THESIS FOR THE DEGREE OF DOCTORATE OF ENGINEERING

Ambient Direct Arylation Polymerization

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CHALMERS UNIVERSITY OF TECHNOLOGY

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ABSTRACT

Conjugated polymers hold a vast array of applications as organic semiconductors owing to their light weight, flexibility and tunability. This enables their implementation in wearable and implantable devices, advancing next-generation bioelectronics through their use as organic mixed ionic-electronic conductors (OMIECs) in organic electrochemical transistors (OECTs). Though promising materials, conjugated polymers often require lengthy, toxic, and energy-intensive syntheses. To develop sustainable technologies, environmentally benign synthesis at large scale to high-performance conjugated polymer materials is essential. This thesis covers the synthesis of conjugated polymers, addressing green chemistry principles and the production/performance trade-off, along with their subsequent evaluation as OMIEC materials.

Direct arylation polymerization (DAP) is a promising green synthesis method to conjugated polymers but still requires high temperatures, toxic solvents and is prone to side reactions. Optimization of DAP parameters led to ambient direct arylation polymerization (ADAP), an open-flask, room-temperature, green-solvent process, yielding over 100 grams of polymer. Mechanistic studies reveal a bimetallic Pd/Pd catalytic system with an initial homocoupling initiation cycle that allows the reaction to proceed at lower temperatures. Unexpectedly, improved structural order arose from the created homocoupling defects, which led to state-of-the-art performance in OECTs. Batch-to-batch variation was addressed by translating ADAP to a continuous droplet-flow reactor. As the reaction in flow tolerated high water content, fully aqueous synthesis was explored using water-soluble monomers and catalysts, showing promising results. Given the robustness of ADAP, instructions for cost-effective synthesis and application teaching labs are outlined, allowing students from diverse scientific backgrounds to engage with advanced polymer chemistry.

Ultimately, the cost, safety and scalability considerations developed throughout this work will aid the advancement of conjugated polymer synthesis.

Keywords: *conjugated polymer synthesis, catalysis, organic mixed ionic-electronic conductors, organic electrochemical transistors, hands-on learning*

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NOMENCLATURE

Symbols and abbreviations

ADAP	ambient direct arylation polymerization
C^*	volumetric capacitance
CMD	concerted-metalation-deprotonation
DAP	direct arylation polymerization
DP	degree of polymerization
DSC	differential scanning calorimetry
E_{redox}	redox potential
EX	exchange
GIWAXS	grazing-incidence wide-angle X-ray scattering
HOMO	highest occupied molecular orbital
HT-NMR	high-temperature ^{1}H nuclear magnetic resonance
LE	ligand exchange
$M_{\mathrm{n,NMR}}$	number-average molecular weight by nuclear magnetic resonance
$M_{\mathrm{n,SEC}}$	number-average molecular weight by size exclusion chromatography
NC	number of columns
NH	number of hazard codes
NMR	nuclear magnetic resonance
NO	number of operations
NSS	number of synthetic steps
OA	oxidative addition
OECT	organic electrochemical transistor
OLED	organic light-emitting diode
OMIEC	organic mixed ionic-electronic conductor
PEPER	problem-exploration-planning-execution-reflection
RE	reductive elimination
rr	regioregular
rra	regiorandom

RY	reciprocal yield
$S\cdots O$	sulfur-oxygen
SCI	synthetic complexity index
SEC	size exclusion chromatography
SXRD	single crystal X-ray diffraction
TLC	thin-layer chromatography
T_m	melting temperature
UV-vis-NIR	ultraviolet-visible-near-infrared
V_T	threshold voltage
WaDAP	water direct arylation polymerization
μ	mobility
σ	conductivity

Chemicals

aTT	3,6-bis(decyloxy)thieno[3,2-*b*]thiophene
Br-3HT-Br	2,5-dibromo-3-hexylthiophene
Br-F8-Br	2,7-dibromo-9,9-dioctylfluorene
BrT-g_3TT-TBr	2,5-bis(5-bromothiophen-2-yl)-3,6-bis triethylene glycol monomethyl ether)thieno[3,2-*b*]thiophene
CAT-K	potassium 3-(2-(2-(2-((2,5-dibromothiophen-3-yl)oxy)ethoxy)ethoxy)ethoxy)propanoate)
D18	poly[(2,6-(4,8-bis(5-(2-ethylhexyl)-4-fluoro)thiophen-2-yl)-benzo[1,2-*b*:4,5-*b*’]dithiophene)-*alt*-5,5'-(5,8-bis(4-(2-butyloctyl)thiophen-2-yl)dithieno[3',2':3,4;2",3":5,6]benzo[1,2-*c*][1,2,5]thiadiazole)]
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DMA	*N*,*N*-dimethylacetamide
DMF	*N*,*N* -dimethylformamide
DMPA	2,2-dimethoxy-2-phenylacetophenone
EDOT	3,4-ethylenedioxythiophene
EH	2-ethylhexyl
PFEDOT	poly(3,4-ethylenedioxythiophene-*alt*-9,9-dioctylfluorene)

g_0TT	3,6-bis(methoxy)thieno[3,2-*b*]thiophene
g_1TT	3,6-bis(monoethylene glycol monomethyl ether)thieno[3,2-*b*]thiophene
g_2TT	3,6-bis(diethylene glycol monomethyl ether)thieno[3,2-*b*]thiophene
g_3	triethylene glycol monomethyl ether
g_3TT	3,6-bis(triethylene glycol monomethyl ether)thieno[3,2-*b*]thiophene
g_4TT	3,6-bis(tetraethylene glycol monomethyl ether)thieno[3,2-*b*]thiophene
g_xTT	3,6-bis(*x*-ethylene glycol monomethyl ether)thieno[3,2-*b*]thiophene
HP	4-hexylphenyl
K_2CO_3	potassium carbonate
KBr	potassium bromide
MEH-PPV	poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene)
NBP	*N*-butyl-2-pyrrolidone
NBu_4PF_6	tetrabutylammonium hexafluorophosphate
NMP	*N*-methyl-2-pyrrolidone
OD	2-octyldodecyl
P3HT	poly(3-hexylthiophene)
PCAT-K	poly(potassium 3-(2-(2-(2-(thiophen-3-yloxy)ethoxy)ethoxy)ethoxy)propanoate)-*alt*-2,5-thiophene-diyl)
PCPDTBT-SO_3K	poly[2,6-(4,4-bis-potassium butanylsulfonate-4H-cyclopenta-[2,1-*b*;3,4-*b′*]-dithiophene)-*alt*-4,7-(2,1,3-benzothiadiazole)]
$Pd(NH_3)_4Cl_2 \cdot H_2O$	tetraamminepalladium(II) chloride monohydrate
$Pd(NO_3)_2 \cdot 2H_2O$	palladium(II) nitrate dihydrate
$Pd(OAc)_2$	palladium acetate
$Pd(OH)_2$	palladium(II) hydroxide
$PdCl_2$	palladium(II) chloride
$PdCl_2$(en)	ethylenediaminepalladium(II) chloride
$PdCl_2(PPh_3)_2$	bis(triphenylphosphine)palladium(II) chloride
PE	polyethylene
PEDOT:PSS	poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate)
PEDOTT	poly(3,4-ethylenedioxythiophene-*alt*-3-hexylthiophene)

PEO	polyethylene oxide
PFAS	perfluorinated alkyl substance
PMMA	poly(methyl methacrylate)
PS	polystyrene
S-EDOT	sodium 4-[(2,3-dihydrothieno[3,4-b][1,4]dioxin-2-yl)methoxy]butane-2-sulfonate
S-PEDOT	poly(sodium 4-[(2,3-dihydrothieno[3,4-b][1,4]dioxin-2-yl)methoxy]butane-2-sulfonate)
$T2Br_2$	5,5’-dibromo-2,2’-bithiophene
T-g_3TT-T	3,6-bis(triethylene glycol monomethyl ether)-2,5-di(thiophen-2-yl)thieno[3,2-*b*]thiophene

PUBLICATIONS

This thesis consists of an extended summary of the following appended papers:

Paper I **High-mobility organic mixed conductors with a low synthetic complexity index via direct arylation polymerization**

Joost Kimpel, Youngseok Kim, Jesika Asatryan, Jaime Martín, Renee Kroon, and Christian Müller

Chemical Science, **2024**, 15, 7679-7688

Paper II **Small signal analysis for the characterization of organic electrochemical transistors**

Youngseok Kim, Joost Kimpel, Alexander Giovanitti, and Christian Müller

Nature Communications, **2024**, 15, 7606

Paper III **Open-flask, ambient temperature direct arylation polymerization of mixed ionic-electronic conductors**

Joost Kimpel, Youngseok Kim, Hannes Schomaker, Diego R. Hinojosa, Jesika Asatryan, Jaime Martín, Renee Kroon, Michael Sommer, and Christian Müller

Science Advances, **2025**, 11, eadv8168

Paper IV **Synthesis and single crystals of thieno[3,2-b]thiophene with long oligoether chains**

Joost Kimpel, Iona Anderson, Di Zhu, Jyotsana Kala, Przemyslaw Sowinski, Lars Öhrström, Jenny Nelson, and Christian Müller

Manuscript in preparation

Paper V **A foundational conjugated polymer synthesis teaching lab**

Joost Kimpel, Megan Westwood, and Christian Müller

Manuscript in preparation

CONTRIBUTION REPORT

Paper I	**Main author.** J.K. and C.M. conceptualized the study, visualized the data, and wrote the original draft. J.K. performed all synthetic procedures (small molecule, polymer) and characterization (NMR, SEC, UV-vis, CV) and performed DFT calculations with associated method development, investigation, analysis and validation. Y.K. performed all OECT measurements with associated software programming, method development, investigation, analysis and validation. J.A. and J.M. carried out GIWAXS with associated method development, investigation and analysis. J.K., Y.K., J.A., J.M., R.K., and C.M. reviewed and edited the initial draft. C.M. supervised the overall study.
Paper II	**Co-author.** Y.K. and C.M. conceptualized the study, visualized the data, and wrote the original draft. Y.K. prepared devices and performed all OECT measurements with associated software programming, method development, investigation, analysis and validation, where J.K. and A.G. assisted in analysis. J.K. performed all synthetic procedures (small molecule, polymer) and characterization (NMR, SEC) with associated method development, investigation, analysis and validation. Y.K., J.K., A.G., and C.M. reviewed and edited the initial draft. C.M. supervised the overall study.
Paper III	**Main author.** J.K. conceptualized the study with help of C.M., visualized the data, and wrote the original draft. J.K. performed all synthetic procedures (small molecule, polymer, mechanism, kinetics, upscaling, scoping, post-polymerization, flow) and characterization (NMR, SEC, MALDI-ToF, LCMS, UV-vis) with associated method development, investigation, analysis and validation. Y.K. performed all OECT measurements with associated software programming, method development, investigation, analysis and validation. H.S. provided access to the flow system and LC-MS, and performed the necessary method development and investigation. D.H. further investigated and validated the synthetic procedures. R.K. and M.S. provided access to the SEC and NMR, respectively, and contributed to supervision of synthesis. J.A. and J.M. carried out GIWAXS with associated method development, investigation and analysis.

J.K., Y.K., H.S., D.H., J.A., J.M., R.K., M.S., and C.M. reviewed and edited the initial draft. C.M. supervised the overall study.

Paper IV **Main author.** J.K. conceptualized the study, visualized the data, and wrote the original draft. J.K. performed synthetic procedures (small molecule, crystal growth) and characterization (NMR, single crystal X-ray, DSC) with associated method development, investigation, analysis and validation. D.Z. assisted with synthesis of small molecules. P.S. provided insights into thermal properties of crystals. L.Ö. supervised single crystal X-ray measurements. I.A. performed molecular dynamics simulations with associated method development, investigation, analysis and validation. Jy.Ka. assisted with molecular dynamics simulations. J.N. supervised molecular dynamics studies. J.K., I.A., D.Z., Jy. Ka., P.S., A.G., L.Ö., J.N., and C.M. reviewed and edited the initial draft. C.M. supervised the overall study.

Paper V **Main author.** J.K. conceptualized the study, visualized the data, and wrote the original draft. J.K. performed all synthetic procedures and characterization with associated method development, investigation, analysis and validation. M.W. further investigated and validated the synthetic procedures. M.W. measured SEC and performed the necessary method development and investigation. J.K. and M.W. created the dissemination materials. J.K., M.W., and C.M. reviewed and edited the initial draft. C.M. supervised the overall study.

PUBLICATIONS NOT INCLUDED IN THE THESIS

Paper VI **A route to conjugated monomers and polymers incorporating 2,5-connected oxazole in the backbone**

Joost Kimpel, Waner He, Ye Cheng, and Tsuyoshi Michinobu

Journal of Organic Chemistry, **2022**, 87, 14, 9384–9390

Paper VII **Block poly(carbonate-ester) ionomers as high-performance and recyclable thermoplastic elastomers**

Georgina L. Gregory, Gregory S. Sulley, Joost Kimpel, Matylda Łagodzińska, Lisa Häfele, Leticia Peña Carrodeguas, and Charlotte K. Williams

Angewandte Chemie International Edition, **2022**, 61, e202210748

Paper VIII **On the conformation of dimeric acceptors and their polymer solar cells with efficiency over 18 %**

Jingnan Wu, Zhaoheng Ling, Leandro R. Franco, Sang Young Jeong, Zewdneh Genene, Josué Mena, Si Chen, Cailing Chen, Prof. C. Moyses Araujo, Prof. Cleber F. N. Marchiori, Joost Kimpel, Xiaoming Chang, Furkan H. Isikgor, Qiaonan Chen, Hendrik Faber, Yu Han, Frédéric Laquai, Maojie Zhang, Han Young Woo, Donghong Yu, Thomas D. Anthopoulos, and Ergang Wang

Angewandte Chemie International Edition, **2023**, 62, e202302888

Paper IX **Impact of oligoether side-chain length on the thermoelectric properties of a polar polythiophene**

Mariavittoria Craighero, Jiali Guo, Sepideh Zokaei, Sophie Griggs, Junfu Tian, Jesika Asatryan, Joost Kimpel, Renee Kroon, Kai Xu, Juan Sebastian Reparaz, Jaime Martín, Iain McCulloch, Mariano Campoy-Quiles, and Christian Müller

ACS Applied Electronic Materials, **2023**, 6, 2909-2916

Paper X **Impact of doping on the mechanical properties of conjugated polymers**

Sri Harish Kumar Paleti, Youngseok Kim, Joost Kimpel, Mariavittoria Craighero, Shuichi Haraguchi, and Christian Müller

Chemistry Society Reviews, **2024**, 53, 1702-1729

Paper XI **A facile membraneless method for detecting alkali-metal cations using organic electrochemical transistors**

Waner He, Yurika Kashino, Naoya Nozakia, Joost Kimpel, Hidetoshi Matsumoto, Yuhei Hayamizu, and Tsuyoshi Michinobu

J. Mater. Chem. C, **2024**, 12, 18282-18290

Paper XII **A practical synthesis of multi-Site functionalized norbornadiene-quadricyclane as molecular solar thermal energy storage**

Monika Shamsabadi, Joost Kimpel, Christian Müller, and Kasper Moth-Poulsen

Synlett, **2025**, doi: 10.1055/a-2560-0282

Paper XIII **Benchmarking the elastic modulus of conjugated polymers with nanoindentation**

Sri Harish Kumar Paleti, Shuichi Haraguchi, Zhiqiang Cao, Mariavittoria Craighero, Joost Kimpel, Zijin Zeng, Przemyslaw Sowinski, Di Zhu, Qifan Li, Junda Huang, Alexei Kalaboukhov, Besira Mihiretie, Simone Fabiano, Xiaodan Gu, and Christian Müller

Macromolecules, **2025**, 58, 3578-3588

Paper XIV **Enhanced photoresponsive transistor memory performance through [2 + 2] cycloaddition-retroelectrocyclization of Tröger’s base-carbazole copolymer**

Chia-Yang Lin, Mei-Nung Chen, Joost Kimpel, Waner He, Guey-Sheng Liou, Yu-Cheng Chiu, and Tsuyoshi Michinobu

ACS Appl. Polym. Mater., **2025**, 7, 9286-9293

TABLE OF CONTENTS

Chapter 1

The conjugated polymer production/performance trade-off

Conjugated polymers receive widespread attention as semiconductors and as mixed ionic-electronic conductors for numerous application areas, from wearable electronics to bioelectronics.[1-5]

Considering the synthesis of conjugated polymers, keywords such as "*low-cost production*", "*low toxicity*", "*ease of upscaling*", "*high tunability*", and "*high performance*" are often advertised.[6-15] While conjugated polymers can live up to these expectations, nuance is essential, as these qualities rarely coexist. This is especially true for ease of production *versus* performance, which thus necessitates a trade-off; simpler structures are more easily synthesized but tend to lack optimal properties and *vice versa*.[16-20]

Conjugated polymer materials that can be produced on an industrial scale are often homopolymers.[20-24] Given the use of a single building block, these systems can generally be made via simple synthetic routes. However, this proves to be a double-edged sword. Seeing that homopolymers lack structural variability, they often have confined inherent property portfolios and hence tend to be limited in scope.[7,25,26]

Conjugated copolymers comprising two or more monomer building blocks constitute some of the most promising candidates considering tunability and high performance. Their diverse monomer building blocks can be selected to fit a particular application, e.g., donor-acceptor systems for photovoltaics or polymers with polar side chains in the context of electrochemical transistors.[27-29] However, unlike the synthesis of homopolymers, these systems often involve complex syntheses with low yields that require toxic starting materials and intermediates. These factors complicate large-scale production.[17,24,30,31]

This thesis reports the development and further implications of a novel polymerization technique that provides access to conjugated copolymers: ambient direct arylation polymerization. High-performance and tunable conjugated copolymers can be produced by a straightforward synthetic route with low toxicity at large-scale.

Chapter 2

From sketch to synthesis to application

To improve the production/performance trade-off associated with conjugated copolymers, it is essential to understand the design and synthesis of their molecular building blocks. Equally important is identifying the structural factors that influence their electronic performance in the final application.

2.1 Design and synthesis of conjugated copolymers

The structurally simplest conjugated polymer is polyacetylene, featuring alternating single and double bonds in a single chain, however it suffers from low ambient stability.[32,33] Aromatic units, such as derivatives of benzene and thiophene, are used instead to impart stability.[34] Their electronic character, be they electron-rich/electron-donating, i.e. donors, or electron-poor/electron-withdrawing, i.e. acceptors, will dictate whether the final polymer is hole-transporting (p-type), electron-transporting (n-type), or presenting both behaviors (ambipolar).[19,35] Here, the focus will be on p-type materials, i.e. electron-donating compounds based on electron-rich thiophenes.

In case unsubstituted aromatic monomers are used, the final polymers will feature strong π-π stacking and tend to remain aggregated, causing their neutral form to be poorly soluble, hence not processable.[36-39] By grafting flexible side chains onto the aromatic units, the polymers can become solution processable since conformational entropy is increased which can disturb π-π stacking.[40-44] Monomers with alkyl (or alkoxy) side chains offer relative ease of synthesis and their hydrophobic nature imparts solubility in many industrial organic solvents.[44-46] Oligoethylene glycol side chains, attached to the aromatics by similar synthetic routes, possess a higher dielectric constant, thus enabling processing in safer, more polar solvents such as acetonitrile and alcohol.[47-51]

Depending on the application, different side-chain contents are preferable. For instance, a balance of alkyl side-chain length is key in photovoltaics, maximizing aromatic content to ensure charge separation events while preserving good solubility in organic solvents.[52] On the other hand, in bioelectronic applications, oligoethylene glycol side chains aid in ionic transport and so make up a large fraction of the conjugated polymer.[30,53,54] Accordingly, a balance must be struck between processability and performance based on prerequisites of the application.

Homopolymers are traditionally synthesized by methods such as electropolymerization to polyaniline,[55] chemical oxidative polymerization to poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS),[56] or Grignard metathesis polymerization to poly(3-hexylthiophene) (P3HT) (Figure 1a).[57] Copolymers can be accessed through similar routes by combining two similarly reactive monomers. However, these routes lack selectivity and thus lead to statistical (random) copolymers which often have inferior properties.[58-60]

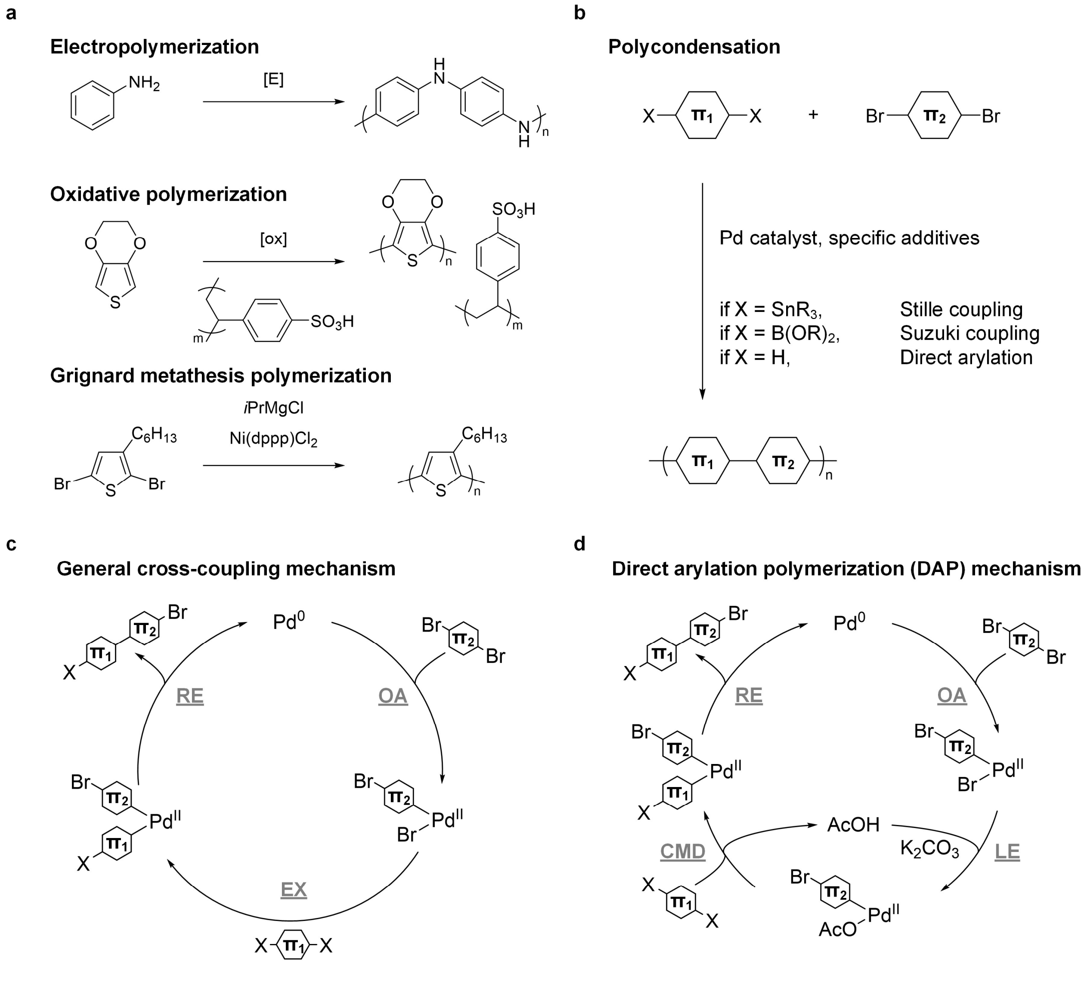


Figure 1. Synthesis of conjugated polymers and reaction mechanisms of conjugated polymer synthesis. (a) Exemplar reaction schemes of common homopolymerizations. (b) General reaction scheme of common polycondensations. (c) General reaction mechanism of polycondensations. (d) Reaction mechanism of direct arylation polymerization (DAP). OA = oxidative addition, EX = exchange, RE = reductive elimination, LE = ligand exchange, and CMD = concerted-metalation-deprotonation.

To realize synthesis of alternating conjugated copolymers, cross-coupling polycondensation of two bifunctionalized aromatics in the presence of an organometallic catalyst is often employed (Figure 1b).[61,62] While different cross-coupling methods proceed through different mechanisms, they all showcase a comparable set of elementary steps, namely oxidative addition (OA), functional group exchange (EX, e.g. transmetalation), and reductive elimination (RE, Figure 1c). For a successful polymerization, the bifunctionalized monomers must have orthogonal reactivity, simplified as the requirement that one monomer must be electrophilic and the other one nucleophilic.[63] In most cases, electrophilic aryl halides are combined with nucleophilic functionalized co-monomers such as aryl stannanes in Stille coupling or aryl boronate esters in Suzuki coupling. Not only does functionalization add an additional synthetic step, but it also makes precursors atom inefficient (Stille, Suzuki) and in some cases highly toxic (Stille).

In direct arylation polymerization (DAP), cross-coupling proceeds by leveraging activated C-H bonds (Figure 1d).[64] However, DAP has several challenges to overcome, such as a limited number of suitable monomers that are sufficiently reactive. Moreover, less orthogonality in reactivity and the lack of C-H regioselectivity often leads to defects in polymers prepared by DAP. Especially the latter, known as β-defects, causes branching defects that lead to cross-conjugation and poor π-π stacking due to steric hindrance chain irregularity.[65,66] By careful construction of the C-H active monomer, formation of defects can be avoided making DAP the technique of choice.[67,68]

2.2 Principles and key metrics of green chemistry

Traditional chemistry is often done at the expense of the environment (through waste and excessive energy consumption) and human health (due to use of toxic compounds). Green chemistry offers a sustainable alternative, aiming to minimize harm through safer materials and cleaner processes.

Anastas and Warner created a green chemistry framework based on twelve principles: (1) prevent waste, (2) maximize atom economy, (3) use less hazardous chemical synthesis, (4) design safer chemicals, (5) use safer solvents and auxiliaries, (6) design for energy efficiency, (7) use of renewable feedstocks, (8) reduce derivatives, (9) use catalytic reagents, (10) design for degradation, (11) apply real-time analysis for pollution prevention, and (12) choose inherently safer chemistry for accident prevention.[69] These principles have already driven other innovations in conjugated copolymer synthesis, e.g., by replacing Stille coupling or Suzuki coupling with DAP, points (1), (2), (3), (4) and (8) are addressed. Through the development of a novel technique based on DAP, I aim to cover more of the principles and move the conjugated copolymer synthesis further towards green chemistry (Figure 2a).

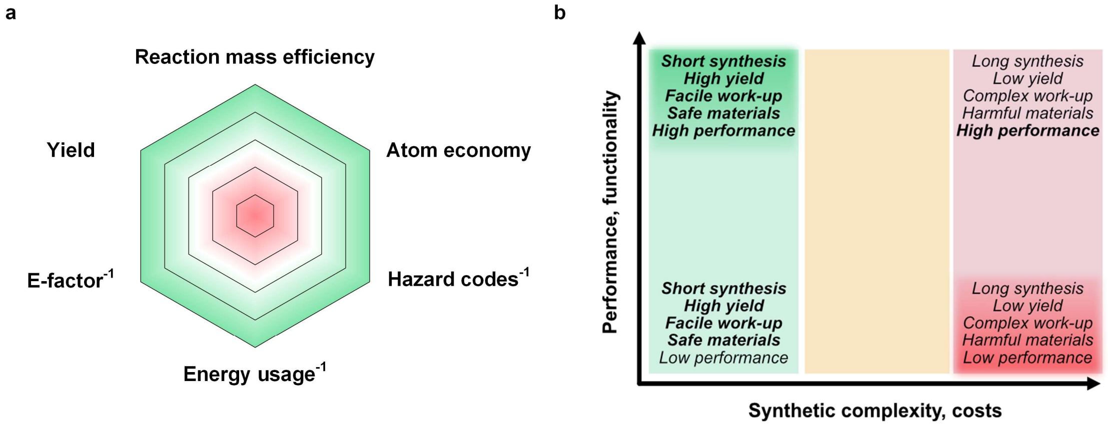


Figure 2. Green chemistry metrics. (a) Quantifiable parameters related to the twelve principles of green chemistry; yield relates to (1), (2) and (8), reaction mass efficiency relates to (1), (2) and (8), atom economy relates to (2), hazard codes relates to (3), (4), (5), (9), (10) and (12), energy usage relates to (6), and E-factor relates to (1), (8) and (9). (b) Representation of synthetic complexity index (SCI) with respect to performance, and associated keywords.

Besides the green chemistry principles as a measure, a key metric explored to evaluate sustainability in this thesis is the synthetic complexity index (SCI).[17] Described by Po *et al.*, the SCI is a method to evaluate the potential of upscaling of synthesis protocols. High-performance devices require high-end materials, which tend to suffer from long syntheses, low yields, and the use of hazardous components. The SCI depicts these factors in order to make an educated decision on whether the synthetic effort is justified (Figure 2b). The SCI considers number of synthesis steps, yield, purification steps and associated hazards of chemicals used. The normalized SCI is defined as Equation 1:

$$SCI = \mathbf{35} \cdot \frac{NSS}{NSS_{max}} + \mathbf{25} \cdot \frac{\log RY}{\log RY_{max}} + \mathbf{15} \cdot \frac{NO}{NO_{max}} + \mathbf{15} \cdot \frac{NC}{NC_{max}} + \mathbf{10} \cdot \frac{NH}{NH_{max}} \qquad (1)$$

where NSS is the number of synthetic steps, RY is the reciprocal yield of the total yield, NO is the number of operations (quenching, precipitation, extraction, filtration/plug, recrystallization, Soxhlet, dialysis, and centrifugation), NC is the number of flash columns or preparative HPLC, and NH is the number of hazard codes. The boldened coefficients have been determined semi-empirically according to overall cost and safety.[17]

2.3 Organic mixed ionic-electronic conductors

Organic mixed ionic-electronic conductors (OMIECs) are a key class of active materials in bioelectronics, wearable electronics, and energy harvesting or storage devices, given their ability to transport both ions and electrons.[1-5] One subclass of OMIECs include conjugated polymers combining polar components, where the aromatic backbone facilitates electronic transport and the polar parts enable ionic transport. Most used examples include conjugated polymers with polar side chains grafted onto the backbone, such as polythiophenes with oligoethylene glycol side chains, [69] or systems like PEDOT:PSS,[70,71] where PEDOT provides electronic conduction and the polyelectrolyte PSS ionic conduction.

Organic electrochemical transistors (OECTs) are among the most explored type of device that incorporate OMIECs, used for e.g., sensing, neural interfacing, and memory devices.[72-76] OECTs operate by modulating the conductivity of the OMIEC channel through redox doping via the electrolyte with simultaneous charge compensation via ion exchange with the electrolyte. Beyond OECTs, other OMIEC-based devices include electrochromic devices which leverage the unique colors of OMIECs in their neutral and doped states, and, by tuning the doping level, modulate the population of these states to get a specific coloration.[77] The desired outputs of these devices, e.g., fast switching and large amplification for OECTs and high coloration efficiency and quick response time for electrochromic devices, as well as other devices such as batteries, are inherently dependent on the properties of the active materials (Figure 3a).

OECTs are sometimes employed to measure the most basic properties of OMIECs such as the charge-carrier mobility (μ) and the volumetric capacitance (C^*), which are also important in other applications (Figure 3a).[70,78] Specifically for OECTs, the transconductance, which is correlated to the product of μ and C^*, i.e. the product of the velocity of charge carriers in an electric field and the number of charge carriers that are accumulated by the OMIEC, is used as a figure-of-merit. The conventional OECT architecture consists of an OMIEC active channel, submerged in an electrolyte solution with a gate electrode suspended into it, connecting a source and drain electrode (Figure 3b).[79] Using a novel technique called small signal analysis designed by Dr. Youngseok Kim, which uses a small alternating current during a voltage sweep, μ and C^* as well as other properties such as conductance, conductivity, and transconductance are acquired simultaneously.[80]

a

Device	Figure(s)-of-merit	OMIEC property
OECT	Transconductance Switching speed Operating window	μ, C^* Transit time, $\sigma_{\text{ion/electron}}$ E_{redox}, V_T
Electro-chromic devices	Coloration efficiency Switching speed Operating window	Band gap, $\sigma_{\text{ion/electron}}$ Transit time, $\sigma_{\text{ion/electron}}$ E_{redox}, V_T
Batteries	Specific capacity Energy density Switching speed Operating window	C^* E_{redox} Transit time, σ_{ion} E_{redox}

b

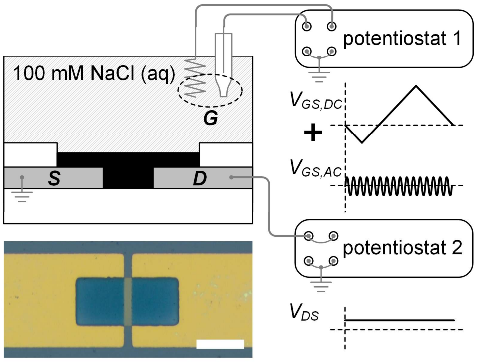


Figure 3. Applications of organic mixed ionic-electronic conductors (OMIECs). (a) Table with outputs from different devices and what OMIEC properties they depend on; μ = mobility, C^* = volumetric capacitance, σ = conductivity, E_{redox} = redox potentials, V_T = threshold voltage. (b) Left: side view of organic electrochemical transistor (OECT) architecture and a picture of a top view of OECT (scale bar = 100 μm); Right: scheme for small signal analysis. From ref [80] (Paper II), adapted and reprinted with permission from Springer Nature.

Throughout this work, OMIEC properties determined via OECT characterization will serve as an electrical performance measure for the synthesized polymers. In this way, after synthesizing materials on a small scale, high-performance candidates can be selected for further investigation into upscaling. Green chemistry principles, the SCI philosophy, and the production/performance trade-off will be integrated into all stages of the synthetic work.

Chapter 3

Aim and objectives

Within this thesis, I explore DAP methods for the preparation of conjugated copolymers that can function as OMIECs. My approach focuses on green chemistry principles and lowering synthetic complexity to facilitate the safe scale up of the preparation of high performance OMIECs – addressing the production/performance trade-off. The following specific research questions are addressed:

1. How can synthetically simple, high-quality monomers be synthesized to suppress direct arylation polymerization β-defect side reactions? (Chapter 4)
2. Which techniques can be used to assess the molecular weight and homocoupling density? (Chapter 5)
3. Which reaction mechanisms enable direct arylation polymerization to proceed under ambient conditions? (Chapter 6)
4. How can ambient direct arylation polymerization be performed in continuous flow? (Chapter 7)
5. How do molecular weight and homocoupling influence the OMIEC electronic properties? (Chapters 5-7)
6. How can direct arylation polymerization be performed in water? (Chapter 8)
7. How can the simplicity and safety of ambient direct arylation polymerization be leveraged in teaching labs? (Chapter 9)

Chapter 4

Insights from thieno[3,2-b]thiophene monomer derivatives

The goal is to synthesize conjugated polymers that act as OMIECs. The total synthesis of the material should address most green chemistry principles, e.g., reaction mass efficiency and derivative minimization, and keep the SCI at a minimum, e.g., by a short synthesis using a minimum of purification operations. Accordingly, direct arylation polymerization (DAP) was chosen to synthesize conjugated polymers as this method aligns well with respect to green chemistry and SCI minimization, by avoiding synthetic steps involving toxic, atom-inefficient, or highly reactive monomer precursors that are required by Stille, Suzuki, and Kumada cross-coupling methods, respectively.

4.1 Synthesis and isolation of thieno[3,2-*b*]thiophene monomer crystals

As a monomer, I chose to use a thieno[3,2-*b*]thiophene with two x-ethylene glycol monomethyl ether chains (g_xTT) as the hydrogen source for DAP. This motif can be accessed in one step, which reflects favorably on SCI.[17,30] The oligoethylene glycol functionality is chosen as it is a common motif to enable a high ion mobility.[3,72,81,82] Given the double substitution, functionalized thieno[3,2-*b*]thiophene only has two reactive C-H bonds, mitigating β cross-coupling that hampers material performance.[65,66] Moreover, the oxygens bound to the thieno[3,2-*b*]thiophene mesomerically impart electron density, which increases the highest occupied molecular orbital (HOMO) making the monomer possess an improved orthogonal reactivity. This is also expected to ultimately facilitate easier oxidation of the conjugated polymer.[37,83-86]

To synthesize g_xTT monomers, I used Ullmann coupling, where copper(I) iodide catalyzes the substitution of bromines on 3,6-dibromothieno[3,2-*b*]thiophene with deprotonated oligoethylene glycol monomethyl ether.[30] Following this protocol with varied conditions (base, solvent), I synthesized a side-chain series from g_0TT to g_4TT (Figure 4). After purification by column chromatography, g_0TT–g_2TT were solids, whereas g_3TT and g_4TT were oils that spontaneously crystallized upon mild cooling, forming crystals that were stable up to 50 °C. This was unexpected as monomers bearing long glycol chains typically require heavy atom substituents (bromine, tin) to crystallize, and such crystals often melt below 0 °C.[87,88]

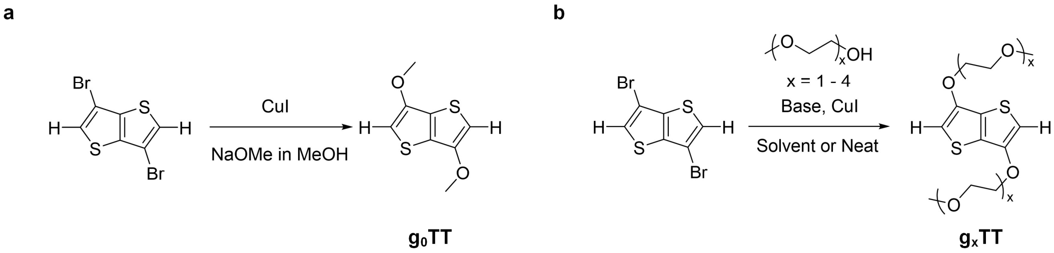


Figure 4. Synthesis of thieno[3,2-*b*]thiophene monomers. (a) Ullmann coupling protocol to g_0TT. (b) Generalized Ullmann coupling protocol to g_1TT to g_4TT. *Unpublished data.*

4.2 Insights of single crystal X-ray analysis and thermal analysis

Single crystals of ample size (20–200 µm) can be analyzed using single-crystal X-ray diffraction (SC-XRD) to elucidate their molecular structure. This confirms molecular isolation and, with thermal data such as melting temperatures obtained by differential scanning calorimetry (DSC), provides insights into molecular interactions.[89-91] These data can then be used for modeling purposes of e.g., the final OMIEC polymers.[88] Accordingly, I grew single crystals of the g_xTT series with vapor diffusion crystallization, in which diethyl ether diffuses into a concentrated solution of g_xTT in chloroform. These single crystals were then analyzed with SC-XRD and DSC (Figure 5).

As the oligoethylene glycol chain extends, molecular packing shifts from π-π herringbone stacking (g_0TT–g_1TT) to a oligoether chain entangled mode (g_3TT–g_4TT) (Figure 5a). The g_2TT compound shows intermediate π-π slip stacking with closely packed oligoethylene chains. This trend appears in DSC thermograms: peak melting temperatures decrease from 140 – 149 °C (π-π stacking) to 56 – 64 °C (entangled oligoether chains) (Figure 5b). The oligoether chains in g_xTT crystals adopt a 7_2-helix conformation identical to the chain conformation in polyethylene oxide (PEO) crystals,[92] analogous to how alkyl chains in alkylated aromatics mimic polyethylene (PE) crystal packing.[93] Unlike alkylated units, that exhibit distinct domains of π-π stacking and PE-like chains as seen for aTT (alkoxylated derivative of g_3TT, see Figure 5c) and other literature compounds,[94,95] these glycolated units with longer chains show no π-π stacking. As oligoethylene glycol chains lengthen, melting temperatures approach that of 7_2-helix PEO (65 – 70 °C),[96] indicating that the encountered crystal polymorphs are primarily dictated by the interactions among the chains. These conformations and interactions have been proposed for conjugated polymers with oligoether side chains but lacked direct evidence until now.[97,98]

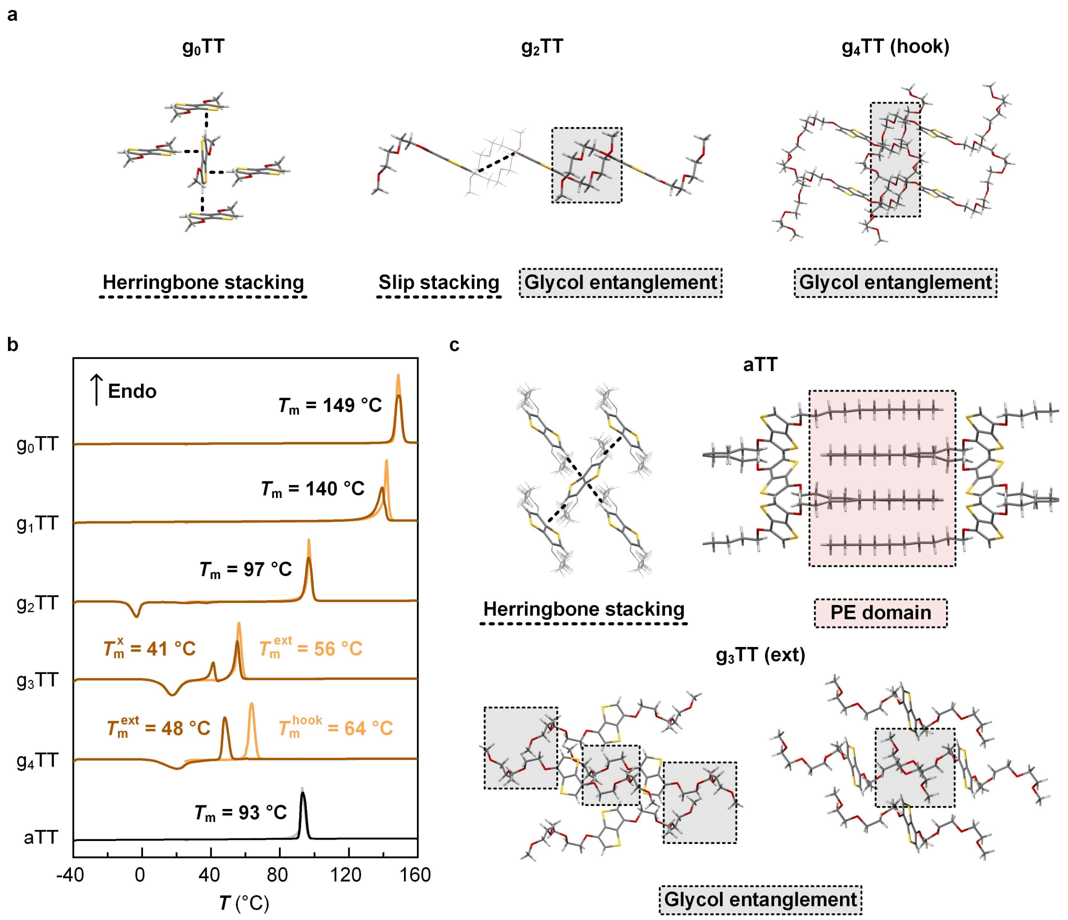


Figure 5. Molecular interactions of g$_x$TT series single crystals. (a) Packing of g$_0$TT, g$_2$TT, and g$_4$TT in solution-grown single crystals. (b) Differential scanning calorimetry heating thermograms of different thieno[3,2-*b*]thiophene crystals (first heating in pale orange/grey; second heating in brown/black). (c) Packing of aTT and g$_3$TT in solution-grown single crystals. Compound aTT synthesized by Di Zhu (Judy). *Unpublished data.*

DSC thermograms of g$_3$TT and g$_4$TT showed multiple melting temperatures (T_m). Melt crystallization was attempted to isolate single crystals of the different T_m, which gave the same polymorph for g$_3$TT and two different polymorphs for g$_4$TT. The lower T_m crystals of g$_3$TT could originate from smaller crystals. For g$_4$TT, the lower T_m polymorph possessed an extended (ext) oligoethylene glycol chain with the same conformation as the PEO 7$_2$-helix. In the other polymorph, the oligoethylene glycol chain makes a 180° twist from the 7$_2$-helix PEO conformation (hook). For g$_4$TT, the hooked polymorph has a higher melting temperature, despite the extended form having π-π stacking, which I attribute to the large increase in Van der Waals contacts in the vicinity of each oligoethylene glycol chain.[99] This showcases the dominance, and hence greater importance, of the oligoether chain interactions compared to π-π stacking at these chain lengths.

To investigate the effect of extending the conjugated system, pendent thiophene groups were attached to g_3TT by *in situ* stannylation of g_3TT followed by Stille coupling with 2-bromothiophene to form T-g_3TT-T. Single crystals were obtained by vapor diffusion crystallization. The resulting polymorph showed π-π herringbone stacking between two aromatic cores and entanglements between four oligoether units, highlighting changes upon extension of conjugation. Unexpectedly, 13 % of thiophene rings adopted a *syn* conformation relative to the thieno[3,2-*b*]thiophene core (Figure 6a). Prior computational and experimental results of comparable conjugated polymers suggest an *anti* conformation, stabilized by through-space electrostatic sulfur-oxygen (S···O) interactions between the thiophene sulfur and glycol oxygen,[98,100] though more recent computational studies challenge this view, suggesting more nuance of the effect.[101] The here presented experimental results suggest that while S···O interactions might be favorable, they are not necessarily the sole thermodynamic minimum of the crystallization process.

Isolated single crystals of the brominated product BrT-g_3TT-TBr featured a planar polymorph with continuous short π-π slip stacking; markedly different from other g_3TT variants (Figure 6b). This originates from halogen bonding combined with π-π stacking, a strong and commonly used interaction in crystal growth and engineering.[102] This shows that, while useful for purification, brominated structures ought to be avoided for modeling and predicting final polymer performance as these interactions may be overestimated and lead to faulty conclusions.

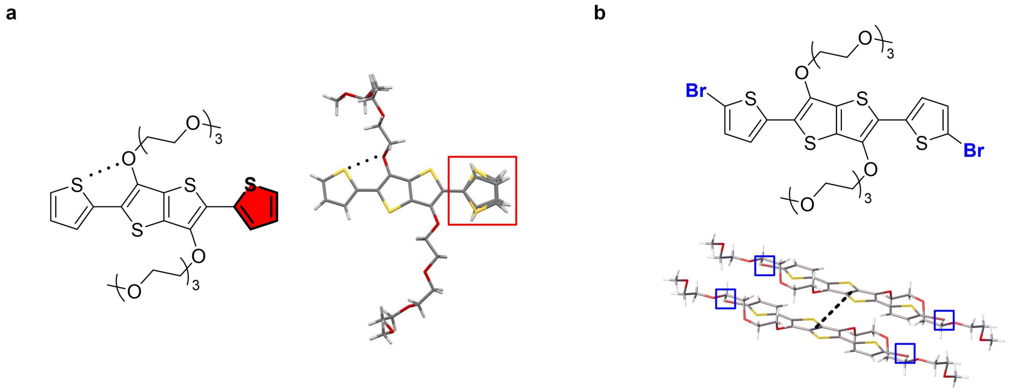


Figure 6. Single crystal X-ray structures of conjugation-extended systems. (a) Structure of T-g_3TT-T structure with (dotted) and without (red) S···O interactions. (b) Structure of BrT-g_3TT-TBr and packing of two molecules in a single crystal where blue boxes indicate bromines and the dotted line slip stacking between aromatic systems. *Unpublished data.*

Chapter 5

Direct arylation polymerization with a thieno[3,2-b]thiophene monomer

Successful synthesis and isolation of the glycolated thieno[3,2-*b*]thiophene series enabled their use for preparing polymers by DAP. The g_3 chain length was chosen as a starting point since it can be expected to provide good processability, impart ionic conductivity, and allow ordering of the final polymer, all while maintaining a high electroactive fraction.[53,54,103]

5.1 Direct arylation polymerization of glycolated thieno[3,2-*b*]thiophene

To assess the versatility of g_3TT, and by extension g_xTT, I initially chose a highly active Ozawa catalyst system for DAP (Figure 7a).[104] I used a Pd(0) catalyst in combination with phosphine ligands, pivalic acid and cesium carbonate under inert conditions in toluene at 110 °C, which would enable coupling of donor-donor, donor-neutral, donor-ambipolar, and donor-acceptor pairs. Using this method, eight novel polymers were synthesized by DAP using g_3TT as the hydrogen source with a variety of dibrominated aromatics as comonomers (Figure 7b). Crude yields were reasonably high, all above 70 %, though the average yield of the chloroform-soluble fraction was only 39 % with the remaining part retained on the filter during Soxhlet purification. This is attributed to the formation of too high molecular-weight polymers, or branching that leads to aggregation, which are insoluble in common processing solvents (and may also gelate and aggregate during the reaction and purification).[66,105]

Cyclic voltammetry of all polymers yielded a clear electrochemical response when using acetonitrile with NBu_4PF_6 as an electrolyte. Instead, only four polymers became conductive in case of an aqueous electrolyte (Figure 7b, top row), a requirement for OMIECs in e.g., bioelectronics. A common feature of these four polymers is their high glycol content (> 50 % mass fraction). This facilitates swelling of the polymer in water, which allows ion ingression, important for OMIECs.[106] These polymers were subsequently used as OECT channel materials by Dr Youngseok Kim using a novel small signal analysis technique that simultaneously determines conductance, conductivity, transconductance, as well as the OECT mobility (μ_{max}) and the volumetric capacitance (C^*_{max}) that make up the figure-of-merit of OECTs, $[\mu C^*]_{max}$.[80] The most promising polymer, p(g_3TT-T2), had a $[\mu C^*]_{max}$ = 432 F cm^{-1} V^{-1} s^{-1}, among the highest values reported for DAP-synthesized polymers. Notably, its μ_{max} exceeded previous DAP compounds, possibly owing to the high degree of order of p(g_3TT-T2) originating from its centrosymmetric thieno[3,2-*b*]thiophene backbone, as compared to many all-thiophene polymers, as well as mitigation of β-defects. Moreover, the shorter synthetic route resulted in a lower SCI than other polymers with comparable $[\mu C^*]_{max}$.[30]

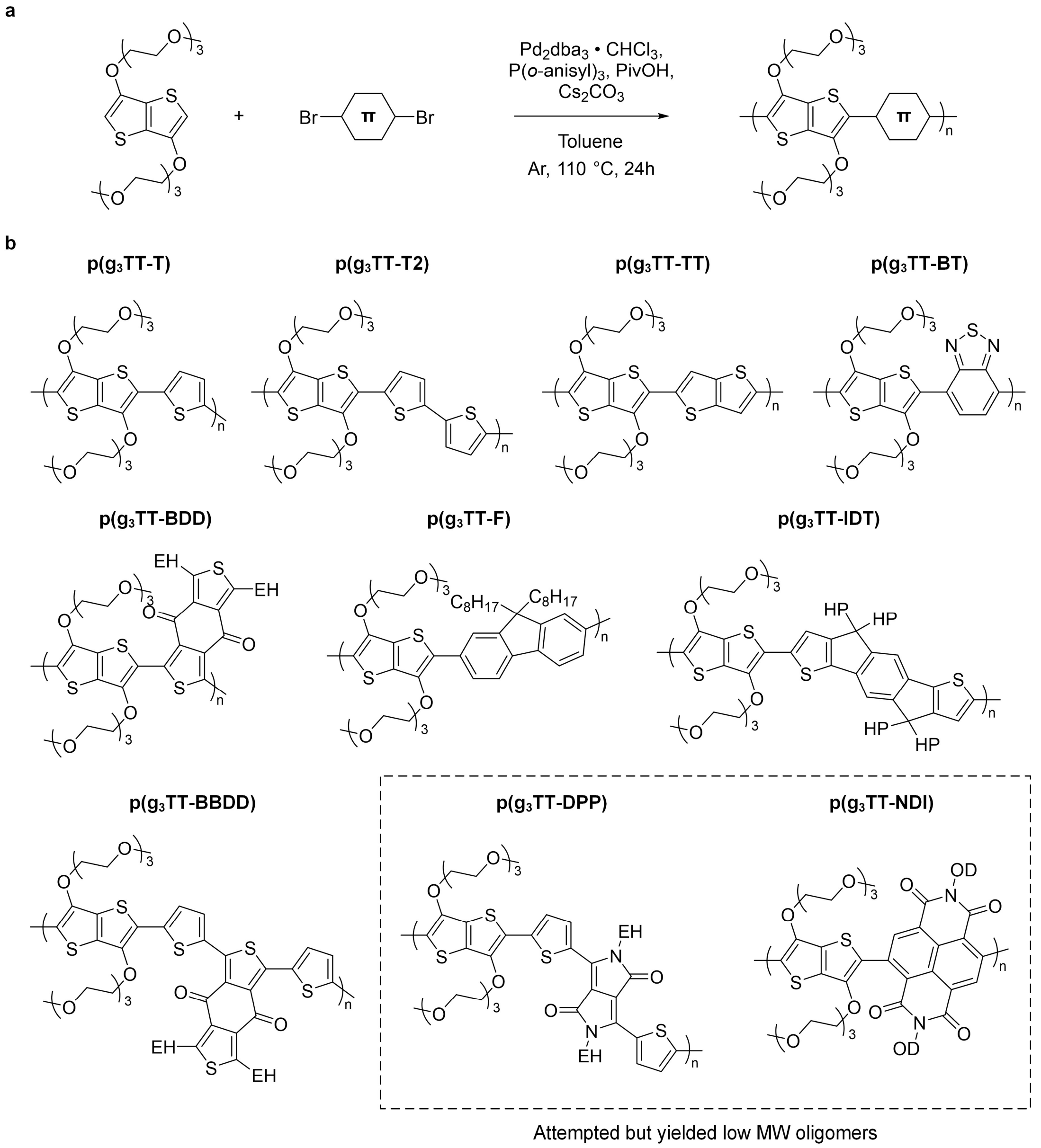


Figure 7 Direct arylation polymerization (DAP) with g$_3$TT. (a) Generalized reaction scheme of DAP under Ozawa conditions for synthesis of g$_3$TT-based polymers. (b) Polymers synthesized by DAP with g$_3$TT. EH = 2-ethylhexyl, HP = 4-hexylphenyl, OD = 2-octyldodecyl.

5.2 Molecular weight determination methods

The properties of polymers depend on their molecular weight, i.e. the chain length.[107-109] Higher molecular weights translate into several beneficial macromolecular properties: adjusted viscosity for processing, improved connectivity via tie chains, reduced influence of end groups, and, specifically for conjugated polymers, a high conjugation length and charge delocalization.[110-114] Thus, determining molecular weight is essential for understanding the material properties and electronic performance of conjugated polymers.

The most employed method is size exclusion chromatography (SEC).[115,116] Polymers pass through a porous gel column; larger chains elute faster, smaller ones slower. SEC is typically calibrated with reference polymers like polystyrene or poly(methyl methacrylate) (PS or PMMA), i.e. a relative calibration, which differ structurally from conjugated polymers leading to systematic errors.[117,118] Universal calibration can correct for this by also considering the intrinsic viscosity of eluding fractions.[119,120] Similar to relative calibration, universal calibration requires Gaussian coil conformations, non-aggregating chains, and consistent polymer-solvent interactions – conditions not easily met by conjugated polymers.[114,121] Successful universal calibration has been done for commercially available P3HT and polyfluorenes,[122] but have not been extensively implemented. Hence, SEC with relative calibration against PMMA was carried out which suggested that some systems only formed oligomers (p(g_3TT-TT) and p(g_3TT-IDT)), while the others had a $M_{n,SEC} > 10$ kg mol^{-1}.

High-temperature ^{1}H NMR (HT-NMR) can be used to determine absolute number-average molecular weight, $M_{n,NMR}$, if end-group signals are visible.[123] The chain length can then be found by comparing the end-group and main-chain signal(s). Heating improves signal resolution by relaxing the polymer chains. Still, it should be noted that errors in HT-NMR are present given the suboptimal signal-to-noise of the end group signals, especially for long polymer chains. For g_3TT-based copolymers, distinct end-group signals appear at 6.40 ppm (TT aromatic proton) and 4.30 ppm (first CH_2 on the side chain) (Figure 8, circles). Hence, absolute $M_{n,NMR}$ can be determined by HT-NMR for the polymers. HT-NMR agreed with results obtained by SEC, corroborating that p(g_3TT-TT) was oligomeric, while the other polymers had molecular weights ranging from $M_{n,NMR} = 13$ to 49 kg mol^{-1}. HT-NMR also supported the likelihood that all polymers were alternating copolymers, as indicated by 1:1 monomer ratios (Figure 8, lines). Thus, HT-NMR successfully provides both insights about molecular weight and composition for g_3TT-based polymers.

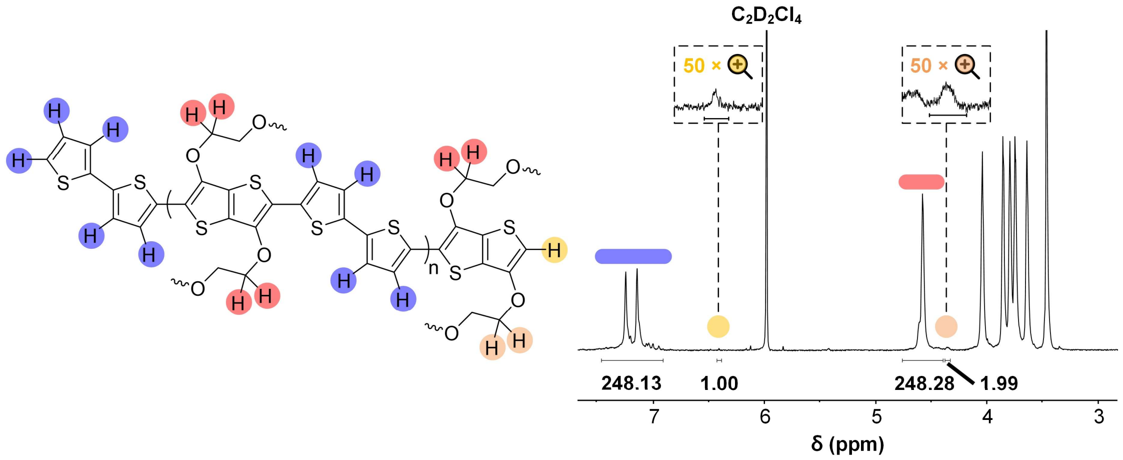


Figure 8. Exemplar high temperature ^{1}H NMR (HT-NMR) spectrum of g$_3$TT-based copolymers. HT-NMR spectrum of p(g$_3$TT-T2) recorded in tetrachloroethane-d$_2$ at 120 °C, allowing end-group analysis by comparing the end-group oligoether CH$_2$ (orange) and the main chain oligoether CH$_2$ (red). By comparison of the main chain oligoether CH$_2$ (red) and aromatic C-H of T2 (blue), chemical composition of the polymer can be determined. From ref [30] (Paper I), adapted and reprinted with permission from RSC.

Both techniques provide molecular weight values but have their shortcomings. SEC is frequently employed in conjugated polymer analysis that provides information about molecular weight distribution and is often regarded as indispensable. Since it only gives relative values based on the standard and column used, changing the analysis conditions (sample, standard, or column) can significantly affect results. This makes comparison between materials more challenging. On the other hand, the use of HT-NMR is limited – the presence of well-resolved end-group signals is not the case for every polymer. HT-NMR only offers absolute number-average molecular weights, not distributions of weights. Moreover, at very high molecular weights, end-group signals become too weak for reliable determination.

Molecular weight measurements of conjugated polymers still require improvement. Ideally, the field should adopt conjugated (co)polymer standards for SEC calibration, as was done for P3HT and polyfluorenes,[122] which can be alkylated, glycolated, or otherwise functionalized. Possibly, given the ability of HT-NMR to accurately determine lower molecular weight g$_3$TT-based polymers, to be combined with insights on viscosity of higher molecular weight polymers, this might serve as an alternative baseline upon which the SEC calibration can be built.

Chapter 6

Ambient direct arylation polymerization

Despite successful DAP to p(g_3TT-T2), chloroform-soluble yield was low (28 %), mostly forming insoluble, high-molecular-weight material. To improve the yield, I attempted to slow the reaction kinetics by switching to a less active catalytic system. I adopted Fagnou DAP conditions, using the Pd(II) catalyst Pd$(OAc)_2$ in presence of pivalic acid and potassium carbonate in *N*,*N*-dimethylacetamide (DMA) at 110 °C.[124] I expected the absence of Pd(0) and phosphine ligands, for reduction of Pd(II) to Pd(0) and ligation, to result in a more gradual polymerization. Instead, the system "supercatalyzed" DAP, producing a gel within one minute.

6.1 Optimization and scope

Intrigued by the fast reaction, I sought to push the system's limits. Conventional DAP often requires high temperatures (> 80 °C), inert conditions, with only limited success in green solvents.[64] Stepwise, I lowered the temperature, removed additives, performed the reaction in air, and switched to the greener solvent *N*-butyl-2-pyrrolidone (NBP) for DAP to p(g_3TT-T2) (Figure 9a). Besides extending the reaction time, lowering the temperature and changing to NBP did not influence the propensity of the polymerization. This would ultimately lead to an air-stable, room temperature DAP, named ambient direct arylation polymerization (ADAP).[125] Reaction under ADAP conditions improved the yield of the chloroform-soluble fraction, likely because lower temperatures cause earlier polymer precipitation. This is reflected in the lower number-average molecular weight for p(g_3TT-T2) isolated in ADAP ($M_{n,NMR}$ = 10 – 20 kg mol^{-1}) compared to DAP ($M_{n,NMR}$ = 39 kg mol^{-1}). The reaction was successfully scaled up to over 100 grams, a feat not often attempted for conjugated copolymer synthesis.

Next, compatibility of other monomers with ADAP was explored. DMA was chosen as the solvent since it showed the fastest kinetics for polymerization to p(g_3TT-T2) during the ADAP optimization. A selection of conjugated polymers was synthesized by ADAP (Figure 9b), spanning a wide range of systems with varying electronic character and glycol, alkoxy and alkyl side chains. A common requirement of ADAP is that the hydrogen source monomer must be electron-rich, which is achieved by a heteroatom on the adjacent carbon to the reactive hydrogen. While this is useful for synthesizing donor materials, it complicates ADAP to acceptor systems.

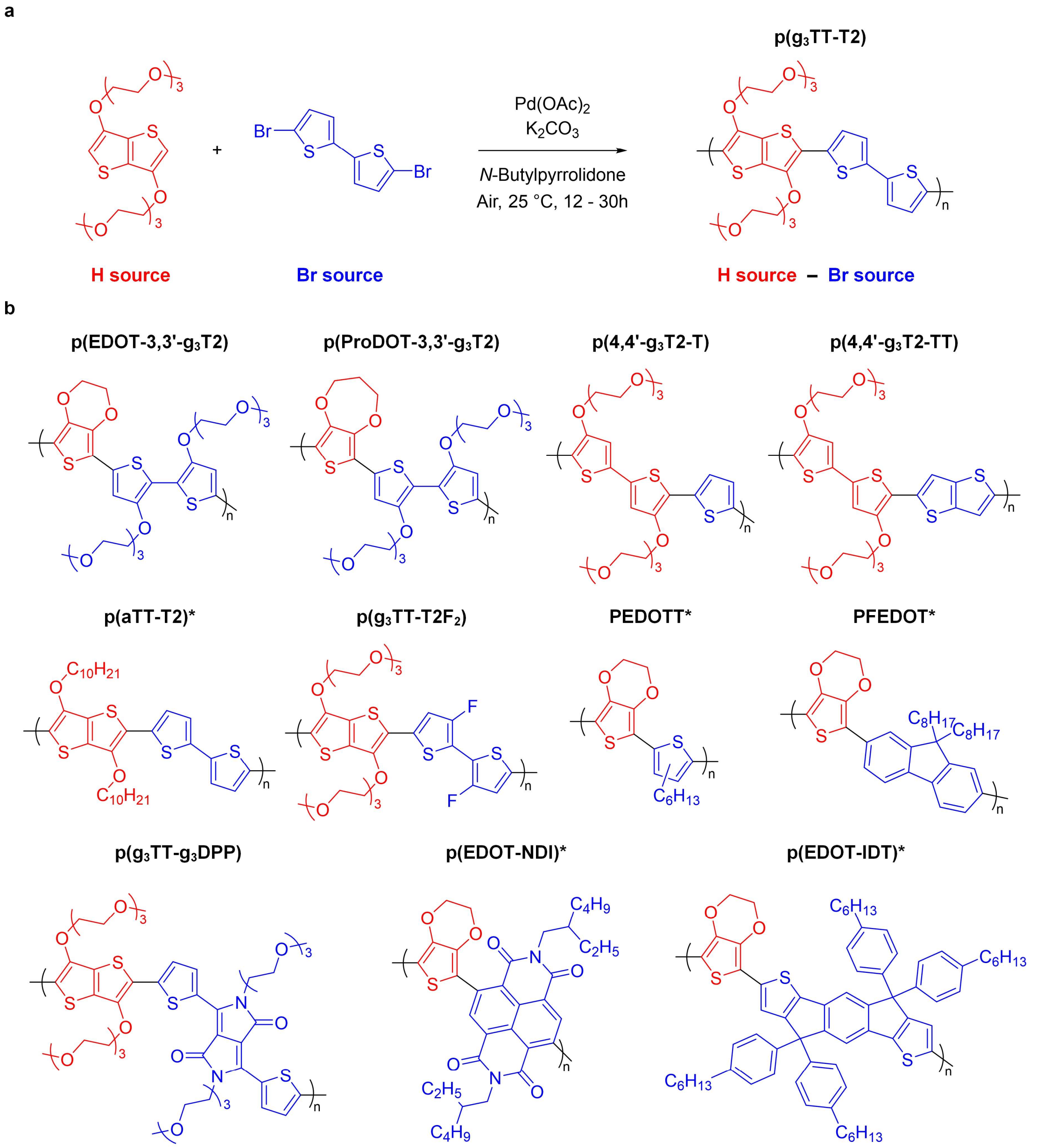


Figure 9. Polymers from ambient direct arylation polymerization (ADAP). (a) Reaction scheme of optimized ADAP for synthesis of p(g_3TT-T2). (b) A selection of polymers synthesized by ADAP with varying electronic character and varying side chains. Polymer p(aTT-T2) synthesized by Di Zhu (Judy). **Unpublished data.*

During this investigation, another study reported inert, room temperature DAP to synthesize p(EDOT-*co*-fluorene) from EDOT and diiodofluorene derivatives.[126] However, there was a striking difference: for my polymers, a higher amount of hydrogen source monomer was incorporated into the final polymer compared to the other work (checked by HT-NMR). This indicated homocoupling of the monomer. Given the change in energy barrier and the presence of homocoupling, I hypothesized the occurrence of a different reaction mechanism.

6.2 Mechanistic and kinetic insights

To study the homocoupling of g$_3$TT, I performed a reaction in absence of the bromine source 5,5’-dibromo-2,2’-bithiophene (T2Br$_2$). Using proton NMR spectra with an internal standard, I identified a diminished aromatic g$_3$TT signal at 6.16 ppm, i.e. consumption of the aromatic hydrogen. LC-MS confirmed the presence of g$_3$TT, the homocoupled product (g$_3$TT-g$_3$TT), and the monomer/palladium complexes (Pd(g$_3$TT)(OAc) and Pd(g$_3$TT)$_2$). This aligns with previously reported observations of bithiophene homocoupling in the presence of 20 mol % Pd(OAc)$_2$.[127] However, while previous reports argued that a double concerted-metalation-deprotonation (CMD) formed Pd(g$_3$TT)$_2$,[127,128] I concluded that homocoupling proceeded via a single CMD to Pd(g$_3$TT)(OAc) (Figure 10, step a) followed by transmetalation between two Pd(g$_3$TT)(OAc) units to form Pd(g$_3$TT)$_2$ and Pd(OAc)$_2$ (Figure 10, steps b and c). This was supported by the absence of conversion at low catalyst loadings (< 1 mol %), indicating a minimum Pd(II) requirement to overcome the bimetallic kinetic bottleneck.[129,130] Since reductive elimination (RE) of Pd(g$_3$TT)$_2$ released g$_3$TT-g$_3$TT and Pd(0) (Figure 10, steps d and e), the homocoupling and oxidative addition of Pd(0) with T2Br$_2$ can be explained.

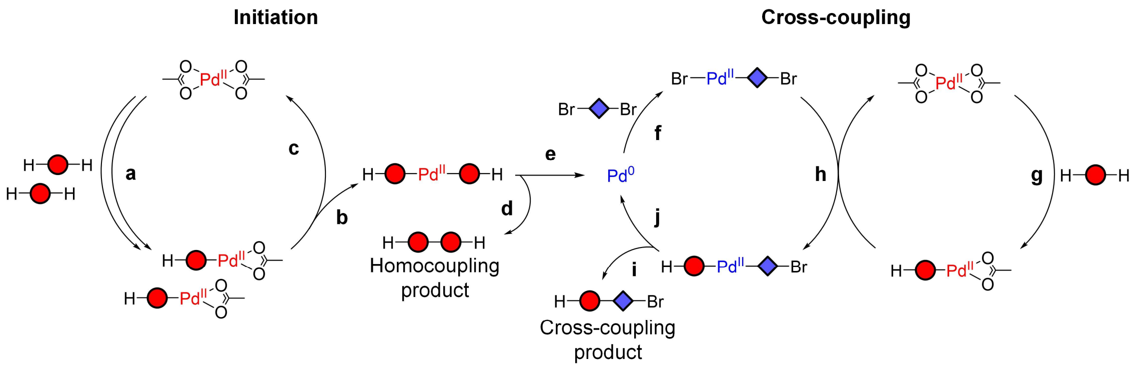


Figure 10. Proposed mechanism for ambient direct arylation polymerization (ADAP). K$_2$CO$_3$ present in excess for acetate regeneration from acetic acid formation and Br abstraction from Pd(II) through KBr formation. From ref [125] (Paper III), adapted and reprinted with permission from AAAS.

Formation of Pd(0) would make it possible for traditional DAP to proceed via OA, LE, CMD and RE (Figure 1d, Chapter 2.1). However, under the same room temperature conditions using a Pd(0) from the start of the reaction, traditional DAP did not initiate. This suggested that i) Pd(II) reacted in some way with T2Br$_2$ in ADAP, ii) Pd(II) was necessary for the cross-coupling step in ADAP, and/or iii) the initiation step of homocoupling in ADAP was essential. The former was disproved by lack of reaction between Pd(OAc)$_2$ and T2Br$_2$ in absence of g$_3$TT.

The latter two points were confirmed. OA can readily occur at room temperature between Pd(0) and $T2Br_2$ to form Pd(T2Br)(Br) (Figure 10, step f).[131] After a CMD between g_3TT and $Pd(OAc)_2$ (Figure 10, step g), transmetalation occurred between Pd(T2Br)(Br) and $Pd(g_3TT)(OAc)$ (Figure 10, step h). This formed $Pd(g_3TT)(T2Br)$ and, in presence of excess acetate, $Pd(OAc)_2$. Subsequent RE of $Pd(g_3TT)(T2Br)$ gave the cross-coupled product g_3TT-T2Br and Pd(0), which restarted the cycle (Figure 10, steps i and j). The minimum palladium requirement for transmetalation was also observed here; at low catalyst loading, neither homocoupling nor cross-coupling would occur.[130] This suggested a Pd(II)/Pd(II) bimetallic initiation cycle, followed by a Pd(II)/Pd(0) bimetallic cross-coupling cycle. This mechanistic change would explain the different energetics involved and hence the low temperature reaction.

To better understand the kinetics of this reaction, several solvent systems were analyzed. ADAP would not initiate in all solvents – at least 20 % (v/v) of a solvent with an amide group was required, possibly owing to its high polarity and ability to ligate to the palladium catalyst.[132,133] This polarity and ligation trend was confirmed by comparing *N*,*N*-dimethylformamide (DMF) and *N*-methyl-2-pyrrolidone (NMP) in the solvent series with DMA and NBP. With decreasing polarity according to DMF > DMA > NMP > NBP,[134] kinetics slowed. It could also be argued that the ligation potential to the palladium catalyst decreases, as the solvent becomes increasingly sterically hindered. Regardless, the reaction proceeded in all solvents, which was promising for systems that might not be as polar as the one considered here (e.g. glycol *versus* alkoxy/alkyl). In fact, in scoping experiments (Figure 9, p(aTT-T2), PEDOTT, PFEDOT, p(EDOT-NDI), and p(EDOT-IDT)) polymerizations in NBP reached higher molecular weights whilst proceeding at similar rates as in DMA. All in all, the use of NBP in ADAP opens the way to more green conjugated polymer syntheses at lower temperatures in air, posing fewer risks for large scale production.

6.3 Correlation between synthesis, nanostructure and performance

Two of the biggest concerns with regard to ADAP are the homocoupling defects and the stoichiometric imbalance leading to a low degree of polymerization (DP). Both factors often result in inferior electrical properties.[135,136] Surprisingly, despite higher homocoupling amount and lower DP, the OMIEC figure-of-merit $[\mu C^*]_{max}$ from ADAP improved upon those from DAP: from 432 to 963 F cm^{-1} V^{-1} s^{-1} for $p(g_3TT\text{-}T2)$, from 5.8 to 38.9 F cm^{-1} V^{-1} s^{-1} for $p(ProDOT\text{-}g_3T2)$, and from 2.5 to 1112 F cm^{-1} V^{-1} s^{-1} for $p(EDOT\text{-}g_3T2)$ (Figure 11a). At the same time, all ADAP compounds had lower SCI values compared to analogous DAP-synthesized compounds which already compared favorably to the rest of the field.

UV-vis-NIR spectroscopy and grazing-incidence wide-angle X-ray scattering (GIWAXS) of thin films of polymers prepared by ADAP showed improved order as evidenced by emergence of vibronic peaks as well as additional lamellar diffractions and π-stacking diffraction, respectively (Figure 11b and Figure 11c). This order possibly originated from the inclusion of more rigid units (especially g$_3$TT and EDOT) and the lower molecular weight since shorter chains can crystallize more easily owing to a lower viscosity.[137,138] The high degree of order aided electrical transport, supported by mostly consistent C^*_{max} values but improved μ_{max}. Another consequence from higher order is that the oxidation onset, measured by cyclic voltammetry, occurs at a lower potential for ADAP polymers. This also translates to earlier onsets in OECT devices, i.e. a lower required threshold voltage to introduce charges. Besides structural order, I suspect that these earlier onsets can also be attributed to a higher content of electron-rich hydrogen source monomer, [121,128] raising the HOMO level. It must be noted that ADAP aids the electrical performance for OMIEC materials, though this is not generic behavior for all applications and monomer combinations.

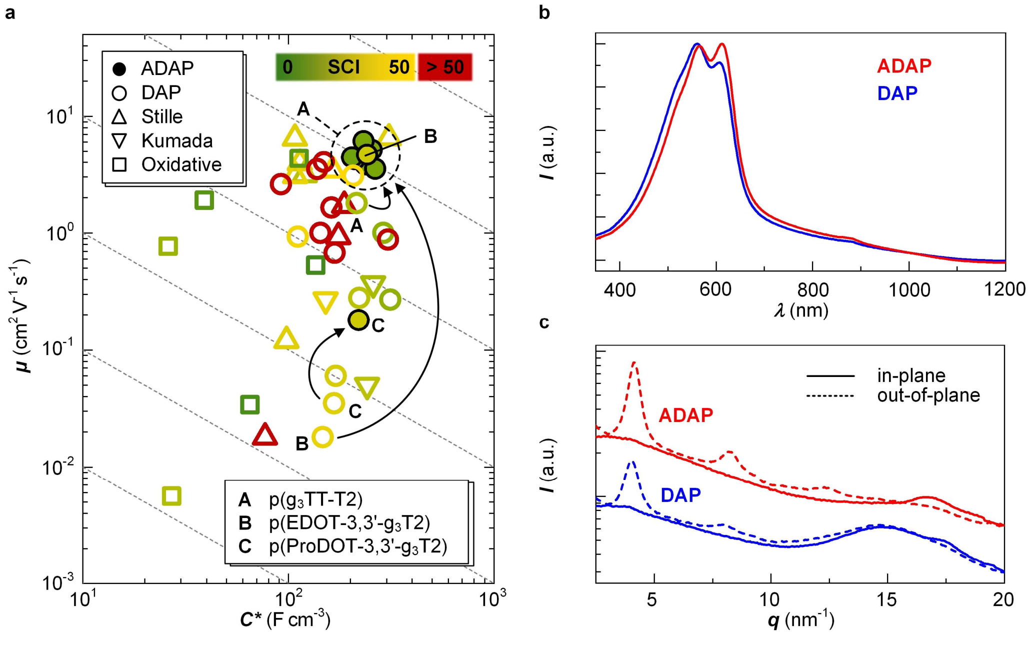


Figure 11. Performance and nanostructure of ADAP-synthesized polymers. (a) Ashby plot comparing C^*_{max}, μ_{max}, and SCI of different OMIECs. (b) Comparison between UV-vis-NIR spectra of ADAP- and DAP-synthesized p(g$_3$TT-T2). (c) Comparison between GIWAXS diffractograms of ADAP- and DAP-synthesized p(g$_3$TT-T2). GIWAXS measured by Jesika Asatryan. From ref [125] (Paper III), adapted and reprinted with permission from AAAS.

Chapter 7

Direct arylation polymerization in flow

Flow polymerization in steady-state conditions is a viable route to obtain materials with more consistent properties, avoiding the variation, e.g., molecular weight that tend to occur in case of batch synthesis.[139,140] The rapid polymerization of g_3TT and $T2Br_2$ under ADAP conditions makes this system an ideal candidate for fast continuous flow synthesis.

7.1 Conjugated polymer synthesis in flow

The aim is to perform the polymerization using droplet flow, where each droplet acts as an individual reactor.[139,140] This improves reproducibility by averaging properties across thousands of microreactions. Previous work relied on highly demixing perfluorinated alkyl substance (PFAS, a "forever chemical") carrier fluid for creation of droplets, which is preferably avoided.[141]

Translating DAP to flow is already inherently difficult,[142,143] since the necessary inorganic bases (e.g., potassium carbonate) are insoluble in common DAP solvents (e.g., toluene). To prevent clogging of the flow set-up, a base-loaded solid-phase reactor is usually connected in-line.[142] However, this approach necessitates frequent base regeneration and negates steady-state conditions. Moreover, a solid-phase reactor is not compatible with droplet flow. For an ideal system, I set four requirements: i) form stable reaction droplets, ii) avoid PFAS as a carrier fluid, iii) eliminate the base-loaded solid-phase reactor and iv) complete the reaction in under 30 minutes.

7.2 Translating ambient direct arylation polymerization in batch to flow

Since ADAP requires polar amide solvents, I first tested their ability to dissolve inorganic bases (Figure 12a). While a potassium carbonate solubility of $0.75\ \mathrm{g\ L^{-1}}$ in DMF has been reported,[144] actual solubility was negligible. Instead, I attempted to dissolve hydroxide, acetate, and phosphate salts at the minimum required 150 mM, without success. Potassium *tert*-butoxide and sodium methoxide were soluble at this concentration in DMF and DMA but did not initiate polymerization.

In case of direct arylation of small molecules, inorganic bases have in some cases been replaced with liquid organic bases like triethylamine and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (Figure 12a).[145-147] However, implementation under ADAP conditions did not initiate polymerization. Next, I explored the possibility of imidazolium acetate ionic liquids and an in-lab created [HDBU][OAc] (DBA + acetic acid) ionic liquid (Figure 12a).[148] Though not used in direct arylation before, I intended to use the ionic liquids as acetate sources that fully mix with the reaction solvent. Despite no phase separation, no reaction occurred, possibly due to strong ion-pair formation and hence lack of reaction.

Instead of changing the base, I searched for a co-solvent that dissolves inorganic bases and mixes with the required amide solvent. This approach was based on two observations that I had made while optimizing the ADAP reaction: i) ADAP requires only ~ 20 % v/v amide solvent to proceed and ii) ADAP works in NMP:water mixtures. Solubility tests showed that an NMP:water (9:1 v/v) mixture dissolved the base (potassium acetate), catalyst, and monomers (Figure 12b). This ratio was chosen as less water precipitated the base while more water precipitated the $T2Br_2$ monomer.

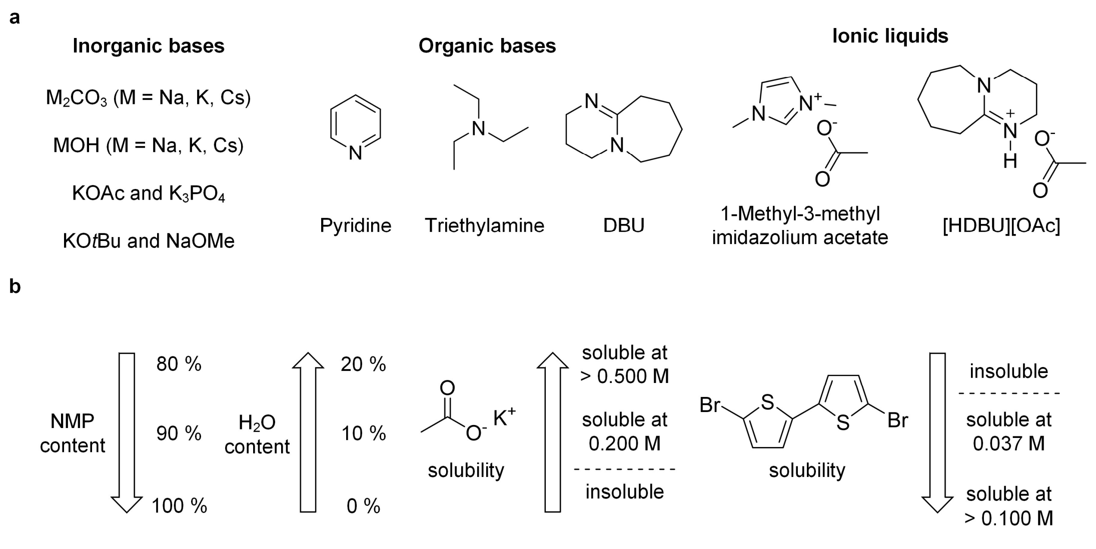


Figure 12. Base solubility tests. (a) Bases checked for solubility in amide solvent. (b) Relation between NMP:water content, solubility of potassium acetate, and solubility of $T2Br_2$.

Given the hydrophilicity of the NMP:water mixture, the solvent choice conveniently allowed for replacement of the PFAS carrier fluid with hydrophobic silicone oil or an isoparaffin solvent. Their suitability was confirmed by the inability to mix with NMP:water. Silicone oil was selected over isoparaffins given the latter is a carcinogen. Stable droplet formation was achieved by feeding NMP:water through a small outer diameter tube into a larger tube carrying the silicone oil. Together with Hannes Schomaker, the polymerization was translated successfully to a Vapourtec flow system. The polymerization proceeded in four steps: i) mixing $Pd(OAc)_2$ stock solution with monomer/base stock solution, ii) droplet formation, iii) polymerization in the reactor, and iv) polymer collection (Figure 13). To complete polymerization within 30 minutes, the reactor was heated to above 100 °C. These high temperatures required deoxygenation and degassing of stock solutions to prevent catalyst deactivation by oxidative side reactions and to avoid expansion of gases in the flow reactor. A backpressure regulator was also needed to prevent boiling of water.

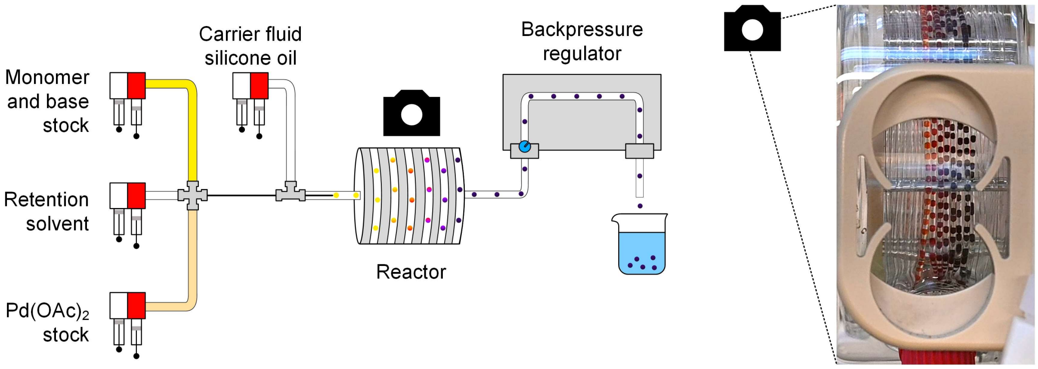


Figure 13. Direct arylation in droplet flow. Schematic of flow synthesis setup; image to the right showcases NMP:H_2O reaction droplets inside silicone oil in the reactor. Flow system set up with help of Hannes Schomaker. From ref [125] (Paper III), adapted and reprinted with permission from AAAS.

The flow reaction was successful, as evidenced by near-stoichiometric conversion to the chloroform-soluble fraction, little molecular weight variation ($M_{n,NMR}$ = 11 ± 1 kg mol^{-1}), and consistent ADAP homocoupling artefacts (1.5 ± 0.8 %), shown by the mean ± standard deviation of ten batches. Flow-synthesized samples show less homocoupling compared to batch samples (3.1 ± 1.4 %). I suspect a shift in preference of initiation and cross-coupling transmetalation at these temperatures – possibly, cross-coupling transmetalation is more endothermic and accelerates more at higher temperatures. Flow samples also show consistent OECT device performance: μ_{max} = 1.7 ± 0.2 cm^2 V^{-1} s^{-1}, C^*_{max} = 224 ± 12 F cm^{-3} V^{-1} s^{-1}, giving $[\mu C^*]_{max}$ = 378 ± 77 F cm^{-1} V^{-1} s^{-1}. These values match batch-synthesized DAP p(g_3TT-T2), despite lower molecular weight and the presence of homocoupling, which indicates that flow-synthesized ADAP polymers are indeed promising.

Chapter 8

Direct arylation polymerization in water

Oxidative homopolymerization of S-EDOT in water to produce highly conductive, water-soluble S-PEDOT (Figure 14) represents a major advancement.[149] This material falls in the library of conjugated polyelectrolytes, which have regained popularity given their relevance in bioelectronics.[14,150] Although there exists a broad library of conjugated copolymers that are ultimately water-processable, the synthesis of such copolymers *directly in water* (without the use of co-solvents or surfactants) remains a significant challenge.[151-154] To realize a water direct arylation polymerization (WaDAP) to copolymers, (at least one of) the reagent monomers, as well as the active catalyst and product polymer must be water-soluble.

8.1 Synthesis of water-soluble monomers

Due to the hydrophobic nature of conventional monomers for organic electronics, water-soluble side chains are needed. Ideally, these have an ionic group such as a carboxylate in case of the water-processable PCAT-K or a sulfonate in case of PCPDTBT-SO_3K (Figure 14).[155,156] As monomers with these side chains are not easily accessible, I designed a general synthetic route for functional diversification.

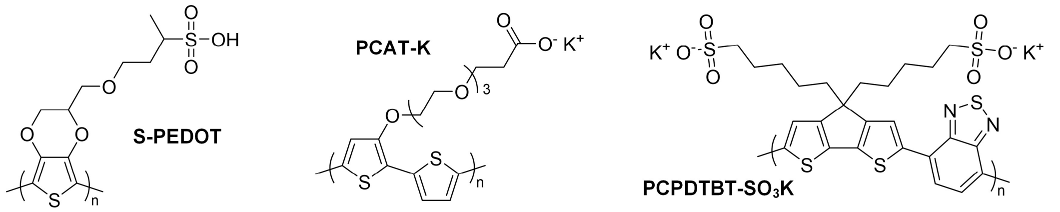
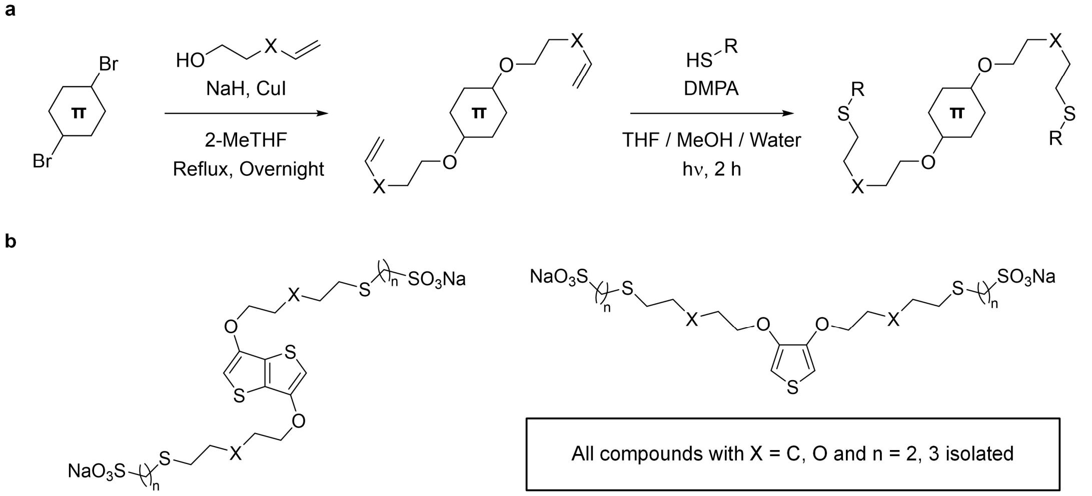


Figure 14. Water-processable conjugated polymers.

Click chemistry is an often-employed, straightforward technique to synthesize compounds in high yields.[157] The thiol-ene click reaction leverages the weak sulfur-hydrogen bond of a thiol and the long lifetime of sulfur radicals to attack alkenes in the primary position.[158] Many commercial ionic thiols, such as sodium 2-mercaptoethanesulfonate, are water-soluble. Alcohols can be attached to aromatics by Ullmann coupling, as seen for bis-glycolated thieno[3,2-*b*]thiophenes (Chapter 4). Ullmann coupling of alkenols (with a terminal alkene on one end and an alcohol on the other) followed by a thiol-ene click reaction with ionic thiols should yield water-soluble monomers (Figure 15a).



All compounds with X = C, O and n = 2, 3 isolated

Figure 15. Synthesis of water-soluble monomers. (a) General synthesis protocol to water-soluble monomers via Ullmann coupling followed by thiol-ene click chemistry. (b) Successfully synthesized water-soluble thieno[3,2-*b*]thiophene and thiophene monomers. Thiophene-based monomers synthesized by Ts-Pei Chen. *Unpublished data.*

With assistance from Ts-Pei Chen, I synthesized eight sulfonated, water-soluble monomers (Figure 15b). Ullmann coupling and isolation of the product were achieved in a similar manner as already described (Chapter 4). The thiol-ene reaction used a THF/methanol/water mixture to dissolve the aromatic unit, radical initiator (DMPA), and ionic thiol. A handheld UV lamp was used to homolytically cleave the central carbon-carbon bond in DMPA to ultimately form methyl radicals, which rapidly abstracted hydrogen from the thiol to yield a sulfur radical species.[158] The initially turbid solution quickly became clear. Stoichiometric conversion within hours was confirmed by TLC, but isolation of the products was non-trivial. One reason is that the thiol-ene click reaction requires a large excess of ionic thiol to maximize yield by making it the highest concentration radical species. This causes some sulfur-sulfur bond formation as a termination side product. The thiol reagent, disulfide side product and the product are all solids that show similar solubilities in various solvents; i.e., precipitation or crystallization cannot be used for purification. Reverse-phase column chromatography, a non-scalable and expensive purification technique, was the only method to reliably isolate the product. Future efforts to avoid chromatography could include lowering thiol excess or using scavengers to remove residuals.[159-161]

8.2 Synthesis of a water-soluble catalyst

In-water polymerization to conjugated polymers has many possible approaches considering the catalyst. Given the presumption that Pd(0) is often necessary while its complexes are unstable in water, heterogeneous catalysis with Pd(0) nanoclusters, and those stabilized by surfactants, is a common method for in-water reactions. This has been employed in e.g., Suzuki coupling of small molecules, and hence could present a possible pathway to the polymers.[162-164] A workaround is the use of water/organic solvent emulsions such as DAP in water/cymene mixtures, where Pd(II) from $PdCl_2(PPh_3)_2$ is reduced *in situ* to Pd(0), and the subsequent Pd(0) is possibly stabilized in the cymene bubbles by phosphine ligands.[165] However, the aim here is to do polymerization exclusively in water.

In situ reduction of a Pd(II) species by a water-soluble phosphine ligand can yield a homogeneous mixture and lead to successful polymerization. For instance, copolymerization of ethene and carbon monoxide in water,[166] and the Suzuki coupling of small arenes,[167] were accessible by using water-soluble sulfonated bidentate phosphine ligands and zwitterionic bidentate phosphine ligands, respectively. Another successful ligand is sulfonated N-heterocyclic carbene used in the aerobic oxidation of phenyl alcohols.[168] All these ligands, however, must undergo expensive, long and anaerobic synthetic routes. Given that ADAP uses monomer homocoupling to reduce Pd(II) (Chapter 6), and it proceeds in the presence of a significant amount of water, as seen in flow (Chapter 7), possibly the ADAP scheme can be used as a starting point for WaDAP.

I started by checking the solubility of multiple commercial Pd(II) catalysts in water (Figure 16a). The water contained potassium carbonate and acetic acid, since carboxylates are necessary for ADAP. Reference $Pd(OAc)_2$ formed a brick-colored suspension with floating solids. Among the other catalysts, namely $PdCl_2$, $PdCl_2(en)$, $Pd(NH_3)_4Cl_2{\cdot}H_2O$ and $Pd(NO_3)_2{\cdot}2H_2O$, the first two exhibited similar behavior while the latter two formed an additional insoluble, fluffy grey precipitate. $Pd(NH_3)_4Cl_2{\cdot}H_2O$ and $Pd(NO_3)_2{\cdot}2H_2O$ have been used prior for creating immobilized Pd(II) nanoparticles, by dissolving in water and then impregnating into a matrix, i.e. they are soluble in water and then bind to reactive surfaces or with reactive ligands.[169,170] In my case, these precursors reacted with acetate to form brick-colored $Pd(OAc)_2$. However, another reaction occurred to form the fluffy grey solid, which I attribute to $Pd(OH)_2$ formation due to the basicity of potassium carbonate. Since ADAP proceeds in basic conditions, this further complicates catalyst synthesis and utility.

To address the insolubility of palladium catalysts in water and the formation of $Pd(OH)_2$, I chose to use multifunctional ligands. At least one carboxylic acid was required to attain carboxylate functionality in the final catalyst necessary for ADAP. Together with Johanna Heimonen, I developed a protocol for preparing water-soluble Pd(II) catalysts (Figure 16b). In simple terms, a water-soluble palladium precursor is dissolved in water and subsequently mixed with a solution of water-soluble ligand. Using this method, we synthesized multiple structurally distinct catalysts. The formation of stable water-soluble catalysts (over 24 hours before precipitation) was confirmed by visual inspection (Figure 16c).

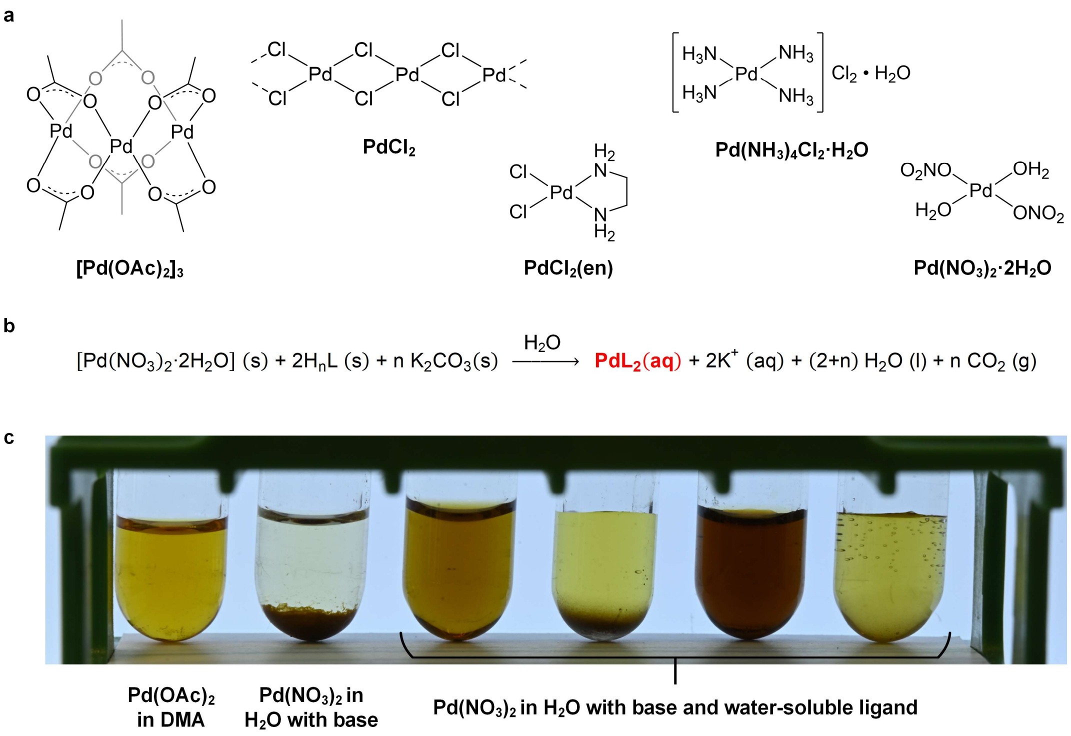


Figure 16. Synthesis of water-soluble palladium catalysts. (a) Most stable structural forms of different palladium catalysts and palladium catalyst precursors. (b) General protocol for preparation of water-soluble palladium catalyst PdL_2 from $Pd(NO_3)_2{\cdot}2H_2O$, water-soluble ligand and base. (c) Stability/solubility test of water-soluble palladium catalysts. *Unpublished data.*

8.3 Initial scoping of direct arylation polymerization in water

With novel water-soluble monomers and catalysts in hand, scoping reactions of WaDAP were conducted (Figure 17a). Catalyst solutions were freshly prepared using the established protocol (Figure 16b). No additional inorganic base was added to avoid precipitation of $Pd(OH)_2$. Instead, the ligand used to solubilize Pd(II) was added in 20-fold excess with respect to the catalyst, serving both as the ligand and the base. This solution was added to a vial containing hydrogen source monomers (described in Section 8.1) and a water-soluble bromine source, a dibrominated thiophene with oligoether chains and a pendent carboxylate (CAT-K), a precursor to PCAT-K synthesized by Johanna Heimonen (Figure 14).[155] To determine the temperature needed to initiate the reaction, the mixture was heated from 30 °C to 100 °C in 10 °C increments. A color change at 60 °C indicated initiation. Aware of possible catalyst degradation in high-temperature solutions containing oxygen (Chapter 7), I ensured that all subsequent reactions were deoxygenated.

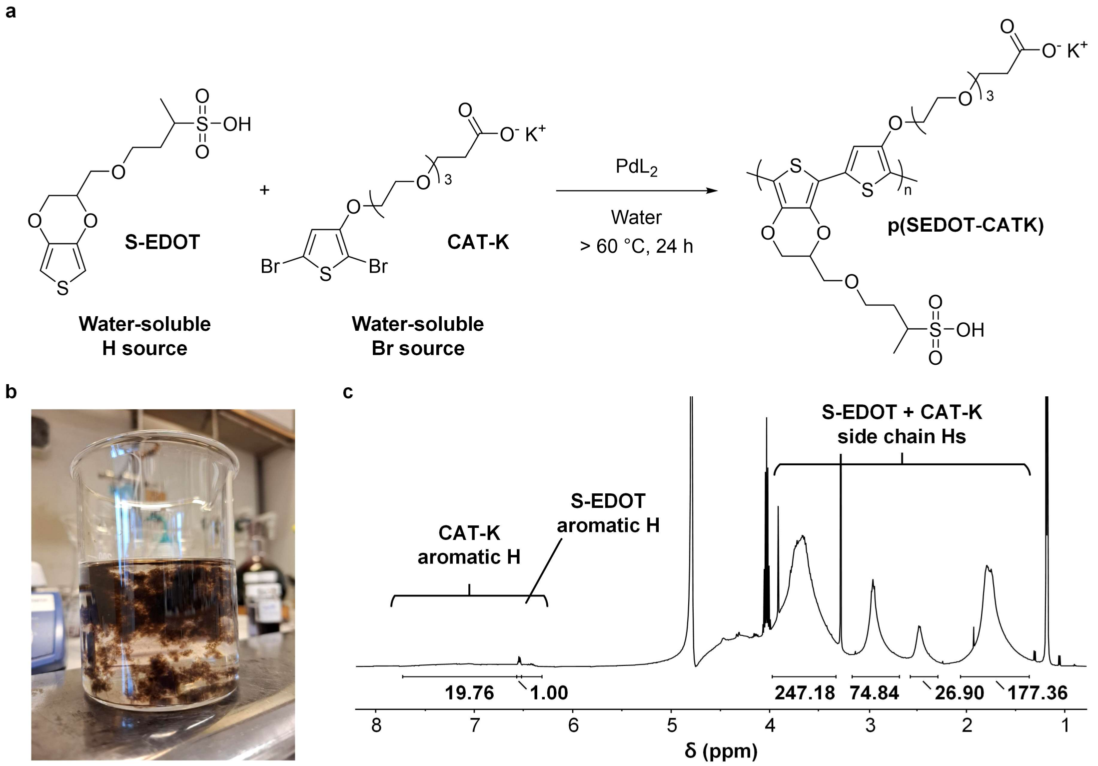


Figure 17. Scoping of water direct arylation polymerization (WaDAP). (a) Exemplar reaction scheme of WaDAP between S-EDOT (hydrogen source) and CAT-K (bromine source) to form p(SEDOT-CATK). (b) Picture of precipitation of WaDAP-synthesized polymer into isopropanol. (c) ^{1}H NMR spectrum of p(SEDOT-CATK) in D_2O (δ 4.80 ppm, 298 K). Monomers synthesized by Johanna Heimonen. *Unpublished data.*

Reactions using thieno[3,2-*b*]thiophene as the hydrogen source proceeded at a similar rate with a comparable final material consistency (brown-red fibrous material upon precipitation in isopropanol; Figure 17b) regardless of the catalyst used. This success prompted polymerization attempts with a water-insoluble bromine source, 2,5-dibromothiophene, which showed promising signs of initiation as indicated by a brown-red reaction mixture. On the other hand, using thiophene with water-soluble side chains as the hydrogen source did not always result in a polymeric product. Possible explanations include the relatively high steric hindrance of the doubly substituted thiophene compared to thieno[3,2-*b*]thiophene with the same functionalization and/or less-activated C-H bonds given the lower electron density of thiophene. These factors could lead to a more sluggish initiation and cross-coupling cycle. Steric hindrance appears particularly convincing, as the water-soluble monomer S-EDOT (Figure 17a),[149] also based on thiophene but more ordered owing to the ethylenedioxy ring, reacted readily when using the WaDAP system, even with 2,5-dibromothiophene.

Initial analysis of the polymerization was performed by NMR (Figure 17c). For p(SEDOT-CATK), the room temperature NMR in D_2O showed a significant reduction in the S-EDOT aromatic proton peak around 6.5 ppm relative to the side chains, along with notable broadening of the side-chain signals. Overall, the WaDAP recipe offers a promising strategy for conducting direct arylation in water when using the novel water-soluble Pd(II) catalysts without the need of any solubilizing or stabilizing additives.

Chapter 9

Ambient direct arylation polymerization; a basis for teaching

Conjugated polymers have become an integral part of natural science curricula. They are now routinely included in lectures on polymer synthesis and optoelectronic materials,[171-173] and even outreach kits exist for high schools.[174] To foster this interest, I set out to create an undergraduate/graduate/PhD lab course suitable for many natural science curricula where students synthesize conjugated copolymers and analyze their properties.

9.1 The conjugated polymer curriculum challenges

Despite the presence of conjugated polymer courses in many natural science curricula, hands-on work with conjugated polymers for students is less common. Not many institutions can offer conjugated polymer teaching labs, and, if they do, oftentimes they would mainly focus on homopolymerizations such as Grignard metathesis polymerization to P3HT or Gilch polymerization to poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV).[175,176] Teaching labs implementing conjugated copolymer synthesis are even less common, as institutions might be dissuaded given several challenges:

1. **Price**: At research scale, monomers for conjugated polymers often cost on the order of €50 to €100 per gram, while the final conjugated (co)polymers themselves can reach €500 to €1,000 per gram.[177]
2. **Equipment**: Synthesis of conjugated copolymers requires specific conditions. For instance, most synthesis protocols must be performed under an inert atmosphere which is most easily safeguarded with e.g., a Schlenk line or a glovebox. These are costly and possibly of limited availability in teaching labs. Moreover, analytical techniques following the synthesis, such as NMR or SEC, are not always available.
3. **Safety**: Robust polycondensation reactions used to synthesize conjugated copolymers carry significant safety concerns for the students, e.g., high toxicity of tin compounds in case of Stille coupling or aromatic solvents in case of Suzuki coupling.
4. **Failure**: Conjugated polymers are difficult to synthesize. Conjugated polymer synthesis is influenced by many factors (e.g., inert atmosphere, catalyst condition, stoichiometric balance, etc.) and prone to fail if even one of these conditions is not perfectly met. Moreover, teaching assistants (usually graduate students) often lack

experience with the synthesis of conjugated polymers (which offer their own nuances *versus* traditional polymer synthesis) to be able to advise during practical lab courses. With respect to the morale of the students, this can have a detrimental effect on their interest in the field.

9.2 Accessible ambient direct arylation polymerization schemes

ADAP has been shown to work with several monomer combinations. As a general requirement, the hydrogen source monomer must be activated by the heteroatom on the carbon adjacent to the reactive C-H bond. As a hydrogen source, 3,4-ethylenedioxythiophene (EDOT) is a commercially available ADAP monomer that is cost-effective compared to many other building blocks for conjugated polymers (€1/g*). As a bromine source, possible lower cost monomers are 2,5-dibromo-3-hexylthiophene (Br-3HT-Br, €3/g*), also used for P3HT synthesis,[175] and 2,7-dibromo-9,9-dioctylfluorene (Br-F8-Br, €1/g*). Combining this with prices of the catalyst, base and NBP solvent, these polymers can be synthesized at a cost of less than €10/g* (70 % yield of reaction), cheaper than e.g., regioregular-P3HT at €135/g*. Br-3HT-Br and Br-F8-Br monomers have not been used in ADAP, so I started by checking their propensity for ADAP with EDOT (Figure 18a). Both reactions readily initiated, as indicated by the quick change from colorless to deep red solutions (Figure 18b).

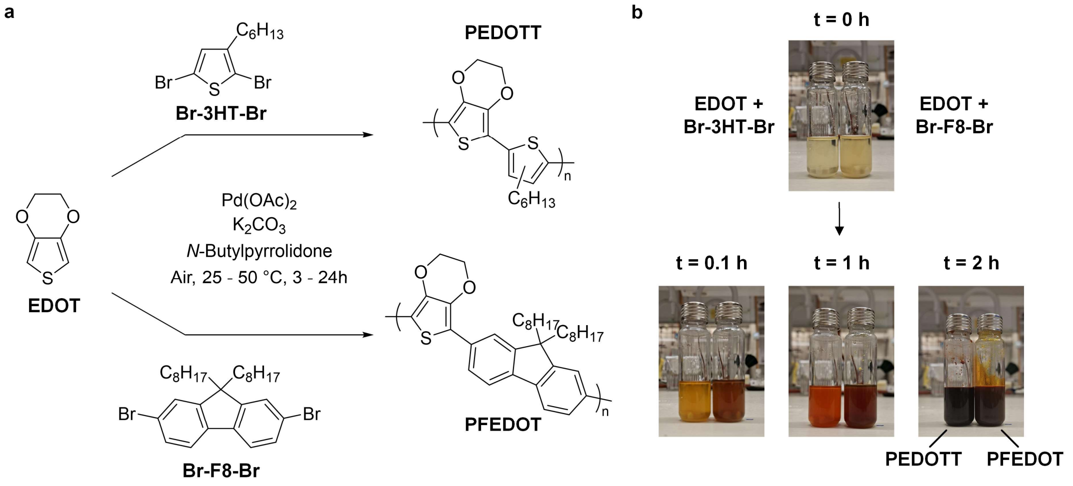


Figure 18. Synthesis of conjugated polymers for teaching lab. (a) Reaction scheme of ADAP to PEDOTT and PFEDOT. (b) Color changes over the course of the reaction performed at 45 °C. *Unpublished data.*

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*Prices (checked 20-07-2025) of common vendors in the Western European market (Sigma Aldrich, VWR, BLDPharm and Ossila), not considering availability and import/export rules in/to other countries.

ADAP can be used to synthesize conjugated polymers in air at room temperature using a green solvent. This tackles most safety and several equipment challenges associated with other common syntheses methods, and this robustness (air stability) of the reaction makes the synthesis less prone to failure. Given the rapid color change upon polymer growth, analytical techniques such as NMR and SEC can now be replaced by more affordable colorimeters.

9.3 Peculiarities of polymers synthesized in the teaching lab

ADAP of EDOT and Br-3HT-Br makes PEDOTT easily accessible (Figure 18a). Previous studies used Grignard metathesis polymerization to create random copolymers of similar monomers,[60] or combinations of Stille coupling and DAP to access polymers with different ratios of EDOT and 3HT.[178] The effects of different compositions and different regioregularities of 3-hexylthiophene in PEDOTT on optical and electrochemical properties were studied, from pure P3HT to pure PEDOT.[178] Based on the study, I used ^{1}H NMR to assign proton signals of the monomers in the polymer for determination of composition and end-group signals for molecular weight determination, as well as regioisomers of 3HT for regioregularity (Figure 19). After synthesizing PEDOTT, students can use room temperature NMR and optoelectronic techniques to elucidate the defect formation in ADAP (homocoupling of EDOT) as well as regioselectivity of this polycondensation method (unselective).

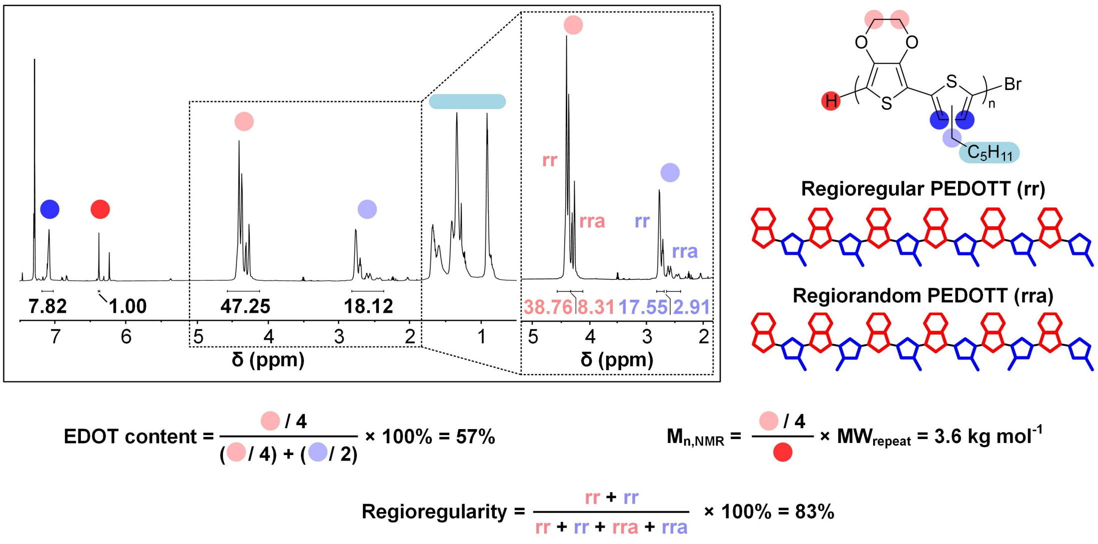

Figure 19. Representative ^{1}H NMR spectrum of PEDOTT. Specific signals are highlighted with circles and lines: EDOT, 3HT, and signals arising due to regioregular and regiorandom are shown in the inset. Underneath the spectrum exemplar calculations of composition, number-average molecular weight and regioregularity are shown. *Unpublished data.*

ADAP between EDOT and Br-F8-Br yields PFEDOT (Figure 18a). Polyfluorenes and copolymers with fluorene often possess strong colors – deep-yellow to deep-red colors with strong blue emissive properties.[179] Not only will the change from colorless monomer to deep-red be an observable indicator of polymer growth, and hence increase in conjugation length, the colors serve purpose in devices. High-molecular-weight PFEDOT was previously synthesized using DAP by Kuwabara *et al.*,[133] and has been used for the fabrication of electrochromic devices, organic light-emitting diodes (OLEDs) and fluorescent chemosensors.[179-181] Perhaps PFEDOT showcases simpler chemistries, but students can expect to employ these polymers in device context to see e.g., its changing color in an electrochromic device or light-emitting properties in OLEDs.[179,180]

9.4 Constructing a lab course

Together with Dr. Megan Westwood, I designed a suitable lab course. Our shared experience in teaching conjugated polymer synthesis labs (e.g., those yielding P3HT and PEDOT) made us aware of difficulties commonly encountered by students, which can be alleviated by ADAP. The lab course is provided in Paper V; considerations that we took into account while preparing the course are listed below.

Defining the pedagogic value and skills obtained by the students is essential for ensuring relevance for the students and streamlining the course. We believe the pedagogic value originates from the interdisciplinarity of organic electronics, which incorporates common themes from chemistry, physics and materials science. Since students are tasked to use multiple disciplines of science, both the pre-existing skills preferable before start of the course and the skills ultimately obtained are manifold:

1. In chemistry,
    a. students must possess basic skills in organic chemistry, polymer chemistry, analytical chemistry and laboratory techniques, which
    b. will allow students to obtain skills in monomer structure determination, synthesis of monomers, synthesis of polymers, understanding reaction mechanisms, polymer purification, and chemical analysis of polymers.
2. In physics,
    a. students should have a basic knowledge of solid-state physics, materials physics and structure-property relationships, which

   b. will allow students to obtain further understanding in ideality of polymer chains, flexibility of polymer chains, and conjugated polymer microstructure.
3. In materials science,
   a. students should understand basics of materials processing, materials characterization methods and application of materials, which
   b. will allow students to obtain skills in polymer processing, thin film fabrication, material properties of polymers, and device preparation with conjugated polymers.

The skills obtained will be associated with the learning outcomes.

While sections 9.1 to 9.3 mainly focus on conjugated polymer synthesis, we decided on a more holistic approach, i.e. we invite synthesis of other polymers through ADAP and exploration of their properties. To make the course as accessible as possible for different institutions and courses, to fit their desired learning objectives, we divided the course into work packages: (1) monomer synthesis, (2) polymer synthesis, (3) polymer characterization, (4) polymer processing, and (5) device fabrication (Figure 20). This way, a teacher can pick-and-choose which parts of the course they want to include. This allows for multi-week lab courses (one or two work packages) to full internships with a duration of several months (most or all work packages). As institutional resources will inevitably vary, i.e. limitations in time, laboratory space and equipment, the flexibility in selecting feasible work packages allows the synthesis of conjugated polymers by students to remain the central focus.

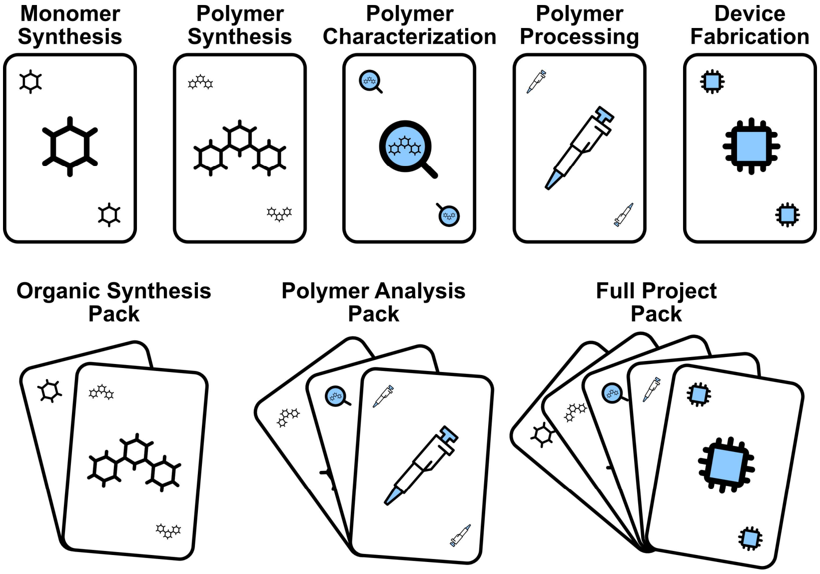

Figure 20. Work packages and exemplary combinations for lab courses.

There are a multitude of approaches when designing a lab course. Traditional lab courses adopted a recipe-driven laboratory approach.[182] Whilst invaluable to learning hard skills of a synthetic chemist, this method lacks the ability to provide deeper understanding and critical-thinking skills.[183] Instead problem-based learning emphasized approaches that encourage the student to go through multiple iterative loops of problem-exploration-planning-execution-reflection (PEPER) cycles, e.g., based on the McMaster problem-solving strategy.[184] We believe that through the work packages and a clear outline of learning goals associated with each one of them, one PEPER cycle equals one work package. For instance, the problem statement and learning outcomes for the monomer synthesis work package could be:

“Design a one-step synthesis to an activated hydrogen source monomer for use in ADAP.”

“The students will be able to

1. recognize a target as a reasonable candidate for polymerization,
2. design a short synthesis procedure,
3. execute synthesis, work-up, and compound purity analysis appropriately, and
4. report their findings in an appropriate format.”

The problem statements and associated learning objectives for each work package can be found in the Supplementary Information of Paper V.

Chapter 10

Conclusions and outlook

In this thesis, I investigated direct arylation polymerization methods for the preparation of conjugated copolymers that function as organic mixed ionic-electronic conductors (OMIECs). Green chemistry principles and lowering the synthetic complexity to facilitate the safe scale up of the preparation of high performance OMIECs have been central to my approach to ultimately address the production/performance trade-off.

Initially, I synthesized a series of x-ethylene glycol functionalized thieno[3,2-*b*]thiophene monomers (g_xTT) for direct arylation polymerization (DAP) designed to avoid β-defects (reaction at incorrect C-H bond). Using an Ullmann coupling protocol, g_0TT to g_4TT were successfully synthesized in one step. Single crystals were isolated, evidence for high purity. As ethylene glycol chain length increases, crystal analysis revealed a change in molecular packing from π-π stacking motifs with high melting points of 140–149 °C to a oligoethylene glycol chain entangled mode with lower melting points of 41–64 °C. A system with increased conjugation, T-g_3TT-T, showed mixed packing (π-π stacking and oligoether chain entanglements). Unexpectedly, 13 % of thiophene rings adopted a *syn* conformation relative to the thieno[3,2-*b*]thiophene (sulfurs on the same side), evidence that S···O interactions do not necessarily 'conformationally lock' the system, a notion often used to guide conjugated polymer design. Furthermore, brominated monomers may not represent the most suitable choice for conjugated polymer modeling, as their structural and electronic properties are strongly influenced by the presence of bromine substituents

Next, I used g_3TT as a hydrogen source in DAP to synthesize eight novel copolymers with donor, acceptor, neutral and ambipolar dibrominated comonomers under Ozawa conditions. SEC and HT-NMR indicated a $M_n > 10$ kg mol^{-1}. Additionally, HT-NMR confirmed equimolar monomer compositions. The four copolymers with > 50 % oligoethylene glycol mass content per repeat unit became conductive in aqueous electrolyte when a bias was applied and thus were plausible OMIEC-active materials. The copolymer with bithiophene, p(g_3TT-T2), had the most promising OECT figure-of-merit $[\mu C^*]_{max}$ = 432 F cm^{-1} V^{-1} s^{-1}.

In an attempt to improve the synthesis yield of p(g_3TT-T2) by slowing polymerization using a Fagnou catalytic system, a serendipitous "supercatalyzed" DAP was observed. By stepwise alteration of reaction conditions, the polymerization could be performed in air at room temperature, in the absence of most additives, in the green solvent NBP, to ultimately scale up the reaction to yield a batch of over 100 grams. Given these conditions, I coined the term ambient direct arylation polymerization (ADAP). ADAP proceeds through a different mechanism compared to DAP: i) an initiation cycle, which simultaneously creates a homocoupled dimer of the hydrogen source monomer and Pd(0), which originates from coordination to $Pd(OAc)_2$, transmetalation between different Pd centers and reductive elimination of Pd(II) bearing two hydrogen source monomers, and ii) a cross-coupling cycle involving two different palladium centers, the Pd(II) from $Pd(OAc)_2$ and the Pd(0) formed by the initiation cycle, which ultimately cross-couple the hydrogen source monomer and the bromine source monomer. One prerequisite for the initiation of ADAP is that the hydrogen source monomer must be electron-rich. With this design strategy, over ten polymers were synthesized with ADAP. OMIEC performance saw an improvement moving from DAP- to ADAP-synthesized polymers, as seen by an in increase in $[\mu C^*]_{max}$ up to three orders of magnitude. This is attributed to improved order of ADAP polymers compared to DAP polymers, possibly an unexpected consequence from the homocoupling that occurs in the initiation step of the ADAP mechanism. Due to the homocoupling, i) less flexible units are introduced into the polymer backbone, which induce rigidity, ii) a stoichiometric imbalance is created leading to shorter polymer chains that crystallize more easily, and iii) high order and/or more electron rich units in the polymer leads to more facile introduction of charges in the OECT devices.

To address batch-to-batch variation, ADAP was translated from batch to continuous droplet flow. Initial solubility tests of the monomers, catalyst and base led to the use of binary solvent mixtures of NMP and water. Given the hydrophilicity of the NMP:water mixture, less harmful silicone oil can be used as the antisolvent carrier fluid to create the reaction droplets, instead of commonly used PFAS “forever chemicals”. By using this combination of solvent and antisolvent, stable droplets were formed which travelled through the reactor and readily polymerized to yield the final product within 20 minutes at temperatures over 100 °C. Near stoichiometric conversion was observed with little variation in molecular weight ($M_{n,NMR}$ = 11 ± 1 kg mol^{-1}) and homocoupling (1.5 ± 0.8 %). Flow samples showed a consistent OECT device performance: μ_{max} = 1.7 ± 0.2 cm^2 V^{-1} s^{-1}, C^*_{max} = 224 ± 12 F cm^{-3} V^{-1} s^{-1}, giving $[\mu C^*]_{max}$ = 378 ± 77 F cm^{-1} V^{-1} s^{-1}.

Polymers synthesized with ADAP possess state-of-the-art OECT figure-of-merit values and large amounts have been synthesized, demonstrating upscaling. Another important step toward upscaling is the translation from ADAP batch synthesis to flow. While DAP already reflects favorably compared to other polycondensation techniques with regards to green chemistry principles and SCI, ADAP addresses additional principles: (5) use of safer solvents and auxiliaries, (6) design for energy efficiency, and (12) the selection of inherently safer chemistry for accident prevention. By comparing ADAP to alternative polycondensations and the oxidative polymerization to PEDOT:PSS using quantifiable parameters related to the twelve principles of green chemistry (Figure 2, Chapter 2.2), ADAP is shown to improve significantly upon these factors approaching values of PEDOT:PSS (Figure 21). Moreover, the SCI of ADAP-synthesized polymers is noticeably lower than other polycondensations given the higher polymerization yields and fewer hazard codes associated with the synthesis (Figure 11a, Chapter 6.3). All this makes ADAP a promising avenue to address the production/performance trade-off, enabling access to the commodity-scale synthesis of high-performance conjugated polymers.

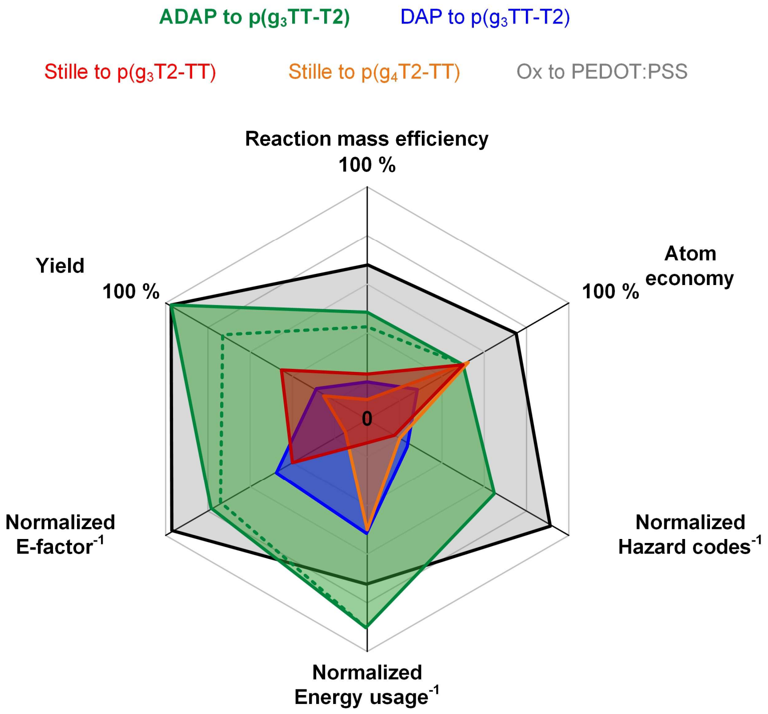

Figure 21. Radar plot of green principles. All environmental impact factors in this plot are calculated for the polymerization step only. The solid lines show the most favorable reported values.[30,56,125,185,186] The dotted line for ADAP to p(g$_3$TT-T2) shows the average value of fifteen reactions. Calculations for reaction mass efficiency, atom economy, energy usage and E-factor are described in the supplementary information of ref [125] (Paper III).

Besides this, further advancements have been made toward direct arylation polymerization in water. Water-soluble conjugated monomers were synthesized by a two-step synthesis: an Ullmann coupling of an alkenol to an aromatic core followed by a thiol-ene click with an ionic thiol to the alkene. Next, a series of novel water-soluble Pd(II) catalysts was synthesized for WaDAP. Pd(II) was chosen since it initiates ADAP and is generally more stable than Pd(0). Combining the synthesized monomers and Pd(II) catalyst, WaDAP was successful at temperatures above 60 °C and yielded brown-red fibrous polymers, which are to be studied further.

Finally, a teaching lab module implementing ADAP was developed. This teaching lab focuses on the safe and robust synthesis of conjugated polymers from commercially available monomers, ideal for students from various natural science backgrounds. Conjugated polymers based on EDOT and 3-hexylthiophene (PEDOTT) and EDOT and fluorene (PFEDOT) can be synthesized in a few hours, meaning that synthesis, work-up and characterization all fit into one or two lab sessions. Students subsequently characterize synthesized polymers by common techniques. For instance, through ^{1}H NMR students can uncover several interesting characteristics, such as composition, molecular weight, and regioregularity.

The ADAP mechanism is a rare example of bimetallic catalysis in the context of conjugated polymer polycondensation reactions. While cocatalytic Pd/Cu-systems have been explored for small molecules,[187,188] a Pd/Pd system is unusual and for polymers, prior to ADAP, unreported. Hence, in future research, I would aim to explore this unique bimetallic mechanism further. Firstly, the energetics of the reaction mechanism must be understood properly, by e.g., computational means, as this would reveal the rate-determining steps and the driving forces within ADAP.[189-191] Once known, the ADAP system can be designed for a greater substrate scope using new catalysts. Candidates range from highly alkaline Pd(II) species, for activation of the hydrogen source monomer, or a specific design of closely positioned Pd(0)/Pd(II) complexes to promote transmetalation.[192] Exploration should not be limited to palladium; more abundant metals are desirable such as iron and copper. Finding a better catalyst is an essential extension to ADAP, especially to n-types, since it has thus far only proceeded in systems with electron-rich hydrogen source monomers. Finally: why would the Pd/Pd bimetallic catalytic system be limited to ADAP? Potentially, the Pd/Pd system can be used in other polymerization methods (Stille, Suzuki) to facilitate the reaction at lower temperatures. Whilst not preferred regarding green chemistry principles, some monomers simply show no activity in DAP methods, making this direction beneficial from an energy- and solvent-hazard point of view.

Droplet flow reactors have shown promising results for conjugated polymer synthesis. In this work, we successfully polymerized p(g_3TT-T2) via direct arylation in droplet flow, the first such case. This prompts investigation of other monomer pairs, requiring optimization of conditions for each case. With regards to commodity-scale synthesis, a major challenge I foresee for droplet flow is space-time yield since droplet flow lags at ~ 0.5 g h^{-1} (e.g., D18, p(g3TT-T2)),[125,193] which would require 8 days for 100 g. Improvements can be made by reducing carrier fluid or increasing tubing volume while retaining constant linear velocity. A multi-capillary 'numbering-up' reactor could also improve time-space yield while preserving previously optimized conditions.[194] The most important step is that an *actual* attempt to prove the possibility of scaling-up with droplet flow – common knowledge of upscaling would suggest this is straightforward but conjugated polymers are notoriously complex.

An underreported factor in the field of conjugated copolymers is the application of green chemistry principle (7) the use of renewable feedstocks. Most monomers used in conjugated polymer synthesis are derived from petrochemical sources, particularly thiophenes which are less prevalent in bio-based and renewable sources compared to nitrogen- and oxygen-containing heteroaromatic compounds. However, levulinic acid derivatives, obtained from lignocellulosic biomass, can be aromatized in the presence of elemental sulfur to form thiophenes.[195] This suggests potential for other bio-sourced 1,4-dicarbonyl compounds to undergo similar transformations. In fact, together with Ramino Peters, I pursued the synthesis of EDOT derivatives from tartaric acid, which proved feasible, albeit with low yields.

This thesis has demonstrated that conjugated copolymers can be synthesized by a novel polymerization technique: ADAP. It has led to high-performance conjugated copolymers for OMIEC applications, specifically OECTs, through a safer and more scalable process. The work offers a deeper understanding of the complexities involved in conjugated copolymer synthesis, highlighting the importance of balancing green chemistry principles, synthetic complexity, and the production/performance trade-off. Beyond synthetic considerations, the results have broader implications for the materials science field. The ability to produce these polymers at scale opens opportunities for integrating classical polymer technologies for processing (e.g., extrusion, molding, blending and composite formation) and characterization (e.g., mechanical testing and rheology). The vast range of conjugated polymer applications, from bioelectronics and bioimaging to polymer electrodes and photocatalysts, can now be accessed more easily through ADAP. In short, the cost, safety and scalability considerations of this work will aid the advancement of conjugated polymer synthesis in any research context.

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四年見て、富士に雪舞う、コタツから。　　　　　あなたは、私にとってのコタツです。