_2 was treated with stoichiometric n-butyllithium (n-BuLi), then excess N,N-dimethylformamide (DMF), and after hydrolysis and purification, the resulting aldehyde **6** was subjected to a Wittig reaction with methyltriphenylphosphonium iodide (Scheme 3.6). This transformation resulted in <50% yields of 2,5-bis((2-ethylhexyl)oxy)-4-iodo-styrene (EH2StI) using BuLi as the base; much higher yields were achieved for related reactions (vide infra) when potassium tert-butoxide (tBuOK) was used instead.



Scheme 3.7: Preparation of BEH-PPV via Mizoroki-Heck homopolymerization.

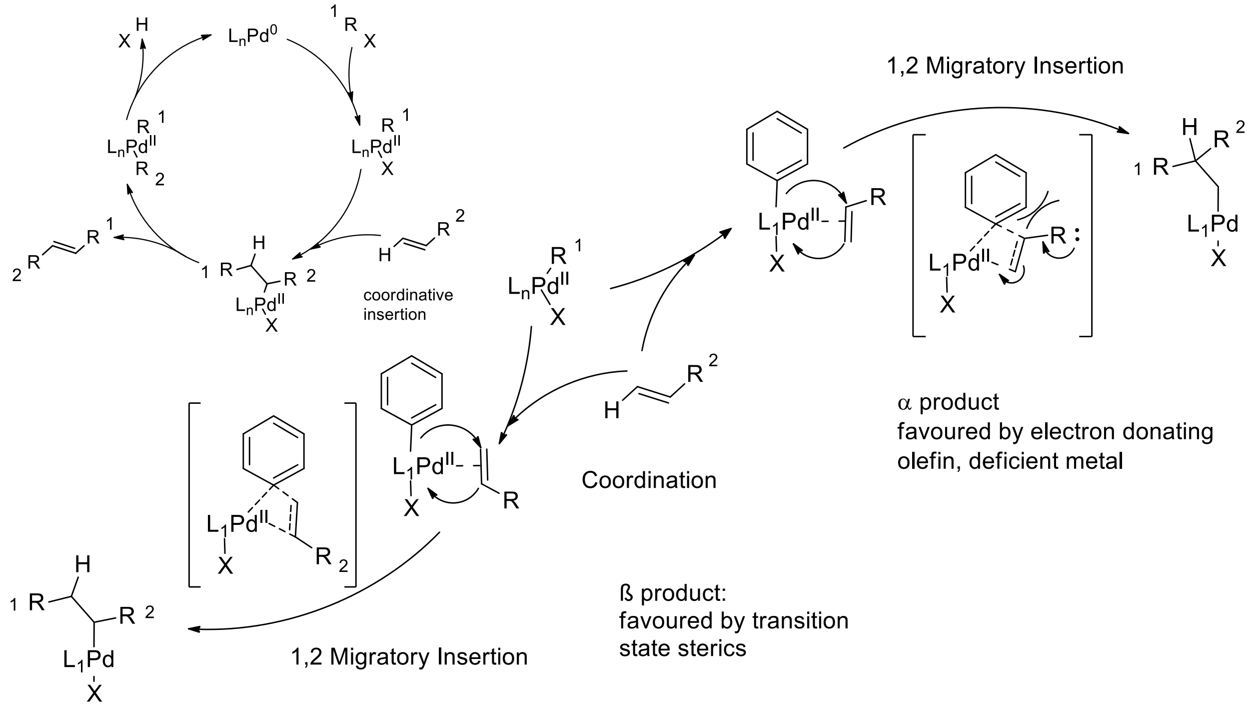
Following protocols from the literature,[146] EH$_2$StI was polymerized in DMF at temperatures between 80 °C and 130 °C using tri-ortho-tolylphosphine and palladium acetate (Scheme 3.7). The bulky phosphine was expected to lead to enhanced catalytic activity, but in all cases, the resulting polymer showed an absorption maximum at 400nm, suggesting of the formation of conjugated trimers as the main product, with a shoulder at 450nm corresponding to pentamers. Gel permeation chromatography indicated the presence of significantly larger macromolecules, with apparent molecular weights on the order of 4kD that would correspond to deca(phenylenevinylene). In certain cases, a very broad, UV-absorbent (254nm) chromatographic peak was observed at much shorter retention times, but vanished when the eluate absorbance was instead measured at 400nm. This suggested that a non-conjugated macromolecular product had also formed, potentially via auto-initiated radical polymerization of the styrene monomer.

In order to simplify the process of optimizing reaction conditions, a model-system in which EH2PhI2 reacted with the commercial para-t-butylstyrene was conceived (Scheme 3.8), and results of the optimization are presented in Table 3.2. Under the polymerization conditions described above, rapid uptake of starting materials was observed, however two products were found to form. Gas chromatography-mass spectrometry indicated that these were two isomers of the desired 1,4-di(2-ethylhexyl)-2,5-di(para-t-butylstyryl)benzene (DSB), having equivalent molecular ions but different retention times and fragmentation patters. The side product was found to produce a pair of very weakly coupled (J=1.5Hz) ^{1}H NMR signals at 5.30 and 5.65 ppm, characteristic of a 1,1-substituted ethylene moiety, that suggested coupling at the vinyl carbon alpha to the aromatic ring. The ratio of these alpha- and beta-coupled DSB products was therefore evaluated along with conversion during optimization.



Scheme 3.8: Heck synthesis of EH$_2$DSB

Regioselectivity in the Mizoroki-Heck reaction is controlled primarily by the electronics and sterics of the planar migratory insertion transition state, and the relative contributions of these two factors are in turn determined by the ionization state of the catalyst complex.[188] For neutral complexes, sterics predominate, and the major product of all but the most electron-rich, least sterically demanding olefins will be beta-substituted. When the catalyst is ionized by the dissociation of an ionic ligand – usually a halide or pseudohalide – the palladium center becomes more electron deficient. This significantly favours the formation of the product in which the more electron-rich pole of the olefin is bonded to the metal. Therefore, π-accepting substituents favour beta-coupling, and π-donors, such as the alkoxy substituents used here, favour alpha-coupling.



Scheme 3.9: Electronics affecting regioselectiity in Heck the Reaction

The preparation of DSB in DMF using palladium acetate and tri(ortho-tolyl)phosphine resulted in complete uptake of the iodide starting material within minutes, but the reaction was less than 70% regioselective. Promising results from Jain et al. suggested that high yields might be achieved using a ‘naked’ phosphine-free catalyst system of palladium acetate in N,N-dimethylacetamide.[189] Indeed, the ligandless catalyst was found to be highly active, however it was less regioselective. In hopes of discouraging catalyst ionization, the reaction was then attempted in the less polar 1,4-dioxane, resulting in slightly improved regioselectivity, but a decreased rate of reaction. This decreased reactivity as remedied by the use of palladium dibenzylideneacetone and tri(tert-butyl)phosphonium tetrafluoroborate catalyst system, as described by Littke et al.,[190] which was found to be significantly more active. Furthermore, this highly electron-rich and sterically demanding catalyst system[191] also offered improved beta-regioselectivity, in agreement with the expectation that the beta-coupling product is sterically favoured. These conditions were first employed with both conventional and microwave heating before it was recognized that this alkylphosphine-palladium complex was sufficiently active to catalyze the reaction at room temperature, and that this resulted in further improved regioselectivity to greater than 90%.

Table 3.2: Optimization of Mizoroki-Heck coupling conditions (Scheme 3.8)

Entry	*Solvent*	*Pd Source*	*Ligand*	*Temperature*	*Unreacted SM*	*target/side products*
AB89	DMF	$Pd(OAc)_2$	$P(o\text{-}Tol)_3$	100°C	6	2:1
AB90a	DMF	$Pd(OAc)_2$	$P(o\text{-}Tol)_3$	100°C	-	3:1
AB91	DMF	$Pd(OAc)_2$	$P(o\text{-}Tol)_3$	60-90°C	16	3:1

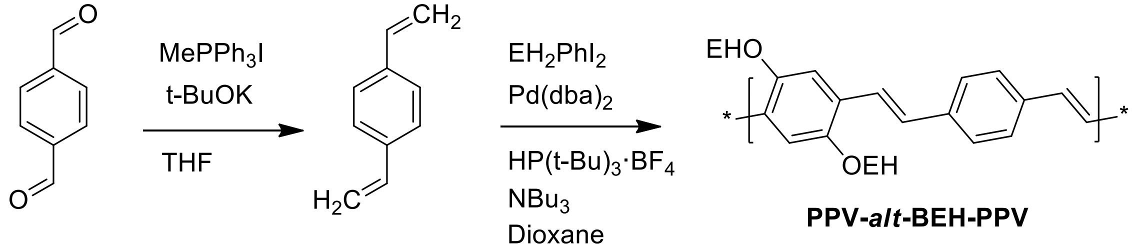
AB92	DMF	Pd(OAc)$_2$	P(o-Tol)$_3$	130°C	25	1:1
AB97b	DMF	Pd(OAc)$_2$	P(o-Tol)$_3$	100°C	4	2:1
AB98	Dioxane	Pd(OAc)$_2$	P(o-Tol)$_3$	100-140°C	-	4:1
AB99[c]	DMF	Pd(OAc)$_2$	P(o-Tol)$_3$	100°C	-	5:1
AB101[c]	Dioxane	Pd(OAc)$_2$	P(o-Tol)$_3$	100°C	-	4:1
AB103[c]	Dioxane	Pd(OAc)$_2$	P(o-Tol)$_3$	90°C	-	5:1
AB104[c]	Dioxane	Pd(PPh$_3$)$_4$	Pd(PPh$_3$)$_4$	150°C	70	1:2
AB105[c]	DMA	Pd(OAc)$_2$	-	90°C	-	1:1
AB106	DMA	Pd(dba)$_2$	-	150°C	-	3:1
AB107[c]	Dioxane	Pd(dba)$_2$	HP(tBu)$_3$BF$_4$	100°C	-	4:1
AB108[c]	Dioxane	Pd(dba)$_2$	P(tBu)$_3$	90°C	100	-
AB109[c]	Dioxane	Pd(dba)$_2$	HP(tBu)$_3$BF$_4$	RT-90°C	-	6:1
AB110[c]	DMF	Pd(dba)$_2$	HP(tBu)$_3$BF$_4$	30°C	40	9:1
AB111[c]	Dioxane	Pd(OAc)$_2$	HP(tBu)$_3$BF$_4$	90°C	25	8:1
AB123[d]	DIoxane	Pd(dba)$_2$	HP(tBu)$_3$BF$_4$	MW ‘80°C’	-	6:1
AB124[d]	Dioxane	Pd(dba)$_2$	HP(tBu)$_3$BF$_4$	MW ’40°C’	-	6:1
AB125[d]	Dioxane	Pd(dba)$_2$	HP(tBu)$_3$BF$_4$	MW ’60°C’	10	6:1
AB128[d]	DMF	Pd(OAc)$_2$	P(o-Tol)$_3$	MW ‘60°C'	-	1:1
AB129[d]	NBu3	Pd(dba)$_2$	HP(tBu)$_3$BF$_4$	MW ‘60°C’	50	-
AB130[d,e]	Dioxane	Pd(dba)$_2$	HP(tBu)$_3$BF$_4$	MW ‘60°C’	-	-
AB131[d,f]	Dioxane	Pd(dba)$_2$	HP(tBu)$_3$BF$_4$	MW ‘60°C’	70	1:1

[a] Excess EH2PhI2 added. [b] Excess styrene added. [c] Freeze-pump degassed. [d] Set-up in glove-box. [e] NBu4Cl added. [f] AgOTf added.

Using these optimized conditions, polymer BEH-alt-PPV was prepared from EH_2StI. GPC of the product indicated a monomodal distribution with a maximum at 20kD; however, the spectroscopic analysis indicated that the average effective conjugation length was not significantly changed compared to previous attempts, with an absorption maximum at 450nm and emission at 540nm (Figure 3.5 left). This discrepancy was reconciled by ^1H NMR analysis, in which the presence of additional signals at ~5.7ppm indicated a much higher rate of α-coupling on the order of 35% in the polymer, resulting in cross-conjugation and chain distortion.

The most significant difference between the model system and the monomer was the presence of an alkoxy substituent adjacent to the styrenic vinyl group. Although catalyst chelation by Lewis acidic functional groups is known to favour beta-substitution when a six-membered transition state would be formed,[171] it is clear from these data that this effect was not extensible to the five-membered cyclic transition state implicated in the current reaction in question. Furthermore, the presence of the two alkoxy substituents raised the HOMO of the olefin by ~0.2eV (DFT using B3LYP functional and LanL3DZ basis set) compared to p-iodostyrene, and this increased donor character is likely responsible for prominence of the electronically favoured pathway (Scheme 3.9).

An alternative strategy was conceived to prepare nucleobase-containing PPV using the existing NB-C12-PhI2, via co-polymerization with para-divinylbenzene (DVB). As commercial DVB contains significant (10-15%) levels of the meta-substituted isomer, regiopure DVB was instead prepared by a double Wittig reaction of terephthalaldehyde with MePPh3I (Scheme 3.10). Concerned that similar, mono-Wittig reactions had only produced 50% conversion in the past, alternate conditions were sought. t-BuOK was found to be a more effective base for this reaction, and pure para-divinylbenzene was isolated in greater than 50% yield after filtration through silica in hexanes; however, due to the instability of the product with respect thermal autoinitiation of radical polymerization, yields were not quantified precisely. Contrary to commercial samples, pure DVB was found to solidify at room temperature, in agreement with the literature.[192]



Scheme 3.10: Wittig synthesis of DVB

Copolymerization of DVB with EH$_2$PhI$_2$ was carried out under the conditions described above (Scheme 3.10), yielding a red precipitate that redissolved with heating. The polymer PPV-*alt*-BEH-PPV was reprecipitated by dispersal of the hot chloroform solution in methanol. UV-visible spectroscopy in chloroform revealed a single absorbance maximum at ≈470nm with a shoulder at 480nm and a steep band edge at 520nm; emission also occurred at 520nm, in agreement with similar alternating PPV co-polymers in the literature.[193] GPC in THF with absorbance detection at 254nm revealed a bimodal distribution of molecular weights, with a sharp peak at 8kD and a broad band centred at 100kD vs polystyrene standards. (Figure 3.5)

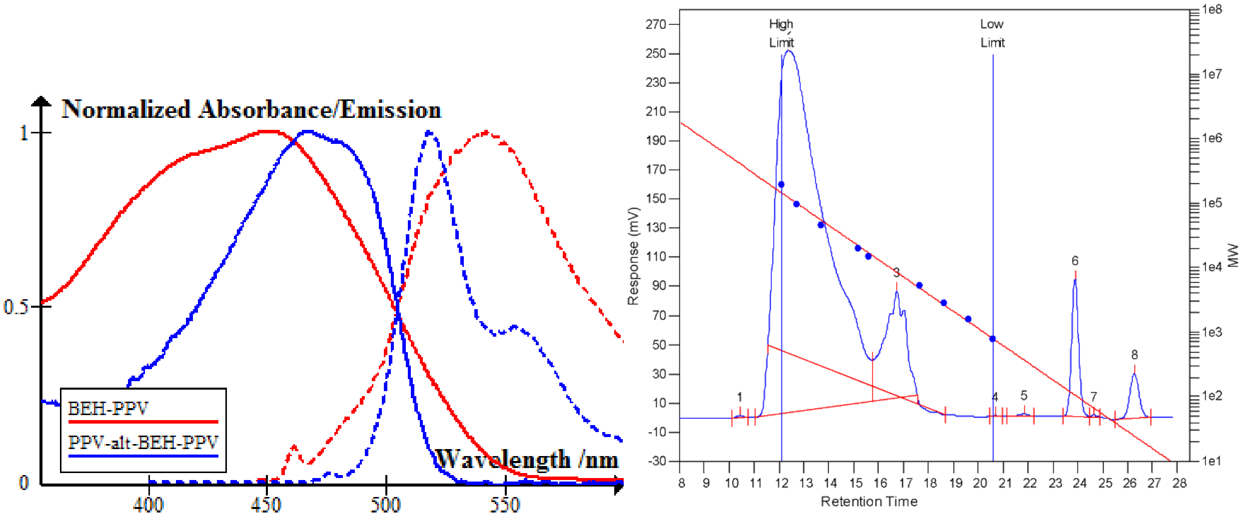
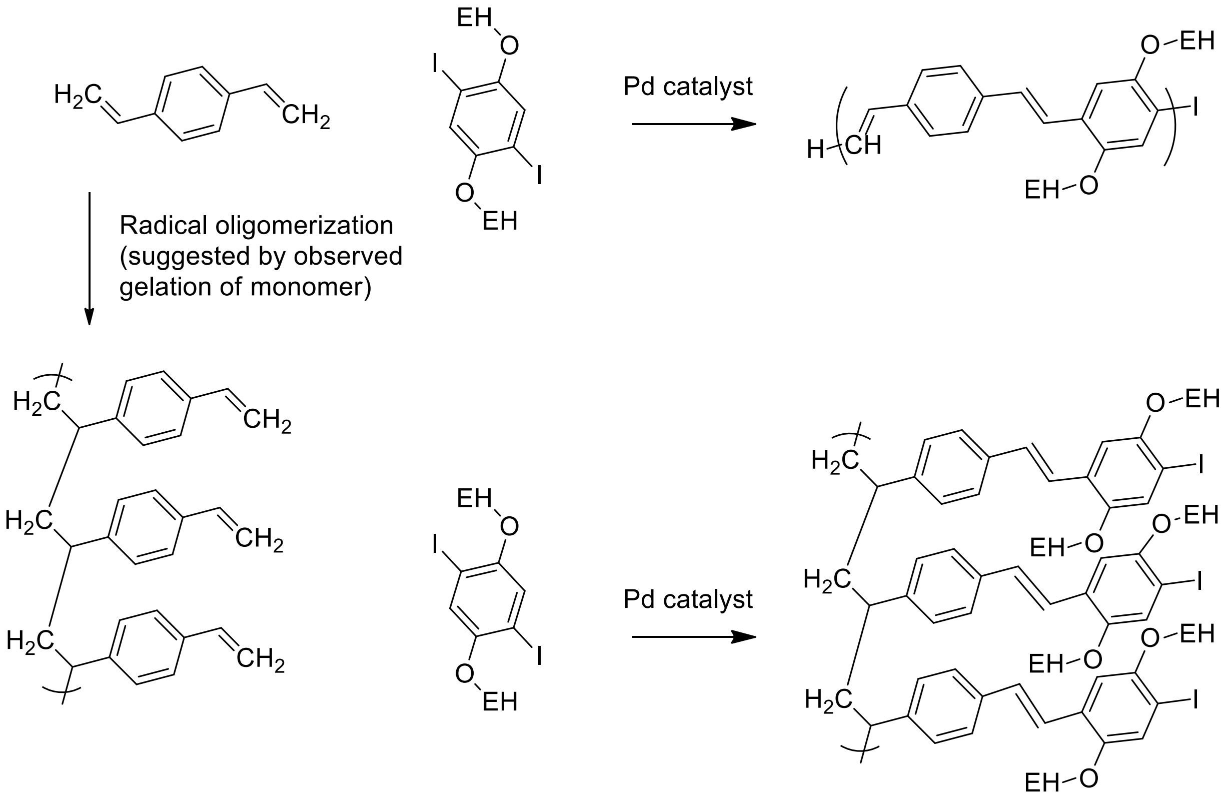


Figure 3.5: (left) Absorbance and emission of polymers prepared by Mizoroki-Heck polycondensation and (right) GPC chromatogram recorded at 254nm for PPV-*alt*-MEH-PPV

^{1}H NMR indicated low incidence of alpha-coupling (5%), but provided little evidence for the origin of the bimodal molecular weight distribution. The GPC chromatogram was reproduced unchanged with detection at 400nm, ruling out the possibility that either peak consisted of radically polymerized PS. This pattern was also conserved during high-temperature GPC at 140°C in chlorobenzene, suggesting that the dual populations were not caused by polymer aggregation, but more likely the result of radical cross-linking (Scheme 3.11).



Scheme 3.11: Proposed mechanism for the formation of high-MW, poorly conjugated materials during the Heck polymerization of PPV

In hopes of reducing possible cross-linking, the reaction was carried out in the presence of a number of radical inhibitors, including BHT, TEMPO, and fullerene. TEMPO and fullerene were both found to inhibit the reaction, while BHT had no observable effect and yielded a comparable bimodal GPC elution profile; however, the effectiveness of BHT is known to be reduced under anoxic conditions such as those employed, and thus these results are not necessarily unexpected.

3.3 Conclusion

Despite excellent results in the synthesis of other polymers,[193] and some derivatives of PPV[181c] in high yields and with molecular weights greater than 20kD, the Stille polymerization was found to produce only oligomeric dialkoxy-PPV, as verified by optical and chromatographic measurements. Varying reaction parameters including temperature, solvent and catalyst, and including accelerant additives in the reaction mixtures did not significantly alter this result; however, significant changes in isolated yield were observed.

Homopolymerization via the Miziroki-Heck reaction was found to produce dialkoxy-PPV containing a large fraction of ethylene-1,1-diyl defects – observable directly by ^{1}H NMR, and indirectly by their effect on the degree of conjugation in the polymer – resulting from poor regioselectivity of coupling, despite the use of electon-rich and sterically-demanding $P(t\text{-}Bu)_3$ ligands. Copolymerization of p-divinylbenzene with 1,4-bis(2-ethylhexyloxy)-2,5-diiodobenzene under similar conditions yielded high molecular weight, highly conjugated material; however, the resulting polymer was found to exhibit a bimodal population distribution via GPC, suggesting that branched products were forming due to radical coupling of divinylbenzene.

3.4 Experimental

General

Reactions were carried out under nitrogen atmosphere using conventional Schlenk technique. Routine NMR spectra were recorded on Varian Mercury 300 and Mercury 400 spectrometers, and polymer NMR on a Varian VNMRS 500 spectrometer. Gel permeation chromatography was performed on a GPC PL 50 using Polyanalytik columns in THF at 30 °C. UV/vis absorption and photoluminescence spectra were measured in CHCl3 with a JACSO V670 UV−vis−NIR spectrometer and a Varian Eclipse Fluorometer, respectively. DFT calculations were performed using the Gaussian 09W program[194] at the B3LYP level with a LanL2DZ basis set.

NB-Dd-PhI_2 materials were kindly provided by Dr. P. K. Lo. Ligands used during catalyst screening were provided by Prof. Bruce Arndtsen. E-bis(tributylstannyl)ethylene was purchased from TCI America. Dry solvents were prepared using an mBraun solvent purification system. Other solvents and reagents were purchased from Sigma Aldrich, VWR and Fisher Scientific and were used without further purification.

1,4- bis(dodecyloxy)-2,5-diiodobenzene (Dd_2PhI_2)

The compound was synthesized as described in ref [49] and recrystallized from ethanol, affording a white powder in 62% yield. Characterization was in agreement with the literature.[49] ^1H NMR (300 MHz, CLCl3) δ 7.17 (s, 2H, ArH), 3.92 (t, J=6.4, 4H, OCH2), 1.79 (m, 4H, CH2), 1.49 (m, 4H, CH2), 1.26 (bm, 36H, CH2), 0.88 (t J=6.7, 6H, CH3).

1,4-bis((2-ethylhexyl)oxy)benzene (EH_2Ph)

Synthetic protocol adapted from ref [195] and isolated as a clear oil in 85% yield after chromatography. Characterization was in agreement with the literature.[196] ^1H NMR (300 MHz, CDCl3) δ 6.83 (s, 4H, ArH), 3.79 (d, J = 5.7 Hz, 2H, OCH2), 1.70 (hept, 2H, CH), 1.33 (m, 16H, CH2), 0.92(m, 12H, CH3). ^{13}C NMR (75 MHz, cdcl3) δ 153.41, 115.33, 71.17, 39.45, 31.59, 30.52, 29.08, 29.05, 23.84, 23.06, 14.09, 11.09

1,4-bis((2-ethylhexyl)oxy)-2,5-diiodobenzene (EH_2PhI_2)

The compound was synthesized in the same manner as **Do_2PhI_2** to afford a pale yellow oil in 86% yield after chromatography. Characterization was in agreement with the literature.[196] ^1H NMR (300 MHz, cdcl3) δ 7.17 (s, 2H, ArH), 3.82 (d, J = 5.4 Hz, 4H OCH2), 1.73 (m, 2H, CH), 1.52 (m, 8H, CH2), 1.33 (m, 8H, CH2), 0.88 (m, 12H, CH3). ^{13}C NMR (75 MHz, cdcl3) δ 152.84, 122.32, 86.06, 72.30, 39.46, 30.52, 29.07, 23.96, 23.07, 14.16, 11.25.

2,5-bis((2-ethylhexyl)oxy)-4-iodo-benzaldehyde ($EH_2PhICOH$)

The compound was synthesized as described in ref [197] to afford a yellow oil in 36% yield after chromatography. Characterization was in agreement with the literature.[196] ^1H NMR (300 MHz, cdcl3) δ 10.42 (s, 1H, CHO), 7.46 (s, 1H, ArH), 7.18 (s, 1H, ArH), 3.91 (d, J = 5.5 Hz, 2H, OCH2), 3.88 (d, J = 5.5 Hz, 2H, OCH2), 1.75 (m, 2H, CH), 1.5 (m, 8H, CH2), 1.32 (m, 8H, CH2), 0.93 (m, 12H, CH3).

2,5-bis((2-ethylhexyl)oxy)-4-iodo-styrene (EH2StI)

Synthetic protocol adapted [198] to afford a clear oil in 50% yield after filtering through silica. Characterization was in agreement with the literature.[196] ^1H NMR (300 MHz, cdcl3) δ 7.28 (s, 1H, ArH), 7.02 (dd, J = 17.8, 11.2 Hz, 1H, Vinyl CH), 6.94 (s, 1H, ArH), 5.77 (dd, J = 17.7, 1.2 Hz, 1H, Vinyl CH2), 5.29 (dd, J = 11.2, 1.2 Hz, 1H, Vinyl CH2), 3.89 (d, J = 5.4 Hz, 2H, OCH2), 3.82 (d, J = 5.5 Hz, 2H, OCH2), 1.75 (h, J = 6.2 Hz, 2H, CH), 1.53 (m, 8H, CH2), 1.35 (m, 8H, CH2), 0.92 (m, 12H, CH3).

Para-divinylbenzene (DVB)

Synthetic protocol adapted from ref [198] and [192] afforded a clear oil that solidified on standing (47% yield). Characterization was in agreement with the literature.[192] ^1H NMR

(300 MHz, cdcl3) δ 7.39 (s, 4H ArH), 6.73 (dd J= 10.9, 17.6 Hz, 2H, Vinyl Alpha-H), 5.77 (dd J=0.9, 17.6 Hz, 2H, Vinyl Beta-H) 5.26 (dd J=0.9, 10.9 Hz, 2H, Vinyl Beta-H).

General Procedure for 1,4-bis(2-ethylhexyl)-2,5-di(*para*-t-butylstyryl)benzene (EH_2DSB)

EH_2PhI_2 (1 eq), t-butylstyrene (2 eq), base (4 eq), soluble palladium source (0.025eq), ligand (0.1 eq) and DMF (50 eq) were transferred to a schlenk tube and freeze-pump degassed three times, then heated to 30C in an oil bath with stirring under nitrogen.

After two days, the reaction mixture was diluted with 1:1 toluene/Et_2O (2 ml), and the resulting solution was washed with brine (2x4 ml), 5% HCl, distilled water, and saturated brine. The organic phase was then filtered through $MgSO_4$. Solvent was removed in vacuuo, and the residue was analyzed by ^{1}H NMR. Yields: 10%-88%

Analytically pure 1,4-di(2-ethylhexyl)-2,5-di(para(t-butyl)styryl)benzene was obtained by recrystallization from hexanes. ^{1}H NMR (500 MHz, CDCl3) δ 7.49 (dd, J = 8.4, 1.3 Hz, 4H, Styryl Otho-H), 7.48 (dd, J = 16.4, 1.5 Hz, 2H, Styrene Alpha-H), 7.40 (d, J = 8.4 Hz, 4H, Styrene Meta-H), 7.14 (d, J = 16.4 Hz, 2H Styrene Beta-H), 7.13 (d, J = 1.3 Hz, 2H, ArH), 3.97 (d, J = 5.5 Hz, 4H, OCH2), 1.82 (h, J = 5.9 Hz, 2H, CH), 1.67 – 1.54 (m, 6H, CH2), 1.49 (m, 2H, CH2), 1.40 (m, 8H, CH2), 1.36 (d, J = 1.4 Hz, 18H, t-Bu CH3), 1.01 (td, J = 7.4, 1.4 Hz, 6H, CH3), 0.94 (dt, J = 7.3, 3.5 Hz, 6H, CH3). ^{13}C NMR (75 MHz, CDCl3) δ 155.50, 154.71, 139.65, 132.67, 131.19, 130.59, 129.95, 127.14, 114.57, 76.08, 44.16, 39.01, 35.67, 35.30, 33.65, 28.62, 27.49, 18.51, 15.72.. HRMS (APCI) calculated for $C_{46}H_{47}O_2$ (M^++H) 651.5136, found 651.5158.

Representative Stille polymerization of PPV

To a flame-dried 25ml Schlenk Tube were added Dd_2PhI_2 (43.6mg,0.0624mmol), 1,2-trans(tri-n-butylstannyl)ethylene (37.2mg, 0.061mmol), copper(I) iodide (3mg, 15mmol), cesium fluoride, (41mg, 270mmol) $Pd(PPh_3)_4$ (7.7mg, 0.0066mmol) and DMF (2ml). The mixture was frozen in $CO_{2(s)}$/acetone and freeze-pump degassed three times, then placed in a 110°C oil bath with stirring. After 36 hours, the reaction mixtures was vacuum filtered through a medium porosity fritted glass filter with additional hot toluene, then precipitated from methanol to give pale red suspension which was stored at -10°C overnight then filtered, affording 23mg red solids (79% yield). Absorbance max 430nm, Emission max 511nm. THF GPC Mp 6.5kD (vs polystyrene). ^{1}H NMR (500 MHz, CDCl3) δ 7.24 (s, 2H, ArH), 4.04 (s, 4H, OCH3), 1.84 (bs, 4H, CH2) 1.23 (b, 38H, CH2), 0.85 (s, 6H, CH3)

Representative Mizoroki-Heck homopolymerization of PPV

To a 20ml screw-cap vial were added 2,5-bis((2-ethylhexyl)oxy)-4-iodostyrene (100 mg, 0.206 mmol) and tri-t-butylphosphonium tetrafluoroborate (5.2 mg, 0.018 mmol). The vial was then transferred to an inert-gas glovebox, where $Pd(dba)_2$ (5 mg, 5.46 μmol), tributylamine (70 μl, 0.295 mmol), and dioxane (Volume: 1 ml) were added. The flask was closed and stirred for 12 hour at ambient temperature, then at 50C for 5 days with monitoring by UV-vis and ^{1}H NMR. The resulting red suspension was precipitated in methnaol to give 43mg of red solid (58%), which was purified by reprecipitation from ethanol. Absorbance max 450 nm; emission max 540 nm. THF GPC Mp 21kD (vs polystyrene). ^{1}H NMR (500 MHz, CDCl3) δ 7.55 (d, 1.1H Vinyl α-H), 7.25 (d, 1.1H ArH), 6.86 (d, 0.8H ArH), 5.66 (d, 0.7H, vinyl β-H), 3.97 (d, 2.3H OCH2), 3.75 (d, 1.7H OCH2), 1.85 (d, 1H), 1.46 (m, 24H), 1.85 (m, 13H).

Representative Mizoroki-Heck copolymerization of PPV

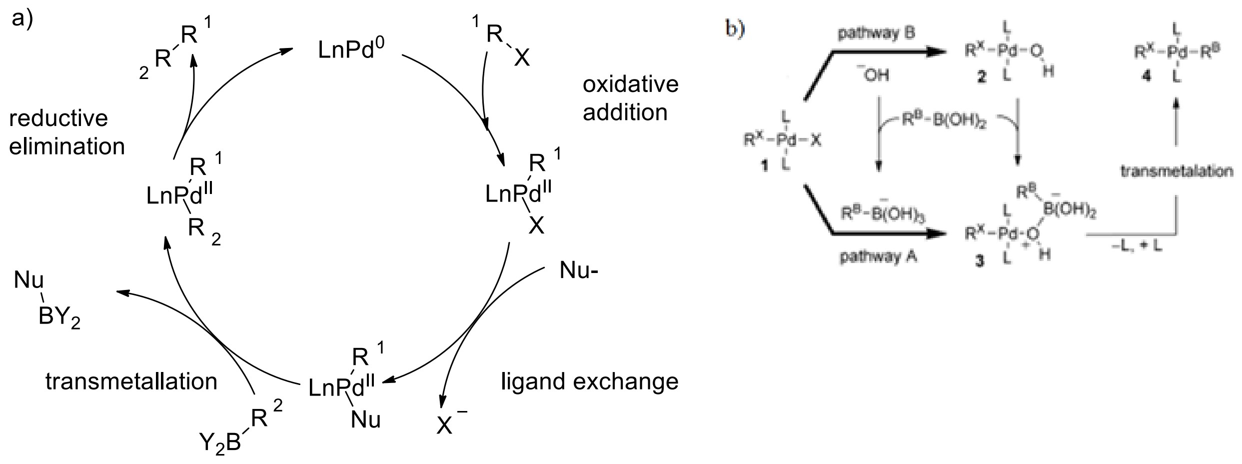
In a 20ml screw-cap vial were combined tri-*tert*-butylphosphonium tetrafluoroborate-(5mg, 0.017 mmol), 1,4-bis((2-ethylhexyl)oxy)-2,5-diiodobenzene (0.057 ml, 0.135 mmol), and TEMPO (4 mg, 0.026 mmol) with a stir bar. The vial was transferred to an inert-gas glove box, where Pd(dba)$_2$ (5 mg, 5.46 µmol), tributylamine (0.1 ml, 0.421 mmol), dioxane (1 ml) and 1,4-divinylbenzene (0.02 ml, 0.140 mmol) were added. The mixture was stirred at room temperature. After 24h, a red suspension had formed, which dissolve on heating. The reaction mass was precipitated in methanol to yield 73mg of red powder (88% yield). Absorbance max 470nm, Emission max at 518nm, shoulder at 554nm. THC GPC Mp 8kD, shoulder at 100kD (vs polystyrene). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (s, 4H ArH), 7.54 (d, J=16.4, 2H, vinyl-H), 7.22 (d, J=16.4, 2H, vinyl-H), 7.18 (s, 2H ArH), 4.05 (s, 4H, OCH3), 1.9 (m, 2H, CH) 1.66 (m, 8H, CH2), 1.48 (m, 8H, CH2), 1.07 (t, J=7.4 Hz, 6H, CH3), 1.01 (t, J=7.0 Hz, 6H, CH3).

Chapter 4: Synthesis and Properties of Nucleobase-Functionalize PPV Prepared By Suzuki Polycondensation

The challenge of this work so far has been to produce a defect-free PPV polymer of sufficient molecular weight to investigate NB-driven self-assembly. In the previous chapter, we detailed attempts to use two palladium-catalyzed reactions – the Mizoroki-Heck and the Stille couplings – to accomplish this. However, it was found that Stille reaction did not occur with sufficiently high conversion to produce appropriate molecular weights, while Mizoroki-Heck polymerization generated ill-defined material due to non-regiospecific reaction of the vinyl group.

4.1 Suzuki Polymerization of PPV

A third palladium-catalyzed coupling was subsequently investigated. The Suzuki reaction is mechanistically similar to the Stille reaction, with the exception that transmetallation occurs from a organoboron reagent instead of organotin, (Scheme 4.1 part a) and is facilitated by the exchange of the palladium halide ligand for a hydroxo, alkoxo, or fluoro ligand that coordinates the incoming boron atom (Scheme 4.1 part b). The site-specificity of transmetallation avoids the poor regiospecificity noted during Mizoroki-Heck polycondenstion, and as noted in Chapter 2, the Suzuki polymerization has been shown to be capable of producing moderate molecular weight dialkoxy-PPV, suggesting that it proceeds with higher conversion than the Stille coupling.



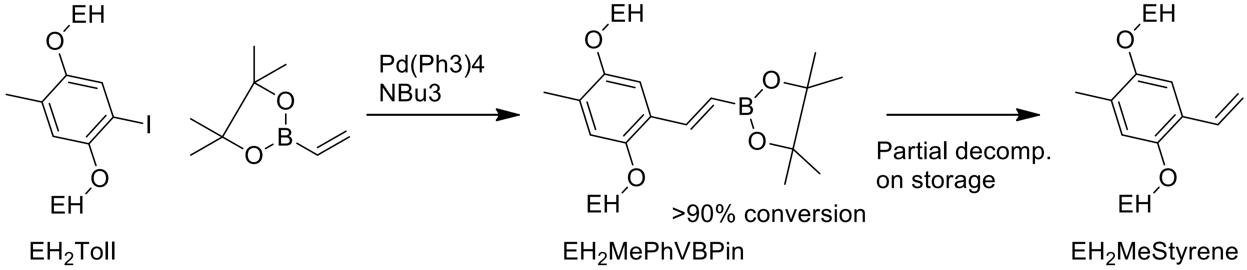
Scheme 4.1: a) Suzuki catalytic cycle b) Transmetallation pathways in the Suzuki reaction. Pathway B has been found to dominate under most conditions.

b) adapted with permission from [199] Copyright Wiley and Sons 2013

As noted in Chapter 2, PPV has been prepared via the Suzuki co-polymerization of para-benzenediboronic acid with both dibromoethylene[174] and para-bis(2-bromoethenyl)benzene.[175] However, the isolation of purely *trans* dibromoethylene is nontrivial,[200] and the synthesis of para-bis(*trans*-bromoethenyl)benzene must be accomplished via multi-step processes with limited overall yields.[201]

In search of a more accessible synthetic approach, an alternate pathway where the positions of the halogen and boron groups are reversed can be conceived. Although *trans*-ethylenediboronic acid does not appear in any recently literature, *trans*-styrylboronic acid derivatives can be prepared using a number of methods, including from the corresponding phenylacetylene,[202] but also via Mizoroki-Heck coupling of a vinyl boronic acid derivative to an appropriate halobenzene compound.[203] In the second case, although the Mizoroki-Heck and Suzuki reactions both occur in basic conditions under palladium catalysis, the use of an amine base and careful exclusion of water can favour the Mizoroki-Heck reaction by preventing the formation of oxopalladium species capable of coordinating the boronic acid, thus precluding transmetallation of the boronate.

To verify the effectiveness of this transformation for dialkoxybenzene compounds, 2,5-bis(2-ethylhexyloxy)-4-iodo-toluene (EH_2TolI) was used as a test substrate. Following procedures developed in our group,[204] EH_2TolI was reacted with an equimolar quantity of vinylboronic acid pinacol ester in dry toluene in the presence of tetrakistriphenylphosphine palladium and tributylamine.



Scheme 4.2: Selective Heck Synthesis of a trans-styrylboronic acid pinacol ester

At 80°C, ^1H NMR tracking of the benzylic methyl singlet indicated 75% conversion to a single product after four hours, and complete conversion after twelve hours. Unfunctionalized styrenic vinyl groups were not detectable by ^1H NMR during the reaction, indicating >99% selectivity for the Mizoroki-Heck reaction over the Suzuki. Following aqueous workup, however, 5% styrene was found to have formed, indicating that the product was susceptible to deborylation, which was also observed to continue during storage under ambient conditions.

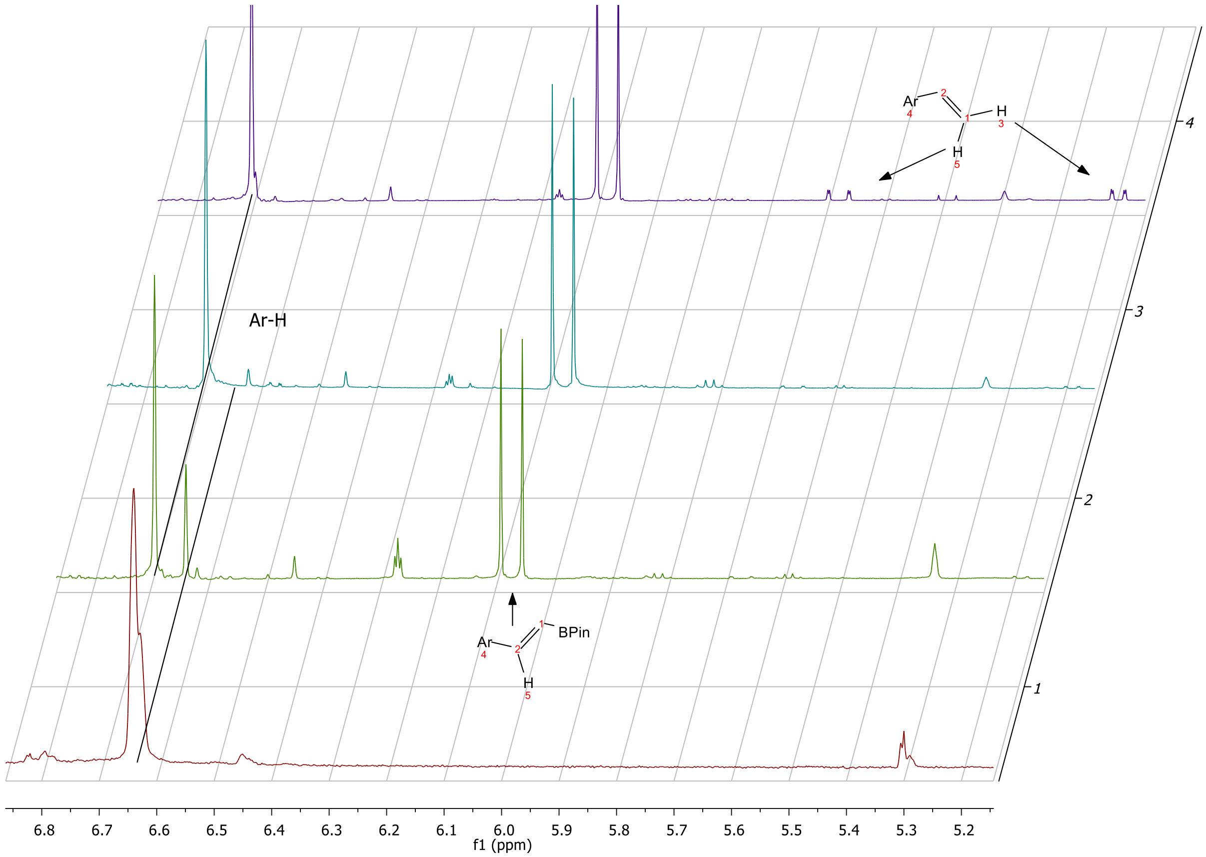
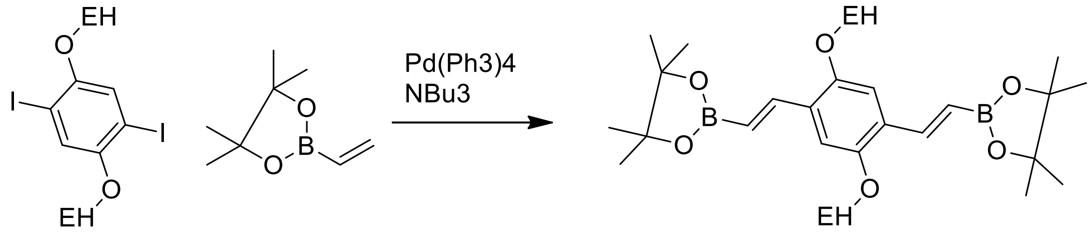


Figure 4.1: Monitoring Heck beta-arylation of vinyl boronic acid pinacol ester by ^{1}H NMR.

Bottom to top: EH2TolI starting material, reaction mass after 4h, reaction mass after 12h, product following work-up.

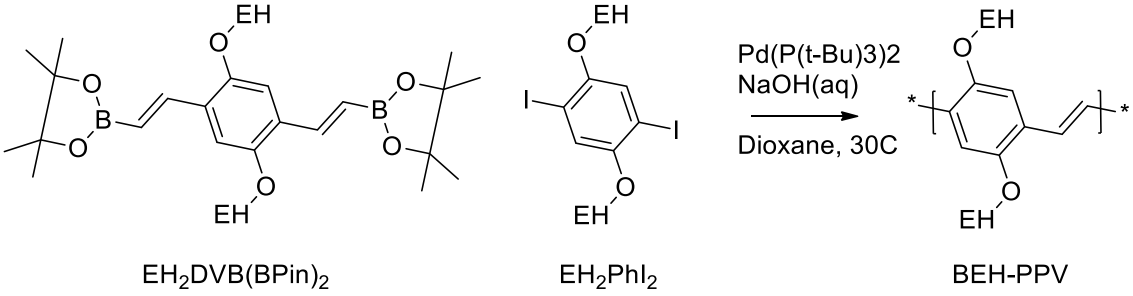
Following the procedure described above, EH_2PhI_2 was coupled with 2 equivalents of vinylboronic acid pinacol ester to produce (E,E)-2,5-bis(2-ethylhexyl)-1,4-divinylbenzene-β,β-diboronic acid pinacol ester $EH_2DVB(BPin)_2$ (Scheme 4.3). The bis-functionalization reaction was found to proceed comparable quickly and selectively, and in nearly quantitative conversion. However, like the test-substrate described above, the product was also found to be vulnerable to deborylation under ambient conditions, as well as during chromatography. As such, although nearly quantitative conversion was obtained, purification proved to be a challenge. Pure material could only be obtained via silica gel chromatography through sequential separation using DCM/hexanes and EtOAc/hexanes, with each step yielding only 50% recovery for a 25% overall purification yield. On C_{18}-silica, however, purification could be achieved in a single elution using acetonitrile with significantly less decomposition. The material could subsequently be concentrated by extraction into hexanes, then isolated in greater than 50% yield by crystallization from water/methanol. The resulting pure solid was found to be significantly more stable to deborylation on storage.



EH_2PhI_2 $EH_2DVB(BPin)_2$

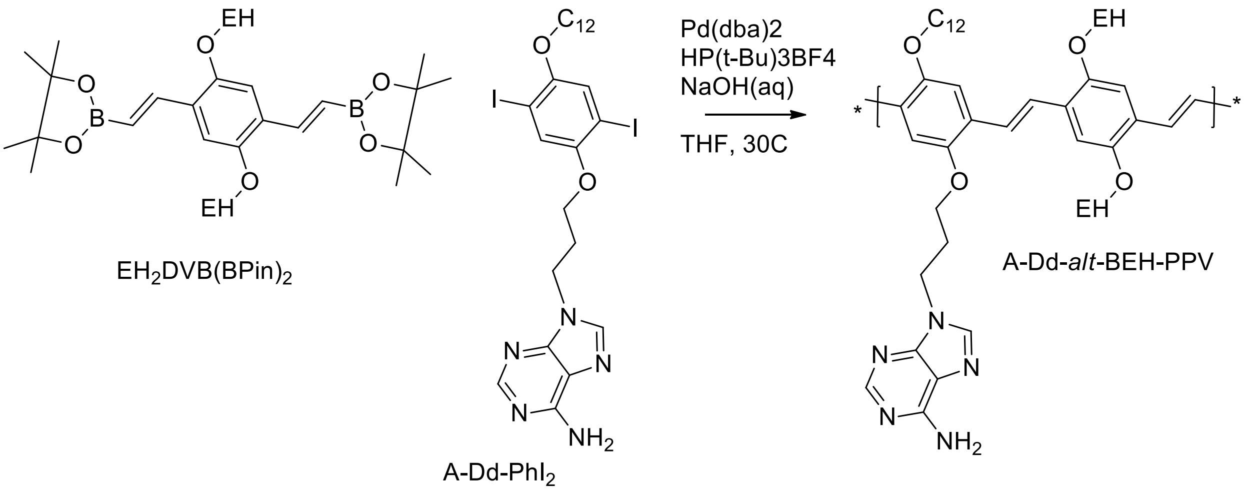
Scheme 4.3: Heck Synthesis of $EH_2DVB(BPin)_2$

Results from recent work on the Suzuki polycondensation of 2,5-dialkoxybenzene-1,4-diboronic acid with (E,E)-1,4-bis(2-bromovinyl)benzene by Wakoka et al. indicate that the highest molecular weights and fewest defects were achieved with a reaction system of sodium hydroxide and bis(tri-tert-butylphosphine)palladium in THF. Similar conditions were used as a starting point for our related polycondensation of EH_2PhI_2 with $EH_2DVB(BPin)_2$ (Scheme 4.4). Polymerization was found to occur very quickly at room temperature in dioxane. The reaction was quenched with phenyl iodide after one day, and the products precipitated in methanol in ~80% yield. The resulting material had an apparent molecular weight of approximately 20kD (GPC vs. polystyrene), and absorbance an emission in the saturation region.



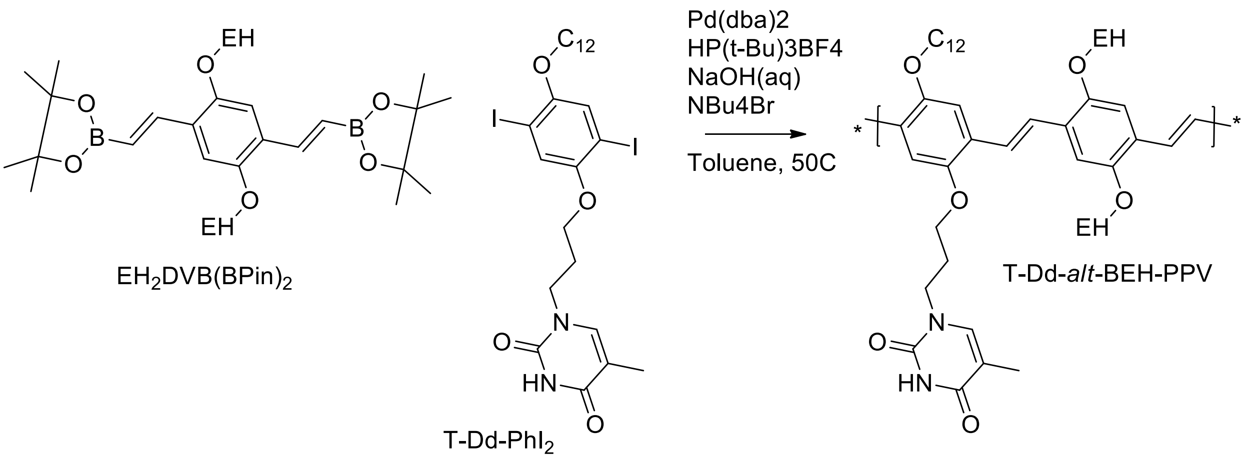
Scheme 4.4: Preparation of BEH-PPV via Suzuki Polymerization

Following the successful preparation of highly conjugated, moderate molecular weight BEH-PPV, the copolymerization of nucleobase-functionalized monomers NB-Dd-PhI_2 with $EH_2DVB(BPin)_2$ to produce NB-Dd-*alt*-BEH-PPV was investigated. Under equivalent conditions, polymerization with adenine-containing monomer A-Dd-PhI2 was not effective, producing no conjugated products. Polymerization the thymine-containing monomer T-Dd-PhI_2 yielded low-molecular weight material, as indicated by its absorption maximum at 472nm, corresponding to a degree of polymerization of 8 (Figure 3.1).



Scheme 4.5: Preparation of A-Dd-alt-BEH-PPV via Suzuki Polymerization

Suspecting the lower solubility of the NB-monomer to be hindering the reaction, other solvents were investigated, and the NB-monomers were identified to have greater solubility in THF. Polymerizations of both monomers were therefore carried out in THF, and the concentration of monomer was lowered from ~0.1M to ~0.01M. This enabled the preparation of the conjugated adenine-containing material A-Dd-*alt*-BEH-PPV with emission approaching saturation, but it was also found to slow the polymerization of T-Dd-PPV unacceptably. Polymerization of the thymine-monomer at 0.1M in refluxing THF yielded comparable results to polymerization in dioxane. The highest molecular weight T-Dd-*alt*-BEH-PPV was produced using conditions derived from the small-molecule optimization of Suzuki conditions carried out by Wakioka et al.. Polymerization was carried out in toluene in the presence of tetrabutylammonium bromide at 50°C. The resulting material had optical properties consistent with defect-free, high-MW PPV.



Scheme 4.6: Preparation of T-Dd-alt-BEH-PPV via Suzuki Polymerization

4.2 Characterization of the nucleobase-functionalized polymer

Polymers were first analyzed by UV-visible absorbance and fluorescence (Figure 4.2). The BEH-PPV was found to have an absorption maximum at 502nm and to emit at 556nm with a shoulder at 600nm, as expected for optically saturated, defect-free dialkoxy-PPV. The nucleobase-functionalized materials had similar properties, with A-Dd-alt-BEH-PPV and T-Dd-alt-BEH-PPV respectively absorbing at 486nm and 502nm, and emitting at 548nm and 552nm. The NB-PPV materials conserved the characteristic shoulder at 600nm, however it was less well-defined. These values all fall within the saturation region described in Figure 3.1.

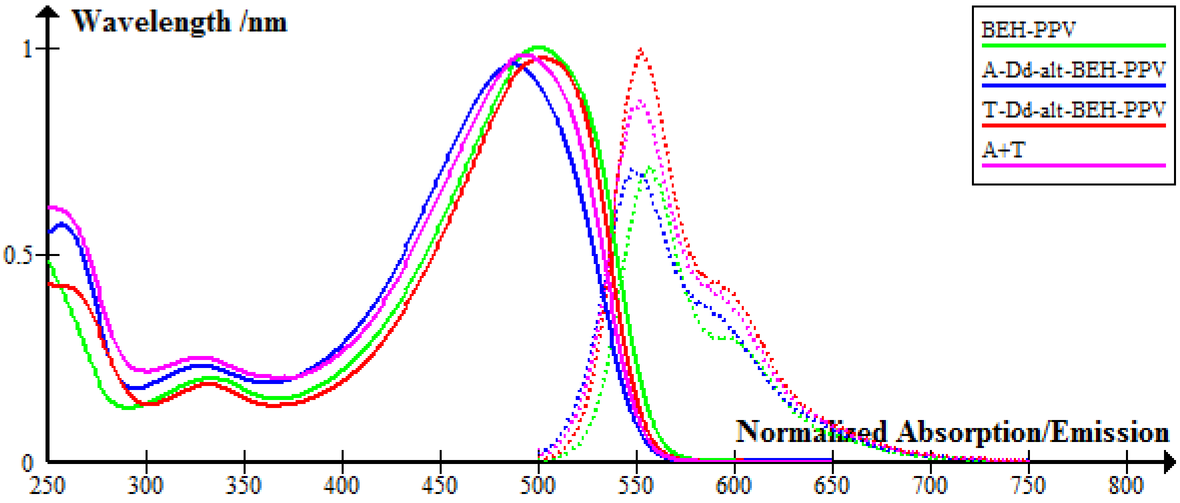


Figure 4.2: Absorbance and emission spectra of BEH-PPV, NB-Dd-alt-BEH-PPV in chloroform.

The photoluminescence quantum yields of the three polymers were measured using rhodamine 6G as a standard; the excitation wavelength (495nm) was well aligned with the absorption maxima of the polymer samples, as well as the absorption shoulder of the standard. The Suzuki BEH-PPV was found to have quantum yield of 19%, which is low compared to the values (42%, 57-60%) observed for dialkoxy-PPV prepared by other methods in the literature.[112a, 205] Contrary to what was found in past work on nucleobase-functionalized poly(phenyleneethynylene),[48] the nucleobase-functionalized PPV copolymers were more emissive than the parent material: the adenine material had a quantum yield of 24%, and the thymine material, 29%. A solution of equal parts (by optical density) adenine and thymine polymers did not have appreciably different quantum yield from the two individual materials (25%).

Table 4.1: Properties of the polymers prepared in this study.

	λmax /nm	*λpl /nm*	*Egap /eV*	*PLQY (95% CL) /%*	*Mn /kD*	*DP*	*Yield /%*

BEH-PPV	502	556	2.22	19 (3)	30	30	94
T-Dd-alt-BEH-PPV	502	552	2.23	24 (1)	~30	>20	65
A-Dd-alt-BEH-PPV	486	548	2.24	29 (1)	18	20	55

pl = photoluminescence

The molecular weights of the polymers were measured using gel permeation chromatography in THF, with light scattering and refractive index detection referenced to polystyrene standards.

As noted above, the BEH-PPV was observed to have an apparent number-average molecular weight greater than 20kD; according to our analysis of data from Meijer et al. and Tilley et al. presented in the previous chapter, this is expected to correspond to a true molecular weight greater than 10kD, and a degree of polymerization of 30 or more. This places the BEH-PPV prepared via Suzuki polymerization within the saturation region of Figure 3.2, in agreement with its observed optical properties.

The adenine-functionalized A-Dd-*alt*-BEH-PPV had an apparent molecular weight of 18kD by GPC. If the hydrodynamic radius of this material in THF solution is not significantly different from alkoxy-PPV, this corresponds to a true molecular weight of 9kD and a number-average degree of polymerization of approximately 20. If this is the true degree of polymerization of the material, it would be expected that the opto-electronic properties of the material should have achieved saturation, however, both the absorption and emission of the adenine polymer were slightly blueshifted with respect to the other two materials.

The thymine-fuctionalized T-Dd-*alt*-BEH-PPV eluted with a similar retention time to BEH-PPV. In agreement with its comparable optical properties, this indicates that the degree of polymerization of T-Dd-*alt*-BEH-PPV greater than 20, and thus this material is also appropriate for further study.

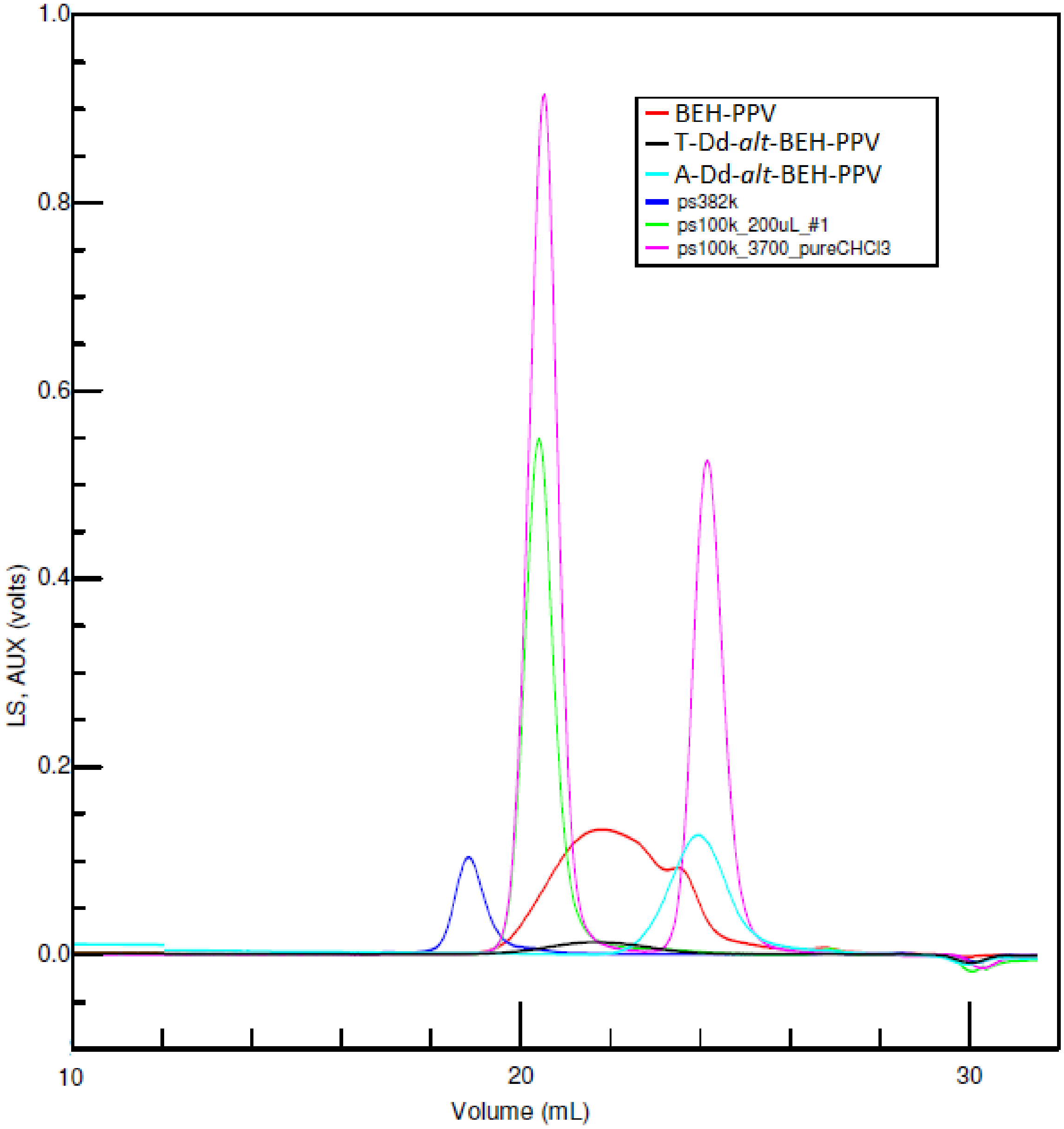


Figure 4.3: Gel permeation chromatograms of the synthesized PPV materials, overlaid with polystyrene standards.

All three materials were analyzed by high-field ^{1}H NMR at 24°C and 99°C in tetrachloroethane-d2, as well as ^{13}C NMR. As expected for a polymeric material, resolution was improved at high temperature due to narrowing off the peaks. Sample concentrations were on the order 20mg/ml to achieve stronger signals in ^{13}C NMR, although this led to gelling of the samples in some cases.

The ^{1}H NMR spectrum of BEH-PPV contained two downfield singlets attributed to the aromatic and vinylic protons respectively, a conspicuous mid-field ether doublet at 3.96ppm, and the group of upfield multiplets originating from the aliphatic 2-ethylhexyl moieties. Also observed in the downfield region were two small signals at 7.4pm and 6.83ppm that are thought to be attributable to phenyl end-groups. ^{13}C NMR included four downfield aromatic and olefinic signals plus the eight expected for the ethylhexyl group, with no other peaks observable.

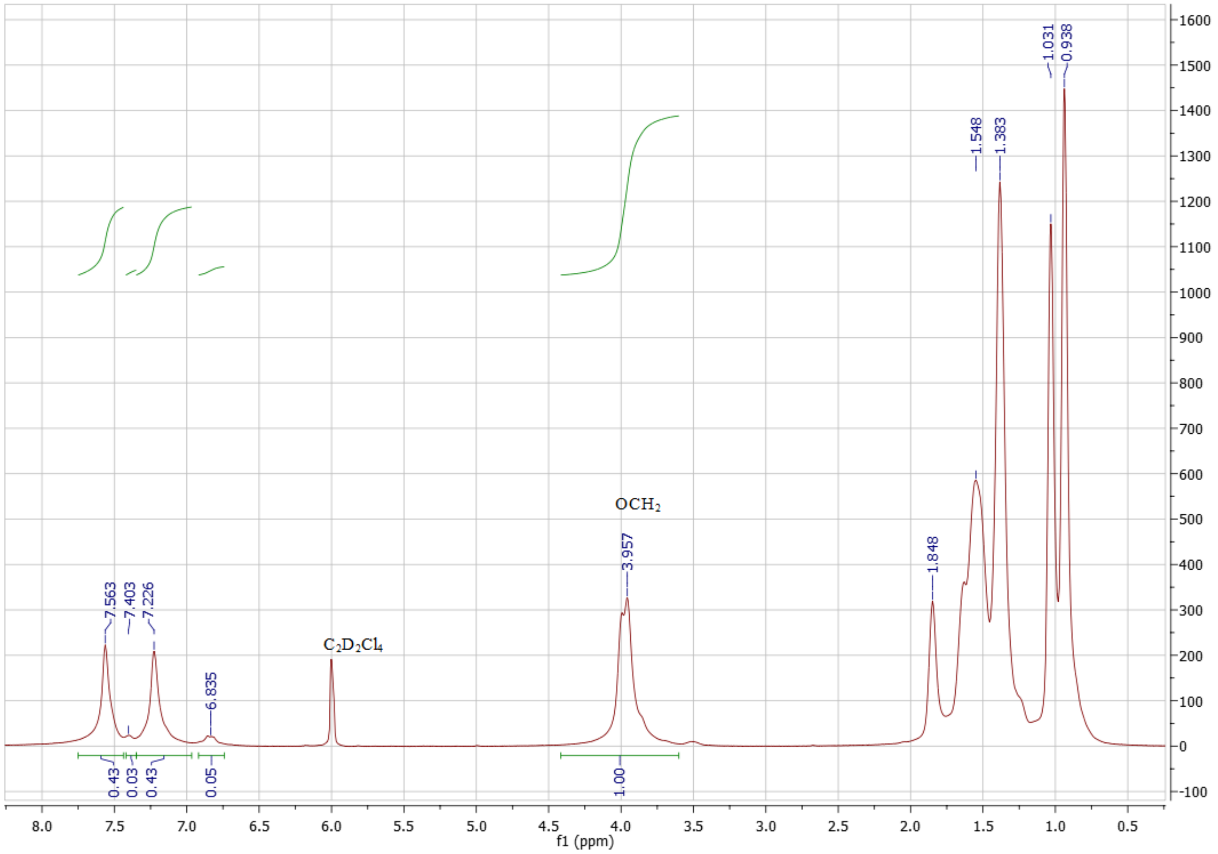


Figure 4.4: ^{1}H NMR of BEH-PPV in $C_2D_2Cl_4$

^{1}H NMR of A-Dd-*alt*-BEH-PPV confirmed the integrity of the adenine base under the polymerization conditions, reproducing the two purine –CH (7.8ppm, 8.4ppm) and the linker NCH2 (4.6ppm) signals of the monomer with little change in chemical shift. The purine –NH2 signal, a singlet in the monomer, became structured in the polymer spectra, suggesting the existence of more than one aggregation state for the nucleobase in non-polar solvent. The copolymer spectrum also contained all of the characteristic peaks described above for the BEH-PPV homopolymer.

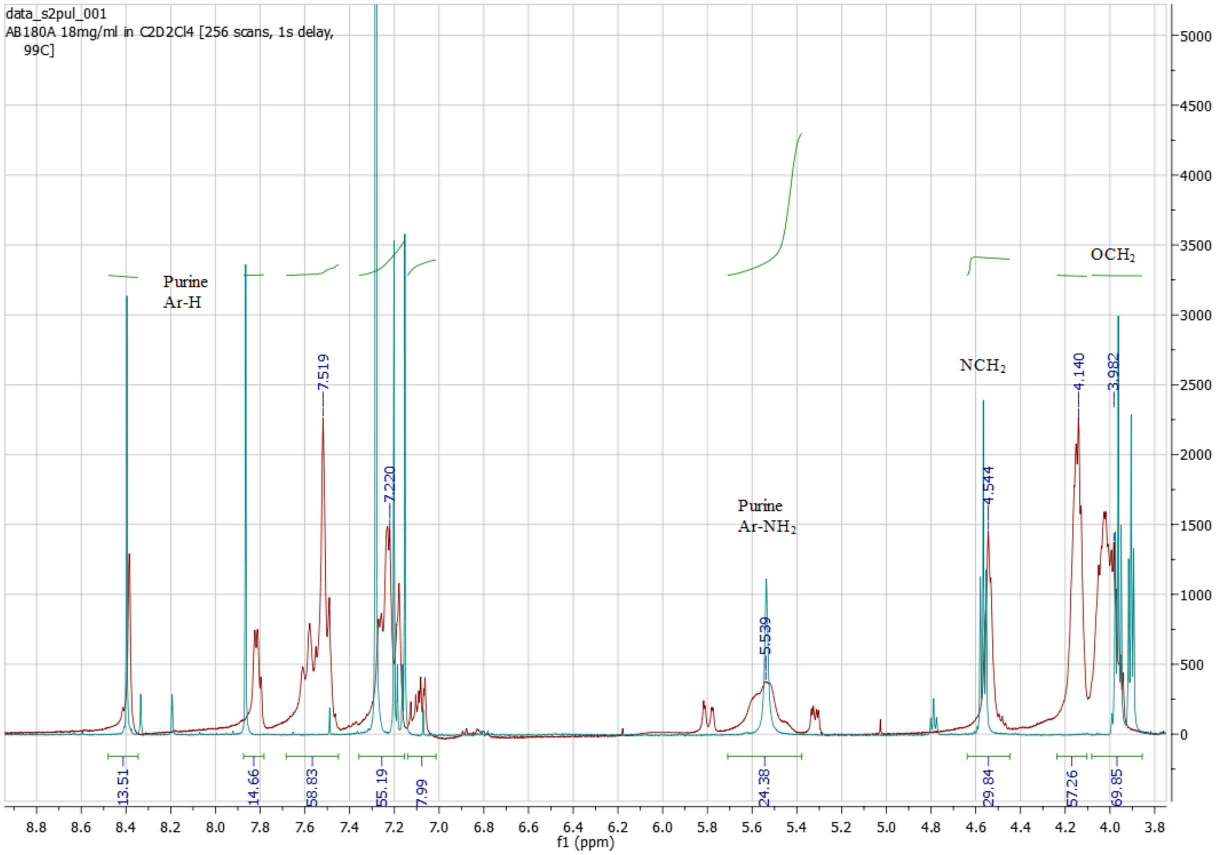


Figure 4.5: High-temperature 1H NMR of A-Dd-alt-BEH-PPV in C2D2Cl4 at 99°C and monomer A-Dd-PhI2 in CDCl3.

C2D2Cl4 signal (6.0ppm) is hidden for clarity. Signal at 5.37 is due to a solvent impurity.

Spectra acquired from T-Dd-*alt*-BEH-PPV were less easily interpreted due to poor peak resolution and the smaller number of characteristic signals originating from the simpler heterocycle. The highly deshielded thymine NH signal was not visible, and the aromatic region of the spectrum is only discernable from the parent BEH-PPV by the presence of a pair of overlapping signals slightly upfield of the polymer backbone protons. In the midfield, the NCH_2 doublet of the linker is clearly visible at 4.25ppm, and a sharp singlet likely attributable to the thymine methyl group can be observed overlapping with a broad aliphatic signal at 1.8ppm in the downfield region of the spectrum.

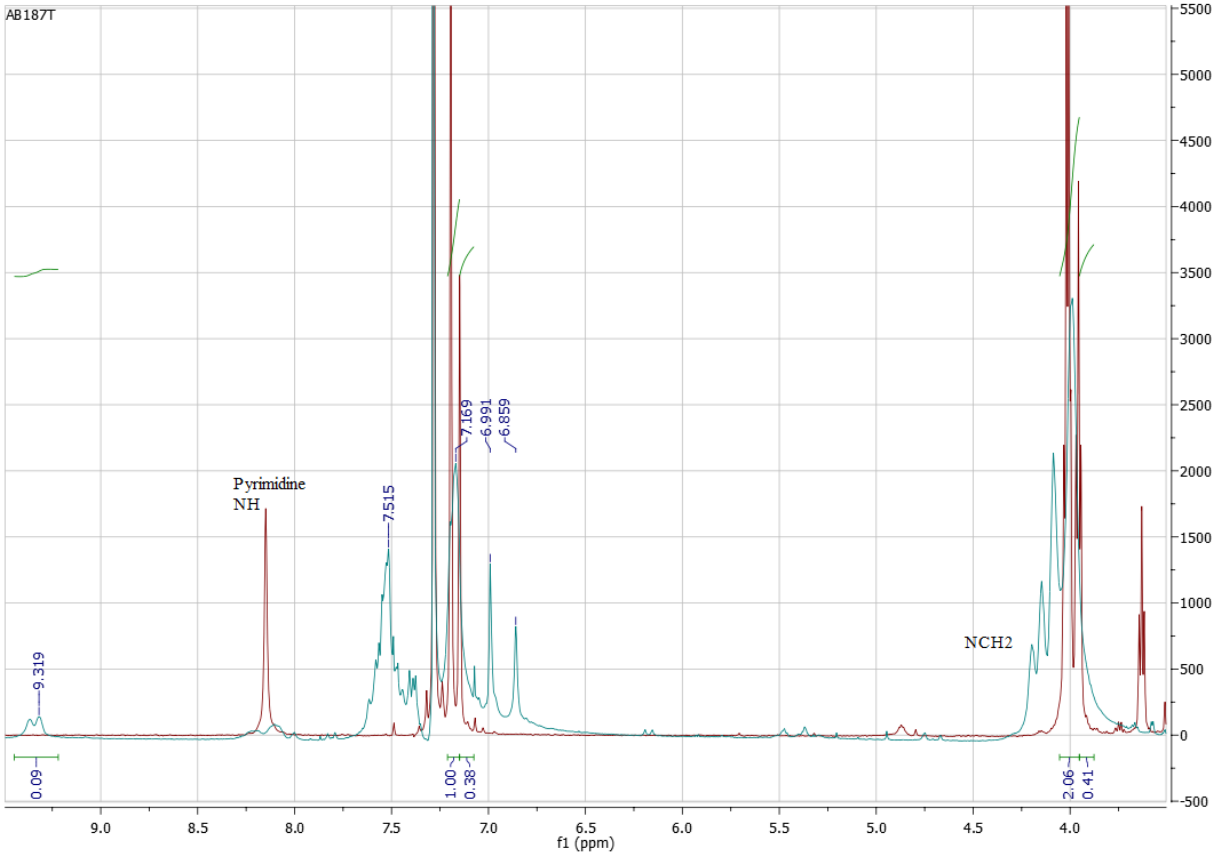


Figure 4.6: High-temperature ^{1}H NMR of T-Dd-alt-BEH-PPV in C2D2Cl4 and monomer T-Dd-PhI2 in CDCl3

4.3 Conclusion

In order to overcome the inability of related synthetic protocols to produce defect-free poly(phenylenevinylene) polymer, a new method was developed based on the Suzuki reaction. This technique offers a general approach to generate poly(arylenevinylenes) from common and synthetically accessible dihaloarenes in two steps. Applied to the synthesis of dialkoxy-PPV, this approach was found to be capable of generating polymers with fewer defects and higher degrees of polymerization than were attained even after extensive optimization of other palladium-catalyzed polycondensations.

This strategy was then employed to prepare two NB-PPVs copolymers with pendant nucleobase moieties connected to every second repeat unit. Under slightly modified polymerization conditions, thymine-functionalized PPV was prepared with similar molecular weight to the dialkoxy-PPV reference material; it is likely that similar degrees of polymerization could be attained for adenine-functionalized PPV.

4.4 Experimental

General

Reactions were carried out under nitrogen atmosphere using conventional Schlenk technique. Routine NMR spectra were recorded on a Bruker AV500 spectrometer, and polymer NMR on a Varian VNMRS500 spectrometer. UV/vis absorption and photoluminescence spectra were measured in CHCl3 with a JACSO V670 UV−vis−NIR spectrometer and a Varian Eclipse Fluorometer, respectively. Photoluminescence quantum yields were determined versus rhodamine 6G (PLQY=95%).

NB-Dd-PhI_2 materials were kindly provided by Dr. P. K. Lo. Dry solvents were prepared using an MBRAUN solvent purification system. Other solvents and reagents were purchased from Sigma Aldrich, VWR and Fisher Scientific and were used without further purification.

2,5-bis(2-ethylhexyloxy)-4-iodotoluene (EH_2TolI)

The compound was prepared analoguously to EH_2PhI_2. Characterization was in agreement with the literature. ^1H NMR (300 MHz, cdcl3) δ 7.16 (s, 1H), 6.64 (s, 1H), 3.79 (dd, J = 15.2, 5.4 Hz, 4H), 2.18 (s, 3H), 1.71 (s, 2H), 1.44 (dd, J = 31.6, 24.1 Hz, 21H), 1.02 – 0.78 (m, 14H).

2,5-*trans*-bis(2-ethylhexyloxy)-4-methylstyreneboronic acid pinacol ester ($EH_2MeSt(BPin)$)

Synthetic protocol followed procedures developed by Ms. Emily Sun in our group.[206] Characterization was in agreement with the literature. ^1H NMR (500 MHz, CDCl3) δ 7.77 (d, J = 18.5 Hz, 69H), 7.03 (s, 49H), 6.70 (s, 54H), 6.08 (d, J = 18.5 Hz, 48H), 3.80 (s, 241H), 2.22 (s, 179H), 1.86 – 1.62 (m, 147H), 1.62 – 1.39 (m, 494H), 1.30 (s, 1309H), 1.01 – 0.77 (m, 843H).

(E,E)-2,5-bis(2-ethylhexyl)-1,4-divinylbenzene-β,β-diboronic acid pinacol ester ($EH_2DVB(BPin)2$)

EH_2PhI_2 (0.456 ml, 1.073 mmol), Pd(PPh3)4 (40 mg, 0.035 mmol), tributylamine (1.3 ml, 5.47 mmol) and toluene (5ml) were combined in a Schlenk tube. The mixture was freeze-pump degassed, then vinyl boronic acid pinacol ester was added (0.60 ml, 3.2 mmol), and the tube was placed in a 95°C oil bath with stirring. The solution turned a rich yellow, but darkened on exposure to oxygen. Heating was removed after 12 hours. The reaction was neutralized with acetic acid (0.2ml) then added to 50ml pentane. Solids were removed by filtration, and the filtrate was washed dil. HCl, distilled water, and sat. NaCl before being filtered through MgSO4. Solvent was removed in vacuuo to yield 725mg of pale yellow oil which was stored under vacuum before being purified by reverse-phase flash chromatography in acetonitrile. The eluate was diluted with water, and the product extracted into hexanes. Solvent was removed, and the resulting white gum was recrystallized from methanol/water to yield approx. 400mg (60% yield) of white crystals. ^1H NMR (500 MHz, CDCl3) δ 7.77 (d, J = 18.5 Hz, 1H), 7.10 (s, 1H), 6.16 (d, J = 18.5 Hz, 1H), 3.84 (ddd, J = 18.2, 9.0, 6.0 Hz, 2H), 1.84 – 1.74 (m, 1H), 1.51 (dt, J = 23.6, 7.4 Hz, 2H), 1.46 – 1.33 (m, 4H), 1.32 (s, J = 12.4 Hz, 8H), 0.95 (dt, J = 9.0, 7.2 Hz, 5H).

Representative Suzuki Polymerization of PPV

EH_2PhI_2 (1 eq), $EH_2DVB(PBin)_2$ (1 eq), tri-tert-butylphosphonium tetrafluoroborate (0.1 eq), and $Pd_2(dba)_3$ (0.025 eq) were weighted into a Schlenk tube. Solvent (~50 eq) was added and the mixture was frozen in CO_2/acetone. 3M aqueous sodium hydroxide was added (6 eq), then the mixture was freeze-pump degassed three times before being allowed warm to room temperature with stirring. Red colour was observed to appear when the mixture was thawed during degassing. After 1h, iodobenzene (2 eq) was added to quench the reaction, and the mixture was stirred overnight. The product was precipitated in methanol, and collected by filtration to yield a red powder (up to 94% yield). The polymer was purified by reprecipitation from ethanol.

Absorbance max 502 nm, Emission max 556 nm. THF GPC Mn 30kD (vs polystyrene). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.23 (s, 1H), 3.96(d, 2H, OCH_2), 1.85 (s, 1H, CH), 1.47 (m, 9H, CH_2), 0.98 (d, 6H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.99, 129.33, 124.51, 111.76, 41.69, 32.56, 30.78, 26.05, 24.50, 15.39, 12.84.

Chapter 5: Conclusions, Future Work, and Bibliography

5.1 Conclusions

In this work, we have identified a potentially important means of advancing the field of polymer electronics by drawing inspiration from the ongoing successes of DNA nanotechnology. The ability to directly organize functional materials with the degree of precision that exists in DNA nanostructures would represent an enormous step towards the goal of creating advanced all-organic electronic devices. To that end, we have begun the investigation into the union of these two fields.

Our first step was to identify a conjugated polymer that is well suited for such investigation. PPV was selected on the grounds of is symmetry and intrinsic electronic properties, the broad base of existing research into its chemistry, and it synthetic accessibility. From a synthetic standpoint, PPV is unique among conjugated polymers in the diversity of ways in which is can be prepared. As a second step, we therefore conducted a thorough review of these varied synthetic methods with an eye to those appropriate for the synthesis of a well-defined, nucleobase-functionalized material.

This review of the field recommended further investigation of palladium-catalyzed cross-couplings as a means of producing defect free, functionalized PPV. Both Stille and Mizoroki-Heck polycondensations were evaluated, but despite extensive optimization, neither was found to be adequate for the task of preparing well-defined NB-PPV: the Stille reaction was found not to proceed efficiently enough to generate polymeric material of consistent molecular weight; meanwhile the regioselectivity of the Mizoroki-Heck reaction was found to too sensitive to the electronics of the monomer, producing defects in the polymer that disrupted its geometry and conjugation.

To remedy this deficiency in the field, an extensible adaptation of the Suzuki polycondensation was developed as an efficient means of producing functionalized PPV polymers from dihaloarenes via their transformation with vinylboronic acid pinacol ester. This technique was found to produce polymers with very low levels of defects, and was subsequently used to produce both adenine- and thymine-functionalized PPV copolymers. To our knowledge, this is the first report of the synthesis and characterization of a pair of complementary NB-CPs.

5.2 Future work

The characterization of the NB-PPV described in this work could be extended using a number of standard methods from the field of DNA science. First and foremost, the self-assembly interactions between the pair of complementary polymers synthesized merit further investigation, and such an investigation could likely take advantage of the well-studied hypochromic effect produced by base-pairing. Such an investigation could contribute to a study of temperature-dependent solution dynamics of these materials, complementing other techniques, such as direct ^{1}H NMR observation of hydrogen-bonding interactions and detailed optical studies into the electronic interactions between conjugated materials. If nucleobase-driven interactions between the complementary

NB-CPs are observed, an important follow-up would be to investigate their effects on the solid-state morphology of the material.

Beyond deeper investigation of the materials that have been prepared, the results of this study also offer opportunities and possibilities to other synthetic chemists. The NB-CPs prepared in this work are alternating copolymers bearing nucleobase moieties on every second repeat unit; however, the synthetic strategies we have developed could be easily extended to produce a more densely-functionalized homopolymer. Furthermore, as our strategy employs dihaloarenes as a substrate, it is expected to be easily extensible to the preparation of NB-CPs with different arene and heteroarene units in the polymer backbone.

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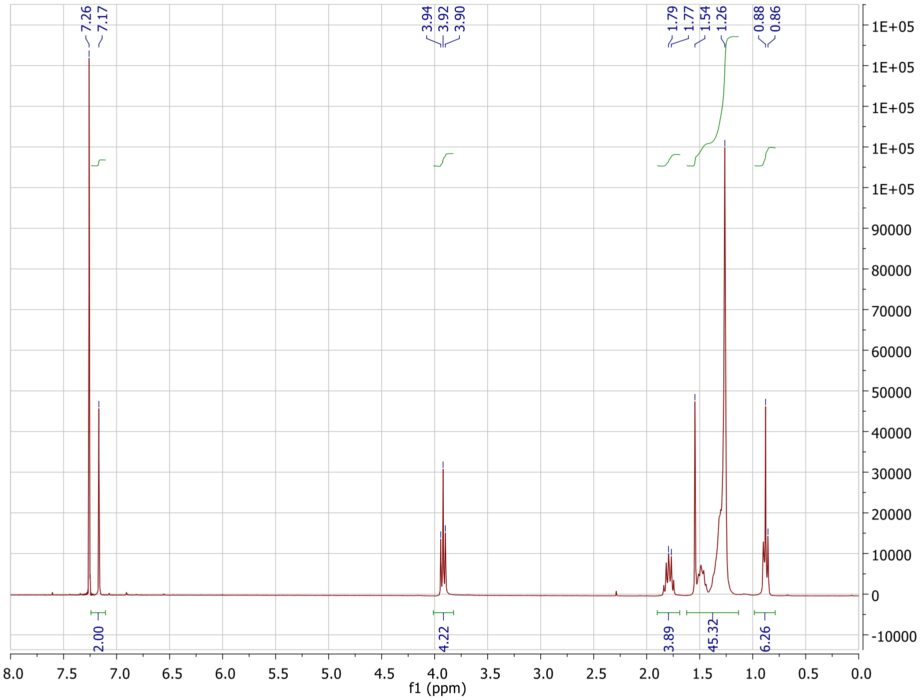
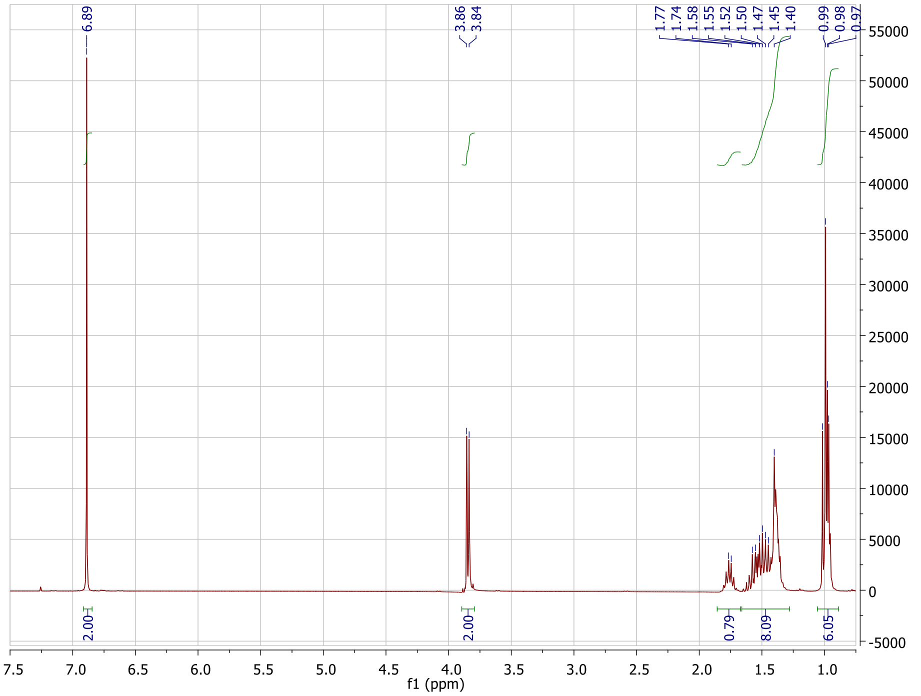
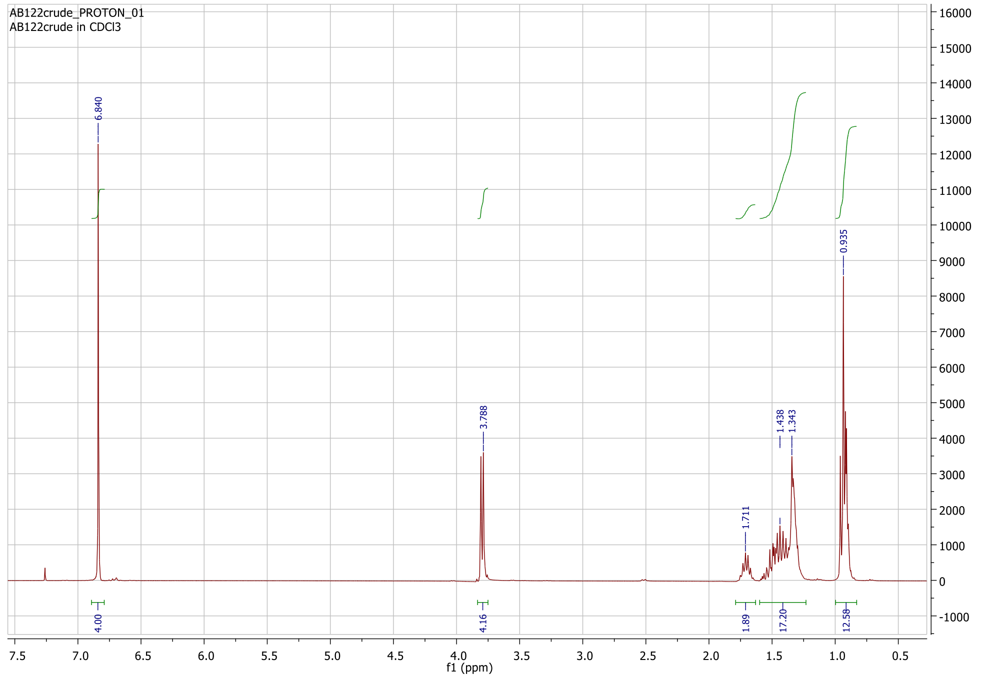
Appendix 1: NMR Spectra



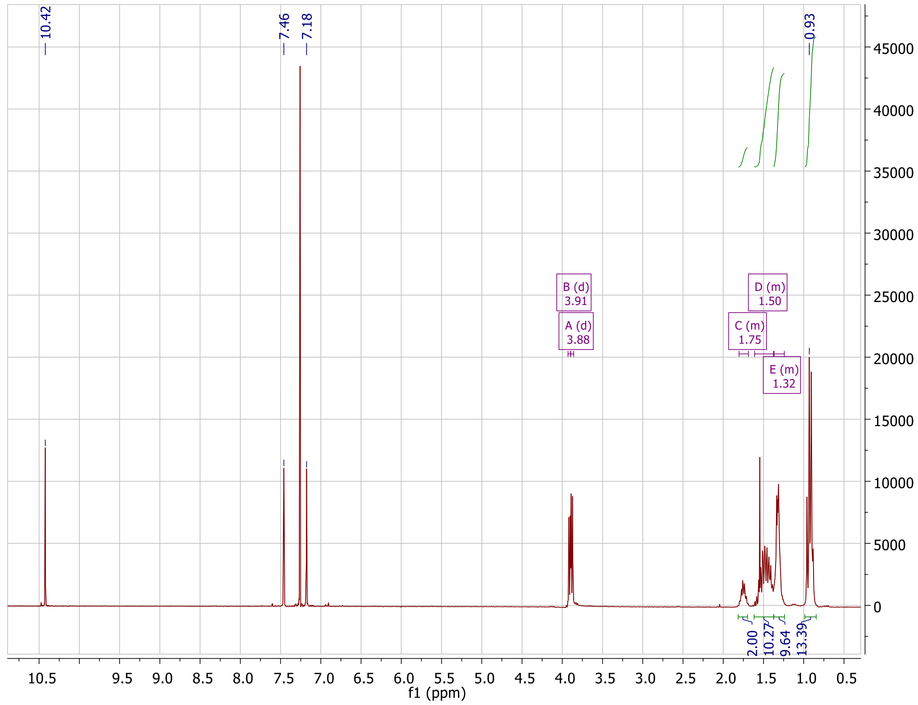
Spectrum 1: 1,4- bis(dodecyloxy)-2,5-diiodobenzene (Dd_2PhI_2)



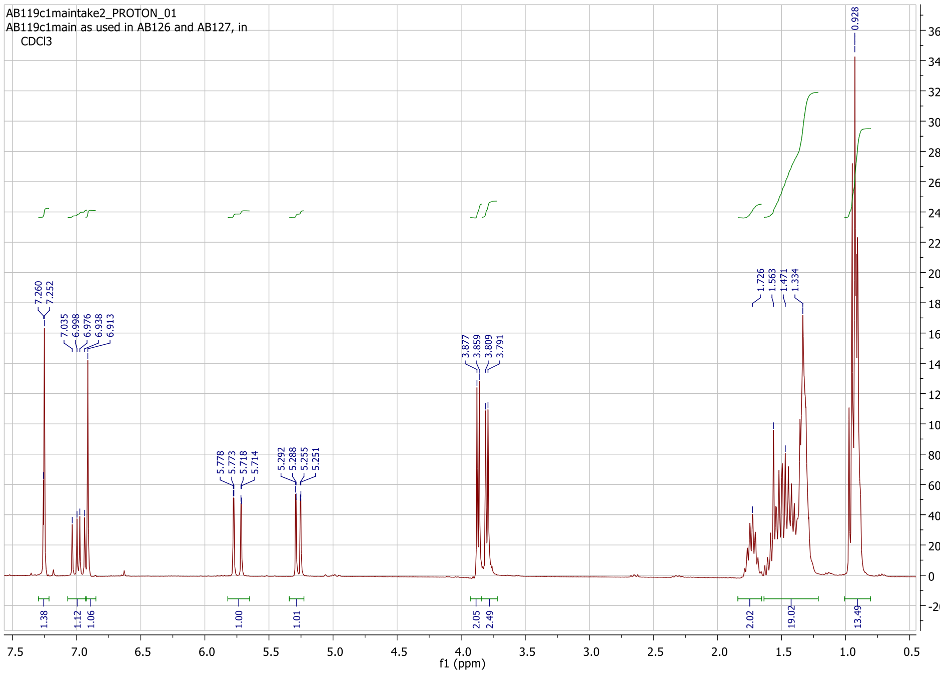
Spectrum 2: 1,4-bis((2-ethylhexyl)oxy)benzene (EH_2Ph)



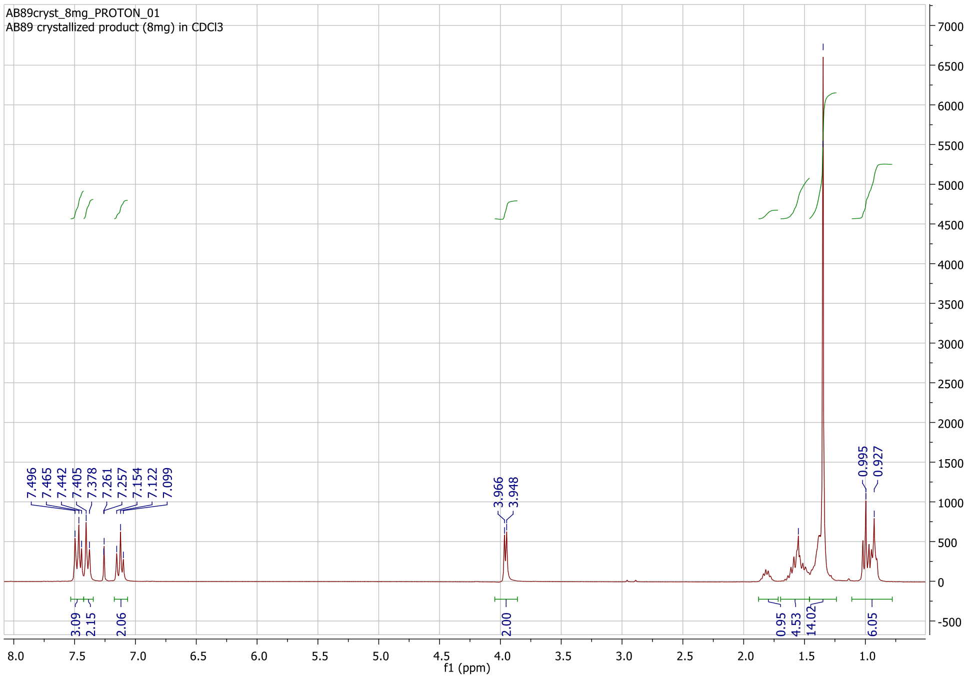
Spectrum 3: 1,4-bis((2-ethylhexyl)oxy)-2,5-diiodobenzene (EH_2PhI_2)



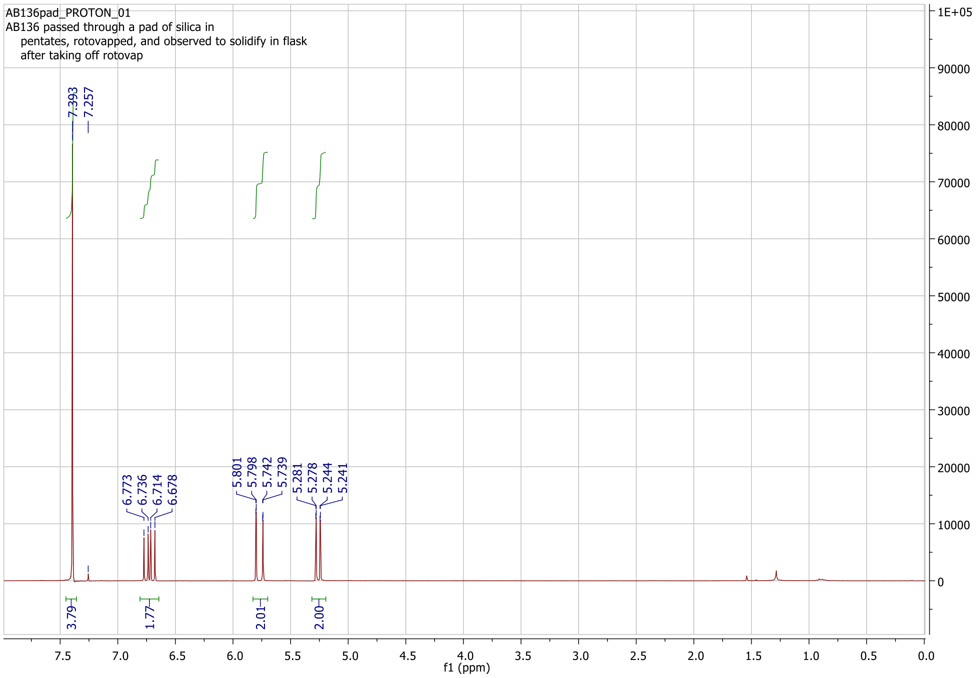
Spectrum 4: 2,5-bis((2-ethylhexyl)oxy)-4-iodo-benzaldehyde ($EH_2PhICOH$)



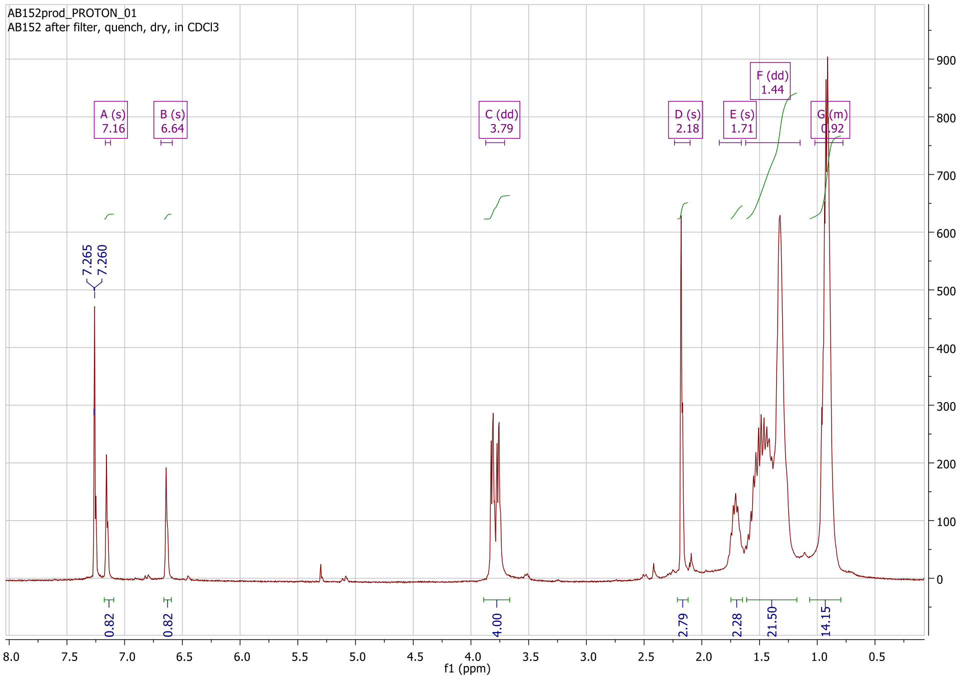
Spectrum 5: 2,5-bis((2-ethylhexyl)oxy)-4-iodo-styrene (EH$_2$StI)



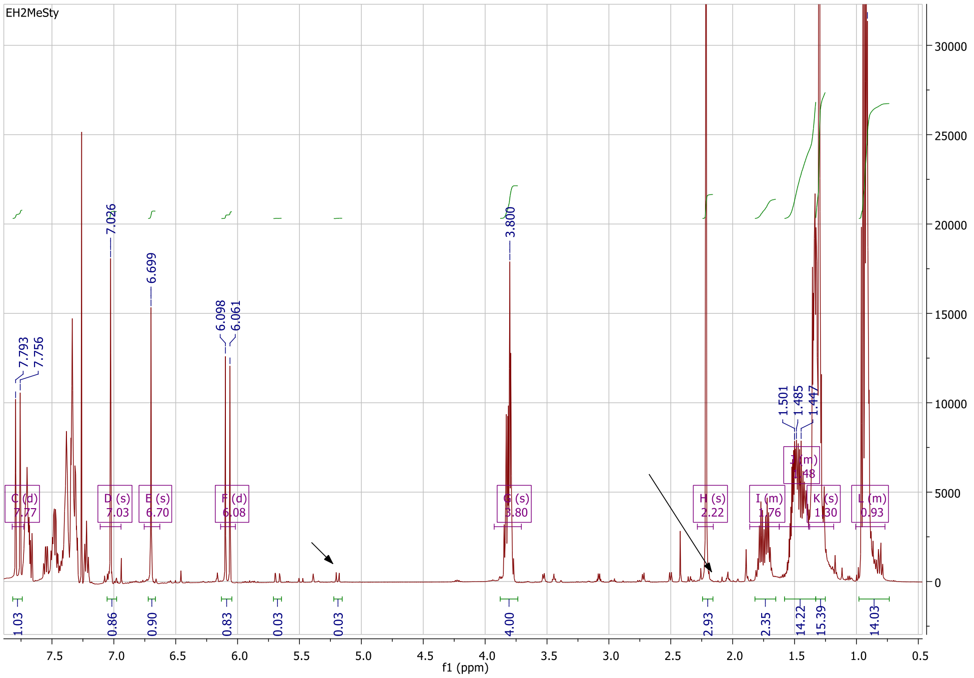
Spectrum 6: E,E-1,4-bis(2-ethylhexyl)-2,5-di(para-t-butylstyryl)benzene (EH$_2$DSB)



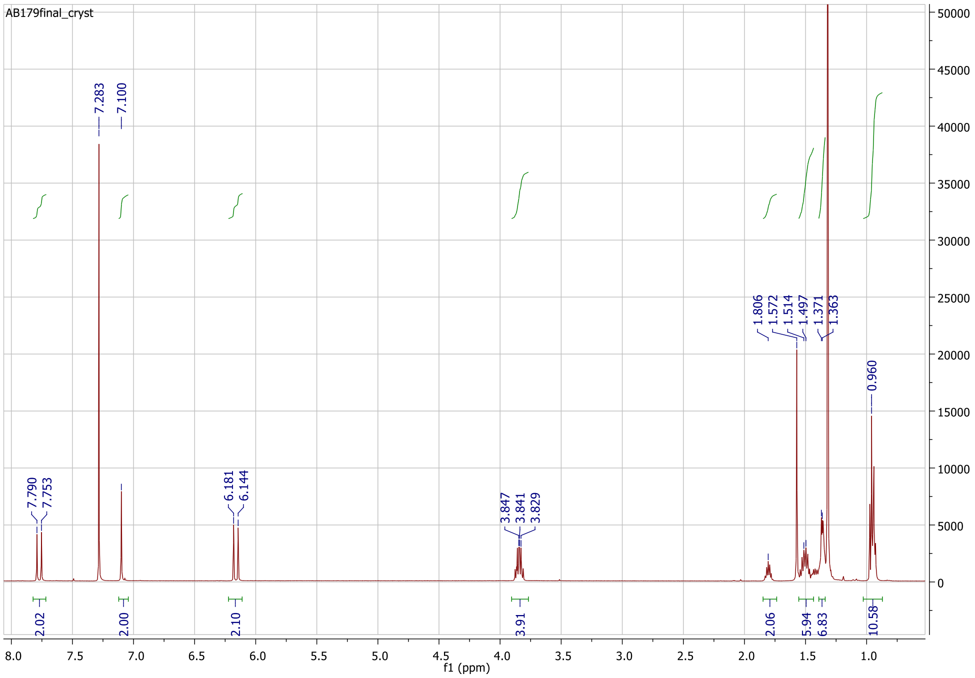
Spectrum 7: Para-divinylbenzene (DVB)



Spectrum 8: 2,5-bis(2-ethylhexyloxy)-4-iodotoluene (EH_2TolI)



Spectrum 9: 2,5-trans-bis(2-ethylhexyloxy)-4-methylstyreneboronic acid pinacol ester ($EH_2MeSt(BPin)$)



Spectrum 10: (E,E)-2,5-bis(2-ethylhexyl)-1,4-divinylbenzene-β,β-diboronic acid pinacol ester ($EH_2DVB(BPin)_2$)