# SYNTHESIS AND CHARACTERIZATION OF CARBAZOLE-BASED CONJUGATED POLYMER VIA DIRECT ARYLATION POLYMERIZATION

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**FACULTY OF SCIENCE AND NATURAL RESOURCES**
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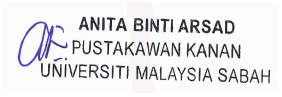


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**WONG XIN LIN**



**THESIS SUBMITTED IN FULFILLMENT FOR THE MASTER OF SCIENCE**

**FACULTY OF SCIENCE AND NATURAL RESOURCES**
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**2020**

# DECLARATION

I hereby declare that this thesis is my own work except for the quotations and references which have been properly acknowledged.

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# ABSTRACT

Conjugated polymers, with excellent optical and electrical properties, have appeared as promising operative materials for a diverse range of applications. Donor-Acceptor (D-A) framework, which copolymerizes electron-donors and electron- acceptors alternatively in conjugated backbones, has proven to be the most effective strategy for obtaining low bandgap polymers that desirable for optoelectronic applications. The synthesis of conjugated polymers is primarily relied on conventional cross-couplings, in particularly, Suzuki and Stille couplings, which involve the use of costly toxic organometallic reagents for monomers' functionalization. Despite robust and effective, these protocols produce stoichiometric quantities of toxic byproducts. Direct arylation polymerization (DArP) is a newly established synthetic strategy that provides a clean and low cost pathway towards conjugated polymers. It allows direct coupling of aryl halides and aromatic compounds without preactivation of Carbon-Hydrogen (C-H) bonds. In this research, an alternating D-A type copolymer based on N-9-hexadecyl-2,7-dibromocarbazole and 4,7-di(2-thienyl)benzothiadiazole was synthesized by DArP. This structure is modified from the classical low bandgap copolymer poly[N-9'-heptadecanyl-2,7-carbazole-alt -5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT) which exhibited excellent devices performance. One-pot DArP reaction was carried out under phosphine-free condition with palladium (II) acetate as the catalyst, pivalic acid as the additive, and potassium carbonates as the base. The resulting copolymer, poly[(9-hexadecyl-2,7-carabzole-alt-4,7-di(2-thienyl)-2,1,3-benzothiadiazole)] (P1) was obtained in 44%. It showed good solubility in organic solvents and has been satisfactorily characterized by FTIR and NMR. UV-Vis absorption spectra show the presence of inter-chain interaction and aggregation in the solid state. The optical bandgap of the copolymer was found to be in between 1.77 – 1.81 eV, which is slightly lower than that of the PCDTBT (1.88 eV).

# *ABSTRAK*

## *SINTESIS DAN PENCIRIAN BAGI POLIMER BERKONJUGAT ASAS-KARBAZOL MELALUI PEMPOLIMERAN ARILASI LANGSUNG*

*Polimer konjugasi, dengan sifat optik dan elektrik yang sangat baik, telah muncul sebagai bahan pengendali yang menjanjikan untuk pelbagai aplikasi. Kerangka Donor-Acceptor (D-A), yang mengkopolimerkan penyumbang elektron dan penerima elektron secara alternatif dalam tulang belakang konjugat, telah terbukti sebagai strategi yang paling berkesan untuk mendapatkan polimer bandgap yang rendah yang diinginkan untuk aplikasi optoelektronik. Sintesis polimer konjugasi ini terutamanya bergantung kepada penyambung silang konvensional, terutamanya, gandingan Suzuki dan Stille, yang melibatkan penggunaan reagen organik organometalit yang mahal untuk kegunaan monomer. Walaupun kuat dan berkesan, protokol ini menghasilkan kuantiti stoikiometrik produk sampingan toksik. Polimerisasi arilasi langsung (DArP) adalah strategi sintetik yang baru ditubuhkan yang menyediakan laluan kos yang bersih dan rendah ke arah polimer konjugat. Ia membolehkan gandingan langsung aril halida dan sebatian aromatik tanpa preaktivasi bon Carbon-Hydrogen (C-H). Dalam hal ini, kopolimer jenis D-A berselang-seling berdasarkan benzothiadiazole N-9-heksadecil-2,7-dibromocarbazole dan 4,7-dalam (2-siyenyl) disintesis oleh DArP. Struktur ini diubahsuai daripada kopolimer rendah band klasik [N-9'-heptadecanyl-2,7-carbazole-alt-5,5- (4 ', 7'-di-2-thenyenyl-2', 1 ' 3'-benzothiadiazole)] (PCDTBT) yang mempamerkan prestasi peranti yang sangat baik. Reaksi DArP satu periuk dijalankan di bawah keadaan bebas fosfin dengan palladium (II) asetat sebagai pemangkin, asid pivalik sebagai aditif, dan karbonat kalium sebagai bes. Kopolimer yang dihasilkan, poli [(9-heksadecil-2,7-carabzole-alt-4,7-di (2-thenyenyl) -2,1,3-benzothiadiazole)] (P1) diperolehi dalam 44%. Ia menunjukkan keterlarutan yang baik dalam pelarut organik dan telah dicirikan oleh FTIR dan NMR dengan memuaskan. Spektra penyerapan UV-Vis menunjukkan kehadiran interaksi antara rantaian dan pengagregatan dalam keadaan pepejal. Penumpukan optik kopolimer didapati berada di antara 1.77 - 1.81 eV, yang sedikit lebih rendah daripada PCDTBT (1.88 eV).*

# LIST OF CONTENTS

# LIST OF TABLES

# LIST OF FIGURES

# LIST OF SCHEMES

# LIST OF SYMBOLS AND ABBREVIATIONS

| | |
|---|---|
| **%** | Percentage |
| ***** | Multiplication |
| **~** | Similarity |
| **°C** | Degree celsius |
| $\Pi$ | Pi |
| $\alpha$ | Alpha |
| $\beta$ | Beta |
| $\delta$ | Delta |
| $\lambda$ | Lambda |
| **(*o*-MeOPh)$_3$P** | Tris(2-methoxyphenyl)phosphine |
| **BHJ** | Bulk heterojunction |
| **brs** | Broad singlet |
| **C-Br** | Carbon-bromine bond |
| **Cbz** | Carbazole |
| **C-H** | Carbon-hydrogen bond |
| **$CHCl_3$** | Chloroform |
| **C-I** | Carbon-iodine bond |
| **CMD** | Concerted metalation-deprotonation |
| **$Cs_2CO_3$** | Cesium carbonates |
| **DArP** | Direct arylation polymerization |
| **DBrBT** | 4,7-dibromo-2,1,3-benzothiadiazole |

| | |
|---|---|
| **DMAc** | Dimethylacetamide |
| **DMF** | Dimethylforamide |
| **DTBT** | 4,7-di(2-thienyl)-2,1,3-benzothiadiazole |
| **$E_g^{opt}$** | Optical band gap |
| **eV** | Electronvolt |
| **FF** | Fill factor |
| **FTIR** | Fourier Transform Infrared |
| **g** | Grams |
| **GPC** | Gel permeation chromatography |
| **$H_2SO_4$** | Sulphuric acid |
| **HOMO** | Highest occupied molecular orbital |
| **$HPCy_3BF_4$** | Tricyclohexylphosphine tetrafluoroborate |
| **ITO** | Indium tin oxide |
| **$J_{SC}$** | Short circuit current |
| **$K_2CO_3$** | Potassium carbonates |
| **KOAc** | Potassium acetate |
| **LUMO** | Lowest unoccupied molecular orbital |
| **$M_n$** | Number average molecular weight |
| **$Na_2SO_4$** | Sodium sulphate |
| **NBS** | N-bromosuccinimide |
| **NDA** | Neodecanoic acid |
| **nm** | Nanometer |
| **NOE** | Nuclear overhauser enhancement |