

Batch and Continuous flow synthesis of Rylenebisimide polymers and their application in Energy Storage

by

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10CC17A26001

A thesis submitted to the
Academy of Scientific & Innovative Research
for the award of the degree of
DOCTOR OF PHILOSOPHY

in

SCIENCE

Under the supervision of

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April-2024

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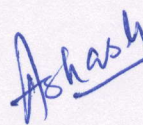
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STATEMENTS OF ACADEMIC INTEGRITY

I, Mr. Aryan Anurath Wavhal, a Ph.D. student of the Academy of Scientific and Innovative Research (AcSIR) with Registration No. 10CC17A26001 hereby undertake that the thesis entitled "Batch and Continuous flow synthesis of Rylenebisimide polymers and their application in Energy Storage" has been prepared by me and that the document reports original work carried out by me and is free of any plagiarism in compliance with the UGC Regulations on "*Promotion of Academic Integrity and Prevention of Plagiarism in Higher Educational Institutions (2018)*" and the CSIR Guidelines for "*Ethics in Research and in Governance (2020)*".

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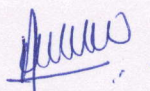
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Declaration

I hereby declare that the matter embodied in this thesis entitled "Batch and Continuous flow synthesis of Rylenebisimide polymers and their application in Energy Storage" is the result of an investigation carried out me at polymer science and Engineering Division, CSIR-National Chemical Laboratory, Pune, India, under the supervision of Dr. Asha S. K.

In Keeping with the general practice of reporting scientific observation, due acknowledgements have been made to the work described on the finding of other investigations.



Mr. Aryan Anurath Wavhal

Student Name and Signature

Date: 01.04.2024

THESIS DEDICATED TO,

DR. BABASAHEB AMBEDKAR, WHO OPENED THE DOORS

OF EDUCATION FOR MILLIONS OF LIVES.

AND

MY MOTHER MRS. ASHA WAVHAL &

MY FATHER MR. ANURATH WAVHAL

FOR THEIR HARD WORK, SUPPORT & LOVE.

AND

FAMILY FOR THEIR ENDLESS LOVE, & SUPPORT THROUGHOUT THE

JOURNEY.

ACKNOWLEDGEMENT

Achieving a doctorate has been a big dream of mine and achieving it brings a lot of happiness and the sense of fulfilment. Undoubtedly, earning a doctorate and completing a dissertation is a lengthy and challenging journey. Throughout this journey, I have been fortunate to receive support, guidance, assistance, and encouragement from numerous individuals. Therefore, I would like to seize this opportunity to express my gratitude to everyone who has helped and supported me throughout my research and academic journey.

*Firstly, I extend my deepest gratitude to my thesis supervisor, **Dr. Asha S. K.**, for her unwavering belief in my capabilities and for granting me the remarkable opportunity to pursue my PhD under her guidance. Throughout this journey, her expertise, patience, and steadfast support have been invaluable. I consider myself incredibly fortunate and privileged to have received her continuous guidance and scientific insights during my doctoral work.*

***Dr. Asha's** mentorship not only shaped the direction of this my research but also established my development as a scholar. Her enthusiasm, encouragement, and firm faith in my abilities have been immensely beneficial. It is thanks to her support that I successfully completed my PhD even after joining job also.*

*I extend my gratitude to **Dr. M. Jayakannan** for his scientific guidance, invaluable knowledge, and numerous insightful discussions and suggestions, which greatly assisted me in the research work. His exceptional teaching abilities played a significant role in providing me with a robust understanding of the fundamentals of polymer science during my coursework at IISER.*

I extend my heartfelt gratitude to my DAC members, Dr. S. P. Chavan, Dr. J. Nithyanandhan, and Dr. S. Kadhiravan, for their invaluable insights, suggestions, and thought-provoking questions during the DAC meeting. Their contributions have significantly contributed to the advancement of my work.

I extend my gratitude to Dr. Ashish Lele, Director of CSIR–NCL, and Dr. Ashwini Kumar Nangia, Former Director of CSIR-NCL, as well as Dr. Suresh Bhat, Head of PSE Division, and Dr. Asha S. K. & Dr. Ulhas Kharul, Former Heads of PSE Division, for granting me this opportunity and for furnishing all the essential infrastructure and facilities required for my work.

I would like to acknowledge the financial support extended by UGC, New Delhi, and CSIR-NCL, which has enabled us to access top-tier infrastructure for our research endeavors. Additionally, I express appreciation for the diligent and prompt cooperation of the Student Academic Office (SAO) staff throughout the duration of my tenure.

I extend my sincere appreciation to Dr. K. Sreekumar and his students, Dr. Meena Ghosh, Mrs. Swati Dilwale, and Miss. Priyanka P., for their active collaboration within NCL, enabling us to delve into the research aspects of energy storage. Similarly, I am grateful to Dr. Amol Kulkarni and his student, Dr. Arun Nikam, for their collaborative efforts within NCL,

Acknowledgement

particularly in exploring the realms of microwave and continuous flow polymerization research. I am genuinely thankful for the privilege of collaborating with such knowledgeable and dedicated individuals.

I am grateful to all the instrumental in-charges of NCL and J-wing for their assistance in carrying out the analysis of my samples. Special thanks are due to the personnel and in-charges of the FESEM and HRTEM instruments. I extend my gratitude to Mr. Manoj Patil for his assistance in BET characterization. Additionally, I would like to express my appreciation to all the members of the NMR division for their support in analyzing my samples.

I extend my sincere gratitude to all my seniors and colleagues who have provided unwavering support and assistance throughout my Ph.D. journey. I am particularly grateful to Dr. Sandeep Sharma, Dr. Shrikant Nikam, Dr. Sarabjot K., Dr. Moumita Roy, and Dr. Navnath Kakde for their invaluable advice and guidance in laboratory practices, which I deeply appreciate. A special thanks to Moumita for her extensive teachings on experimental characterizations and her insightful scientific discussions and friendly support. Additionally, I am profoundly thankful to Dr. Navnath for his helpful suggestions, scientific discussions, and friendly support during this journey. I would also like to express my heartfelt thanks to all my labmates from CSIR-NCL and IISER-Pune, including Ganesh, Shibam, Pooja, Abhijith, Aakashai Kumar, Ashok, Yogesh, Nitin, Utreshwar, Ruma, and Khuduse, for their unwavering support and assistance. I extend my thanks to Ganesh, Shibham, Yogesh, Pooja and Utreshwar for their help during different characterization in lab.

Friends serve as the perpetual wellspring of energy and support in our lives. To all my friends, I express heartfelt gratitude for your understanding and encouragement during moments of crisis. I am particularly grateful to my 12th standard friends, Pradeep, Buddhbhushan, and Pravin, for their unwavering support and love. Similarly, I extend my thanks to my MSc friends, Mr. Indrajeet, Ganesh Kamble, Suryakant Chaudhari, and Amol Jarare, for their constant support. A special acknowledgment goes to Mr. Indrajeet Nawghare for his continuous support, assistance, and fruitful discussions throughout this journey. I am deeply thankful to my seniors from Sutarwadi for their help in study. While I cannot list all the names here, please know that you are always in my thoughts.

I am grateful for the opportunity to express my sincere gratitude to the Indian Oil Corporation Limited. My seniors, and colleagues from the QC department, Indian Oil Corporation Limited. Special thanks are due to Mr. Nitin Udupurkar for his unwavering support and assistance throughout my journey. I also extend my gratitude to my seniors and colleagues, Dr. G. P. Das, Dr. Ravi Gajera, Dr. Jayant Gandhi, Dr. R. Datta, and Mr. Arjun Singh, for their invaluable support and guidance.

I extend my heartfelt gratitude to all the teachers who have played an invaluable role in shaping my academic journey. Their dedication, guidance, and encouragement have been instrumental in my growth and development. I would like to specially thanks to my graduate teachers from

Acknowledgement

Yogeshwari college Ambajogai. I extend thank to Mr. Galphade for strengthening my foundational understanding of chemistry. I grateful to thanks my master degree teachers, Mr. Palve, Dr. Amol Sapkal, Mr. S. Sabhadhinde, Dr. Jadhav, Mr. Khote and Dr. Munde Sir.

I extend my deepest gratitude to my family for their unwavering support, encouragement, and understanding throughout my academic journey.

My parents deserve special mention for their invaluable role in my education. Their unwavering belief in me, coupled with their unconditional love, sacrifices, and tireless efforts, have shaped me into the person I am today. My mother is the strongest pillar of support in my life. She recognizes the life-changing potential of education, so she has dedicated herself to working tirelessly for my academic advancement.

At this juncture, I deeply miss my late Grandfather, Mr. Sukhdev, and Grandmother, Mrs. Subhabai, who passed away during this journey. My grandfather, especially, was a persistent supporter of my education, and his absence is keenly felt.

I extend my heartfelt gratitude to my beloved brother, Mr. Abhijit, whose unwavering support and belief in my abilities have been a constant source of motivation. I would also like to express my appreciation to my sister, Archana, and brother-in-law, Mr. Gautam, for their continuous support, love, and encouragement throughout this journey. I extend my thank to my cousin Diwakar for his support and love.

My sincere thanks go to my uncle, Mr. Vijaykumar, and aunt, Sushma, for their invaluable love, support, and assistance. Furthermore, I extend my gratitude to my uncle, Dharmaraj & aunt, Jayshri and whole Wavhal Family, Gaikwad family (maternal family) and Sarwade family (my in-laws' family), for their unwavering support and encouragement.

Special gratitude is extended to my beloved partner, Mrs. Anjali, for her steadfast support, unwavering motivation, boundless love, and endless encouragement. Thank you for standing by my side, believing in me, and supporting me every step of the way. Your presence has been a constant source of strength through life's ups and downs. And finally, to my cute lovely daughter, you are the shining light in my life. Your presence fills me with joy and brings a smile to my face.

I am very much indebted to my whole family, friends, teachers..... Who supported me in every possible way to see the completion of this research work.

ARYAN ANURATH WAVHAL

ABBREVIATIONS AND SYMBOLS

Mn	Number average molecular weight
Mw	Weight average molecular weight
$\bar{D}$ or $\bar{D}_M$	Dispersity
PDI	Polydispersity index
RT	Room temperature
h	Hours
mg	Milligrams
g	Gram
J	Joule
mL	Milliliter
L	Liter
nm	Nanometer
cm	centimeter
mmol	Millimole
ppm	Parts per million
μ L	Microliter
OPVS	Organic Photovoltaics
R2R	Roll to Roll
HOMO	Highest occupied molecular orbital
LUMO	Lowest occupied molecular orbital
HCl	Hydrochloric acid
HBr	Hydrobromic acid
HI	Hydroiodic acid
OFET	Organic field effect transistor
OLED	Organic light emitting diode
LED	Light emitting diode
PCE	Power conversion efficiency
kDa	Kilodalton
SEC	Size exclusion chromatography
GPC	Gel Permeation Chromatography
FE-SEM	Field Emission Scanning Electron Microscopy
TEM	Transmission electron microscopy

Abbreviations and Symbols

HR-TEM	High Resolution Transmission Electron Microscopy
TCB	1,2,4-trichlorobenzene
TBT	4-ter-butyl toluene
TGA	Thermogravimetric analysis
DSC	Differential Scanning Calorimetry
PVDF	Polyvinylidene fluoride
ODCB	1,2-Dichlorobenzene
μm	Micrometer
mm	Millimetres
rpm	Revolutions per minute
DMF	Dimethylformamide
TLC	Thin Layer Chromatography
NaCl	Sodium chloride
KOH	potassium Hydroxide
DI Water	Deionized water
K_2CO_3	Potassium Carbonate
MeOH	Methanol
ACN	Acetonitrile
ΔH_m	Melting enthalpy
T_m	Melting temperature
T_d	Decomposition Temperature
DCE	1,2-Dichloroethane
TCE	1,1,2,2-Tetrachloroethane
THF	Tetrahydrofuran
MHz	Megahertz
NMR	Nuclear magnetic resonance
CO_2	Carbon dioxide
H_2O	Water
T_g	Glass transition temperature
CDCl_3	Deuterated chloroform
CH_3CN	Acetonitrile
CNT	Carbon Nanotube
MWCNT	Multiwalled Carbon Nanotube
SWCNT	Single walled Carbon Nanotube
rGO or RGO	Reduced graphene oxide

Abbreviations and Symbols

MALDI-TOF	Matrix-assisted laser desorption ionization-time of flight
N ₂	Nitrogen
RI	Refractive index
UV	Ultraviolet
Vis	Visible
SC	Supercapacitor
Au	Gold
Ag	Silver
Al	Aluminum
V	Volt
eV	Electron volt
E _g (opt)	Optical band gap
E _g (ele)	Electronic band gap
mA	Milliampere
A	Ampere
S	Second
λ	Wavelength
Ex	Externally
LiClO ₄	Lithium perchlorate
PC	propylene carbonate
EESDs	electrochemical energy storage devices
E or ED	Energy Density
PD	Power Density
F	Faraday
PVDF	polyvinylidene fluoride
NMP	N-methyl pyrrolidone
CV	Cyclic voltammetry
GCD	Galvanostatic charge discharge
CD	Charge discharge
HSC	hybrid supercapacitor
LS	liquid-state electrolyte
QSS	Quasi solid-state electrolyte
QE	quasi-solid electrolyte
AC	activated carbon

Abbreviations and Symbols

M	Molar
BET	Brunauer–Emmett–Teller
DFT	Density functional theory
K	Kelvin
δ	Chemical Shift
PTFE	polytetrafluoroethylene
EDX	energy dispersive X-ray
EDLC	electric double-layer capacitor
R _{ct}	charge transfer resistance
ESR	equivalent series resistance
EIS	Electrochemical impedance spectroscopy
Ω	Ohm
PMMA	Polymethyl methacrylate
ϵ	Molar absorptivity coefficient
A	Absorbance
C	concentration
W	Watts
D-A	Donor-acceptor
PPy	Polypyrrole
PANI	Polyaniline
P3HT	Poly(3-hexylthiophene)
PEDOT	Poly (3,4-ethylenedioxythiophene)
RB flask	Round bottom flask
NDI	Naphthalene diimide
PDI	Perylene diimide
ICT	Intra/inter molecular charge transfer

SYNOPSIS

1. Introduction

The need for energy generation from renewable energy resources was brought to light by the world's growing energy demands and the depletion of fossil fuels. Energy storage is equally important as energy production for human well-being, industrial development and to fulfill the energy demand of the growing world. Supercapacitors(SC) have shown significant potential in the field of energy storage due to their high power density, stability of devices, excellent reversibility, and quick charging/discharging capabilities.¹ The electrode materials are the central components of these energy storage devices and play a vital role in determining their overall performance.² Conjugated polymers are commonly explored as electrode material in energy storage devices due to several advantages as compared to costly metal oxide and carbon materials.³ Also the Conjugated polymers are promising candidates for various energy-related applications, such as organic photovoltaics (solar cells), organic field-effect transistors (OFETs), and energy storage devices.⁴ The conjugated polymers have exhibited advantages in terms of low cost, good conductivity, flexibility, rich color variations, simple synthetic procedure, and controllable structure.⁵ But the synthesis of the conjugated polymer by efficient synthetic method remains a challenge. The primary objective of this research is to synthesize rylenebisimides based donor-acceptor conjugated polymers and utilize them as electrode material for supercapacitors. The thesis also aims for the synthesis of donor-acceptor conjugated polymers by efficient synthetic methods for taking advantage in terms of reduction of reaction time, scalable approach with reproducible molecular weight, and polydispersity.

2. Statement of the problem

Supercapacitors (SC) have shown significant potential in the field of energy storage. Energy density is one of the key parameters for developing an efficient supercapacitor device and meeting the needs of various applications of energy storage. However, the energy density of a supercapacitor [$E = \frac{1}{2}CV^2$] is proportional to the square of the operational voltage and is linearly dependent on the specific capacitance C.⁶ A small increase in the voltage significantly improves the energy density of the device. The p-type conjugated polymers are commonly used as electrode material with aqueous electrolytes which limits their voltage window.⁷ Whereas, the donor-acceptor polymers are efficient materials to obtain a higher operating voltage window by storing energy in both positive and negative electrodes. However, the

electrochemical performance of the donor-acceptor polymer suffers from limitations such as high equivalent series resistance, low capacitance, cycle stability, and energy density. Therefore, the design and synthesis of electrode material with high surface area and large pore size are of great significance to achieve better performance in supercapacitor devices.⁸ In this work, the donor-acceptor conjugated polymer and their composites with different weight ratios of multi-walled carbon nanotubes were synthesized by a modified Stille polymerization procedure. The donor-acceptor polymers and their composites were utilized as electrode material in supercapacitors. This study illustrated the utilization of a synthetic method to fine-tune the morphology, surface area, and porosity of materials to achieve better electrochemical properties of polymeric supercapacitor electrodes.

Along with this, Conjugated polymers are attractive and promising materials for several applications relating to energy. These conjugated polymers are most commonly synthesized by conventional batch synthesis which has limitations in terms of time taking reactions, non-scalable approach due to batch-to-batch variation in molecular weight, and polydispersity. This research aims to address this problem by investigating the synthesis of donor-acceptor conjugated polymers for energy applications using a continuous flow method. The study will also focus on optimizing the synthesis process in batch, microwave, and continuous-flow synthetic methods.

3. Objective and Outline of Thesis

The primary purpose of the thesis is to synthesize Rylinebisimide-based donor-acceptor conjugated polymers by batch and continuous flow approaches for energy application. The rylenebisimide-based donor-acceptor conjugated polymer and its composites were synthesized to utilize as electrode material in supercapacitors. The thesis also focuses on the continuous flow synthesis of rylenebisimide-based donor-acceptor conjugated polymers for energy application. The detailed outline of the thesis is given below,

Chapter 1. Introduction

The introduction focussed on the need for energy conversion from renewable energy sources and the importance of energy storage to fulfill the energy demand from renewable energy sources. The chapter also discusses the significance of supercapacitors in energy storage devices and the advancements that are necessary for supercapacitors. The donor-acceptor conjugated polymers are interesting materials to use as electrode material in supercapacitors.

Also, the donor-acceptor conjugated polymers exhibited a valuable role in different energy applications. The synthesis of conjugated polymers remains a challenge for commercial purpose and reproducing the device-level performance in different energy applications. However, these issues can be tackled by using an efficient synthetic method such as the continuous flow synthesis.

Chapter 2. Enhanced High-Voltage Symmetric Supercapacitor Electrodes via In-situ Synthesized Multiwalled Carbon Nanotube-Doped Perylenebisimide based Donor-Acceptor Conjugate Polymer P(PDI2OD-T2)

Chapter 3: A high-voltage non-aqueous hybrid supercapacitor based on polymer N2200 supported over multiwalled carbon nanotubes

Chapter 4: Continuous Flow Synthesis of High-Performance n-type Polymers based on Naphthalene and Perylene diimide

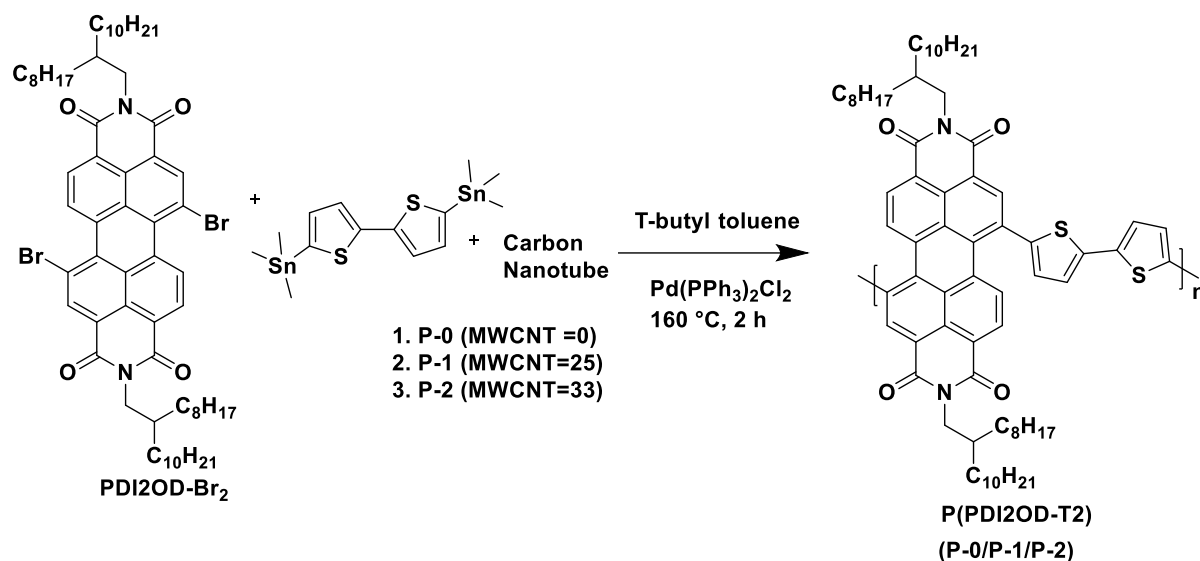
Chapter 5: Conclusion

4. Results and their interpretation

Chapter 2. Enhanced High-Voltage Symmetric Supercapacitor Electrodes via In-situ Synthesized Multiwalled Carbon Nanotube-Doped Perylenebisimide based Donor-Acceptor Conjugate Polymer P(PDI2OD-T2)

In this study, the P(PDI2OD-T2) or poly{[N,N'-bis(2-octyldodecyl)-3,4,9,10-perylenedicarboximide-(1,7&1,6)-diyl]-alt-5,5'-(2,2'-bithiophene)} or P-0 donor-acceptor conjugated polymer and their composites were synthesized by modified Stille polymerization procedure (Scheme 1). The P(PDI2OD-T2) was synthesized by using PDI2OD-Br₂ and 5,5'-bis(trimethylstannyl)-2,2'- bithiophene monomer in dry 4-ter-butyl toluene solvent using bis(triphenylphosphine)palladium(II) dichloride (Pd(Ph₃)₂Cl₂) catalyst at 160 °C. The P(PDI2OD-T2) polymer (P-0) and their composites were synthesized by in situ addition of different weight ratios of multi-walled carbon nanotubes (MWCNTs). The polymer and polymer composites were studied by different characterization techniques and finally utilized as electrode material in supercapacitors. The in-situ synthesized polymer composites show better electrochemical performance compared to pristine polymer due to improvement in surface area, pore size distribution, and uniform mixing with carbon nanotube and it further provides the enhancement of the active participation of redox-active groups of polymer composites. The polymer composites showed better electrochemical performance in a three-

electrode setup and which further utilized as efficient electrode material in symmetric supercapacitor devices.



Scheme 1. Synthetic scheme for P(PDI2OD-T2) (P-0) polymer and its composites with MWCNT C-X (P-1 and P-2).

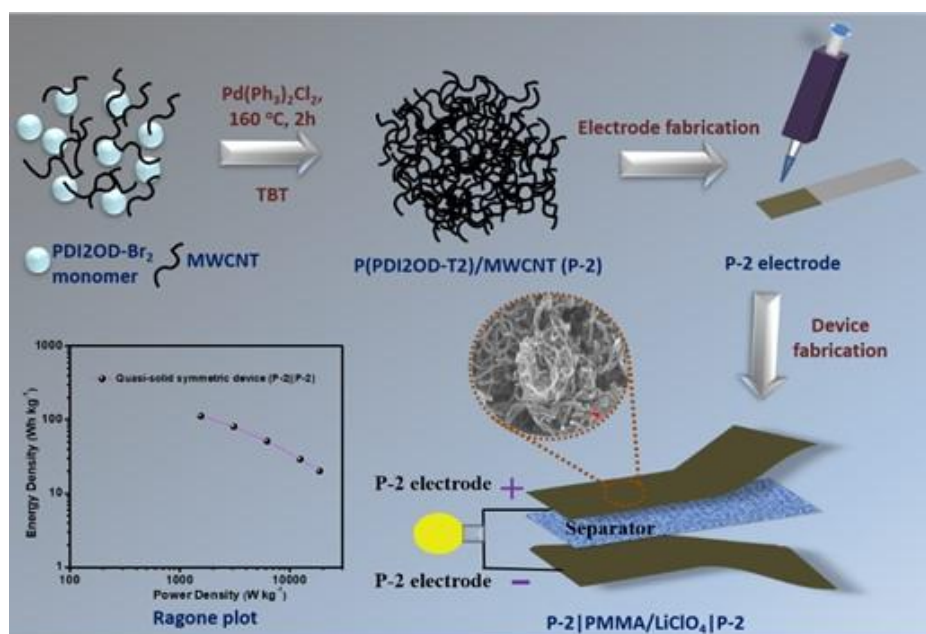


Figure 1. Schematic diagram summarizing the *in-situ* polymerization of P(PDI2OD-T2) with MWCNTs along with their electrochemical analysis in quasi-solid state symmetric supercapacitor device.

The outcome of the synthesis of P(PDI2OD-T2) polymer and their composites for the application as electrodes in supercapacitors are summarized below,

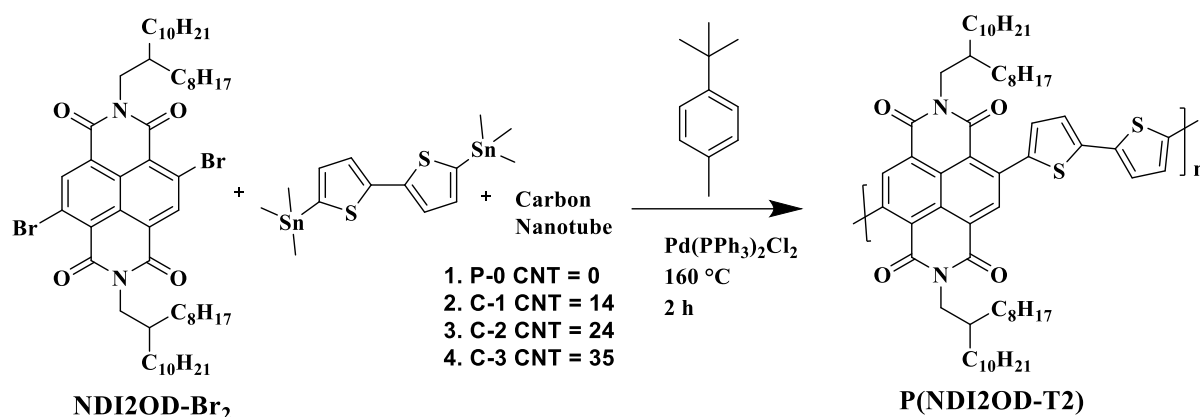
- The P(PDI2OD-T2) polymer was synthesized by a modified Stille reaction where polymerization was completed within two hours by avoiding long reaction time.
- The percent incorporation of multi-walled carbon nanotube (MWCNT) is quantified using absorption spectra and thermogravimetric analysis.
- The structural morphology, surface area and pore size distribution of polymer composites studied further help for electrochemical performance.
- The P-2 polymer composites showed a good capacitance of 93 F g^{-1} in a three-electrode system.
- The P-2 polymer composites showed good performance in liquid-state symmetric supercapacitor devices and quasi-solid state symmetric supercapacitor devices with high operating voltage windows and capacitance of 84 F g^{-1} with good cycle stability.
- The LED device demonstration using a QSS-symmetric device has been established to show the real device-level application.
- The highest Energy density of 112.4 Wh Kg^{-1} and high-power density of 18600 W kg^{-1} are obtained for the QSS-symmetric device.

Chapter 3: A high-voltage non-aqueous hybrid supercapacitor based on polymer N2200 supported over multiwalled carbon nanotubes

In our last chapter, we demonstrated the electrochemical performance of supercapacitors based on perylenebisimides with excellent voltage window and electrochemical performance, indicating the potential of donor–acceptor polymers as efficient electrode materials. The present chapter takes this research forward towards developing a new electrode material and extending the in-situ synthesis strategy to obtain a controlled morphology for improvement in electrochemical performance. In this chapter, we choose a naphthalene bisimide-based donor-acceptor conjugated polymer [N2200/P(NDI2OD-T2)] with carbon nanotubes (CNTs) having the potential to improve its electrical properties and extend its applicability. The P(NDI2OD-T2) or N2200 based polymer composites were synthesized by in situ addition of MWCNTs with various weight ratios following a modified Stille polymerization procedure (Scheme 2). These polymer and polymer composites were synthesized in a very short reaction time, with excellent yield and a very high molecular weight polymer.

We have also prepared externally mixed polymer composites by physical mixing of pristine polymer with 30% of multi-walled carbon nanotubes. The electrochemical performance of the composite materials was tested in an organic electrolyte (1 M LiClO₄/propylene carbonate) in

a standard three-electrode configuration. The in situ prepared polymer composites delivered 80 mA h g⁻¹ specific capacity (Capacitance ~256 F g⁻¹), a value substantially higher compared to that of the pristine polymer and the physically mixed polymer/MWCNT composite. Moreover, the in situ prepared composite showed promising performance as a negative electrode coupled with an activated carbon positive electrode in a hybrid supercapacitor (HSC) cell. The preparation and electrochemical characterization of the in situ and physically mixed polymer/MWCNT composites are schematically summarized in Figure 1.



Scheme 2. Synthetic scheme for the P(NDI2OD-T2) (P-0) polymer and its composites with MWCNTs (C-X).

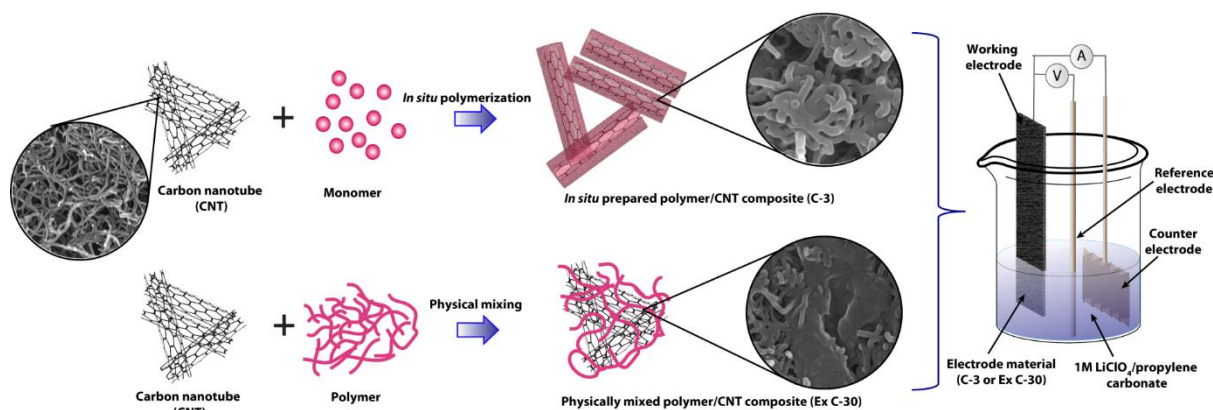


Figure 2. Schematic representation summarizing the polymerization of P(NDI2OD-T2) supported over MWCNTs following in situ and physical mixing approaches, and their electrochemical analysis in a three-electrode cell.

The outcome of the in-situ synthesis of P(NDI2OD-T2) polymer with MWCNT and benefits to use as electrode material in supercapacitors are summarized below,

- P(NDI2OD-T2) polymer was synthesized with very high molecular weight and within very little (2 hours) of reaction time for the first time.
- The in-situ synthesized Polymer composites with MWCNT achieved improvement in the surface area, porosity, and morphology of the polymer composites.
- Among the polymer composites, the in-situ synthesized C-X polymer composites show 80 mA hg⁻¹ (256 F g⁻¹) which is much higher than the pristine polymer and Ex-situ C-30 sample.
- Good discharge capacity of 8.5 and 11 mA hg⁻¹ obtained in high-voltage (2.4 V) for LS-HSC & QSS-HSC hybrid supercapacitor.
- The 80% retention of the maximum capacity after 2500 cycles with 92% coulombic efficiency.
- The device-level application by demonstrating the lighting of a red LED bulb with a 2.4 V for QSS-HSC device.

Chapter 4: Continuous Flow Synthesis of High-Performance n-type Polymers based on Naphthalene and Perylene diimide.

Donor-acceptor conjugated polymers are promising candidates for various energy-related applications, such as organic photovoltaics (solar cells), organic field-effect transistors (OFETs), and energy storage devices. These conjugated polymers are most commonly synthesized by batch polymerization. The batch polymerization reactions have limitations in terms of being time-consuming, and non-scalable, hindering commercialization and batch-to-batch variation in molecular weight and polydispersity. The batch-to-batch variation in molecular weight and dispersity shows further impact on the low and variable performance of polymer material when it is used in energy applications. The continuous flow method is an attractive technique for scaling and commercializing the conjugated polymer with reproducible molecular weight and polydispersity.

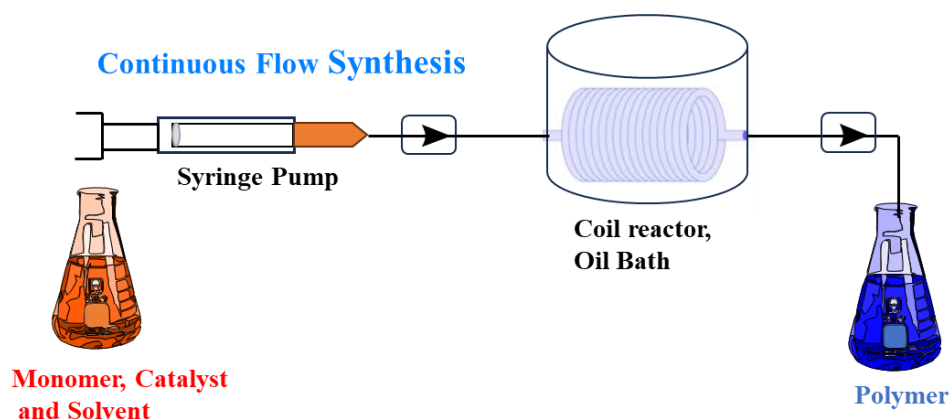
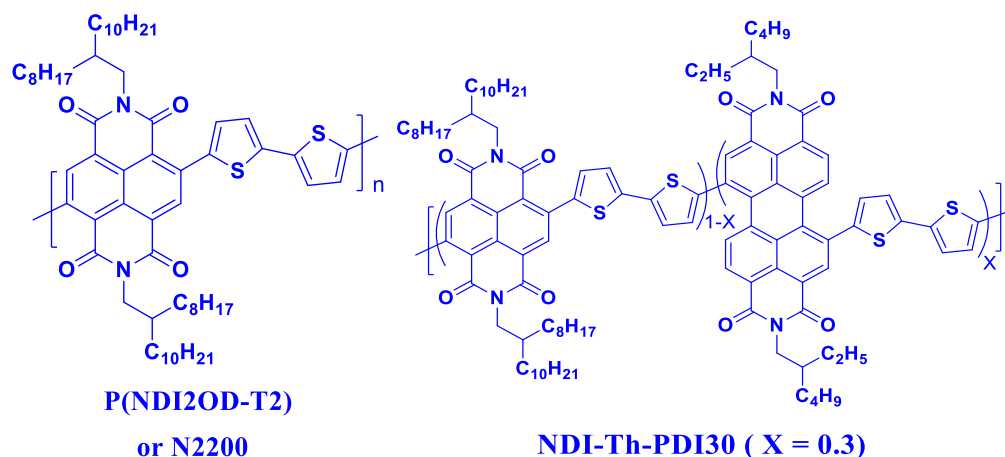


Figure 3. Schematic presentation for the synthesis of polymers by continuous flow Process.

In the thesis chapters 2 and 3, we have focussed on the batch synthesis of rylenebisimide-based donor-acceptor conjugated polymer and their composites for application as electrode material supercapacitors. In this chapter, we are mainly focused on the synthesis of rylenebisimide-based donor-acceptor conjugated polymers by continuous flow method (Figure 2). The N2200 or P(NDI2OD-T2) has been used as an acceptor polymer in all-polymer solar cells, where high power conversion efficiencies have been achieved in combination with suitable donor polymers under well-controlled device fabrication conditions. However, it exhibited a strong tendency to form aggregates in several organic solvents that resulted in large-scale phase separation in contrast to the microphase separation of the desirable pure donor-acceptor polymers. The previous report from our group by Sandip Sharma and coworkers synthesized a series of new n-type NDI-bithiophene/PDI-bithiophene random copolymers (NDI-Th-PDIx) by incorporating varying amounts of perylene diimide (PDI) as co-acceptor along with NDI. Furthermore, they were utilized as acceptors in combination with commercially available donor polymers such as PTB7 or PTB7-Th. The NDI-Th-PDIx showed a high power conversion efficiency of 5.0% in comparison with P(PDI2OD-T2) of PCE 2.97%. The P(NDI2OD-T2) and NDI-Th-PDI-30 donor-acceptor conjugated polymers are efficient acceptor polymers for all-polymer solar cells. These and many more highly efficient conjugated polymers are synthesized by batch process which limits their application for large-scale device fabrication due to batch-to-batch variation in molecular weight and polydispersity. In this chapter, we are mainly focussing on the synthesis of these rylenebisimide-based donor-acceptor conjugated polymers by batch method, microwave polymerization, and continuous flow polymerization. The synthesis of P(NDI2OD-T2) and NDI-Th-PDI-30 donor-acceptor conjugated polymer by different methods are summarized below,



Scheme 3. Chemical structures of P(NDI2OD-T2 and NDI-Th-PDI-30 polymers.

- The synthesis of P(NDI2OD-T2) and NDI-Th-PDI-30 polymers have been successfully optimized in batch polymerization.
- The synthesis of P(NDI2OD-T2) polymer optimized by Microwave Synthesis and achieved benefits in terms of reaction time reduction by energy efficient technique.
- The synthesis of P(NDI2OD-T2) and NDI-Th-PDI-30 polymers has been successfully achieved by a Continuous Flow Process which is a scalable and commercially viable technique.
- The continuous flow synthesis gives benefits to achieve high molecular weight polymers within a short reaction time and extra benefits to improve the structural order.

Chapter 5. Conclusion

The thesis described the synthesis of rylene-bisimide-based donor-acceptor conjugated polymers which were utilized as electrode materials in supercapacitors. This thesis also explored the different methods for synthesizing donor-acceptor conjugated polymers, including Stille coupling in batch, microwave, and continuous flow polymerization approaches.

In Chapter 2, The P(PDI2OD-T2) polymer and its composites with multiwalled carbon nanotubes(MWCNT) were synthesized by a modified Stille reaction within two hours by avoiding long reaction time. The in situ synthesized polymer composite was used as an electrode and showed better capacitance in three-electrode. The P-2 polymer composites are further utilized as electrode material in symmetric supercapacitor devices with liquid organic electrolyte (LE-P-2||P-2) and quasi-solid gel electrolyte (QE-P-2||P-2). The polymer

composites showed good performance in liquid-state symmetric supercapacitor devices and quasi-solid state symmetric supercapacitor devices with high operating voltage windows and good cycle stability. The real device-level application was checked using LED device demonstration for a QSS-symmetric device where it operates with a high operating voltage window and exhibited the highest Energy density and high power density. In Chapter 3, we have developed a facile synthesis protocol for the P(NDI2OD-T2) (P-0) polymer with a high molecular weight within a short period of time (2 h) for the first time by means of the modified Stille polymerization method. The inclusion of MWCNTs during the polymerization reaction was found to improve the physicochemical properties of the composite material compared to that of the pristine polymer and externally mixed sample. The in situ synthesized polymer composite C-3 sample exhibited a better discharge capacity, which is substantially higher than those of the pristine polymer and the composite prepared by physically mixing MWCNTs. The C-3 polymer composite was further used for fabricating a high-voltage (2.4 V) hybrid supercapacitor taking the C-3 composite as a negative electrode (battery-type) and activated carbon (AC, capacitive electrode) as a positive electrode material. The electrochemical performance of the AC||C-3 device was analyzed in 1 M LiClO₄/PC liquid electrolyte (LS-HSC) and a PMMA/PC/LiClO₄ polymer gel electrolyte (QSS-HSC) and both devices show comparable performance. This work provides new opportunities for the design of conducting polymer-based robust electrode materials for non-aqueous hybrid supercapacitors. The last chapter of the thesis describes the synthesis of rylenebisimide-based donor-acceptor conjugated polymers by batch method, microwave polymerization, and continuous flow polymerization. The synthesis of P(NDI2OD-T2) and NDI-Th-PDI-30 polymers have been successfully optimized in batch polymerization. Along with this, the synthesis of P(NDI2OD-T2) polymer optimized by Microwave Synthesis and achieved benefits in terms of reaction time reduction by energy efficient technique. Finally, the synthesis of P(NDI2OD-T2) and NDI-Th-PDI-30 polymers has been successfully synthesized by a Continuous Flow Process which is a scalable and commercialized technique. This continuous flow synthesis gives benefits to achieve high molecular polymer within a short reaction time and extra benefits to improve the Structural order.

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1. **Aryan (Bhaiyyasaheb) A. Wavhal**, M. Ghosh, S. Sharma, S. Kurungot and S. K. Asha, A high-voltage non-aqueous hybrid supercapacitor based on the N2200 polymer supported over multiwalled carbon nanotubes. *Nanoscale*, **2021**, 13, 12314–12326.
2. **Aryan A. Wavhal**, S. Dilwale, N. R. Kakde, P. P. Puthiyaveetil, M. Prakash, S. Kurungot and S. K. Asha, High-Voltage Symmetric Supercapacitor Electrodes Via In Situ Synthesized Multiwalled Carbon Nanotube-Doped Perylenebisimide-Based Donor–Acceptor Conjugate Polymer P(PDI2OD-T2). *J. Phys. Chem. C* **2024**, 128, 12808–12821.
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Table Of Content

Content	Page No.
Acknowledgement	i
Abbreviations and symbols	iv
Synopsis	viii
 CHAPTER 1	
	1-44
General Introduction and Literature	
1.1 Overview	1
1.2 Organic Semiconductors	2
1.2.1 P-Type Organic Semiconductors	2
1.2.2 N-Type Organic Semiconductors	3
1.2.3 Donor-Acceptor Conjugated polymers	4
1.3 Application of Conjugated polymers	5
1.3.1 Organic Light Emitting Diode (OLED)	6
1.3.2 Organic Photovoltaics (OPV or solar cell)	8
1.4 Energy Storage: Supercapacitor	10
1.4.1 Battery	11
1.4.2 Supercapacitor	12
1.4.3 Types of Supercapacitors	15
1.4.4 Conjugated Polymer as Electrode material for supercapacitors.	19
1.5 Synthesis of Donor-acceptor conjugated polymers	29
1.5.1 Suzuki Polymerization	30
1.5.2 Stille Polymerization	31
1.5.3 Batch polymerizations and its limitation	32
1.5.4 Microwave Polymerization	33
1.5.5 Continuous Flow Polymerization	35
1.6 Aim of The Thesis	36
1.7 References	38

CHAPTER 2

Enhanced High-Voltage Symmetric Supercapacitor Electrodes via In-situ Synthesized Multiwalled Carbon Nanotube-Doped Perylenebisimide based Donor-Acceptor Conjugate Polymer P(PDI2OD-T2) 45-80

2.1	Introduction	45
2.2	Experimental Section	48
	2.2.1 Material	48
	2.2.2 Measurements	48
	2.2.3 Sample Preparation	48
	2.2.4 BET Experimental Setup.	49
	2.2.5 Electrode preparation for three electrode studies	49
	2.2.6 Flexible Electrode for device	49
	2.2.7 Quasi Electrolyte Preparation	49
	2.2.8 Electrochemical Measurements	49
	2.2.9 Flexible Device Fabrication	50
2.3	Synthesis of Monomers and polymers	50
	2.3.1 Synthesis of Monomers	50
	2.3.2 Synthesis of P(PDI2OD-T2) Polymer and their composite polymers with MWCNT by Stille Coupling Approach	57
2.4	Results and Discussion	60
	2.4.1 Synthesis and Characterization	60
	2.4.2 Calculation for percentage of MWCNTs in polymer composites determined using absorption spectroscopy	65
	2.4.3 Morphology	66
	2.4.4 Surface Area and Pore Size.	68
2.5	Electrochemical Characterization	69
2.6	Electrochemical Calculation	76
2.7	Conclusion	77
2.8	References	78

CHAPTER 3

High-Voltage Non-Aqueous Hybrid Supercapacitor Based on N2200 Polymer Supported Over Multiwalled Carbon Nanotube

81-119

3.1	Introduction	81
3.2	Experimental Section	84
	3.2.1 Materials	84
	3.2.2 Measurements.	84
	3.2.3 Sample Preparation.	85
	3.2.4 Electrode Fabrication.	85
	3.2.5 Electrochemical Measurements.	85
	3.2.6 BET Experimental Setup.	87
3.3	Synthesis of Monomers	87
3.4	Synthesis of Polymers and their composites	90
	3.4.1 Synthesis of P(NDI2OD-T2) (P-0).	90
	3.4.2 Synthesis of Polymer Composite C-X.	91
3.5	Results and Discussion	91
	3.5.1 Synthesis and characterization	91
	3.5.2 Calculation for quantification of the MWCNT	97
	3.5.3 Morphology	98
	3.5.4 Surface Area and Pore Size	100
3.6	Electrochemical Characterization.	102
3.7	Electrochemical Calculation	113
3.8	Conclusions	115
3.9	References	116

CHAPTER 4

Continuous Flow Synthesis of High-Performance n-type Polymers based on Naphthalene and Perylene diimide

120-145

4.1	Introduction	120
-----	--------------	-----

Table of Content

4.2	Experimental Section	123
4.2.1	Materials	123
4.2.2	Measurements.	123
4.3	Synthesis of Monomers	124
4.4	Batch Synthesis of P(NDI2OD-T2) polymer for time optimization	126
4.5	Microwave polymerization	127
4.6	Optimization of continuous flow polymerization	129
4.7	Batch and Continuous flow synthesis of P(NDI2OD-T2) polymer with Optimized conditions	130
4.7.1	P(NDI2OD-T2) polymer synthesis by Batch Method	130
4.7.2	Synthesis of the P(NDI2OD-T2) polymer by Continuous flow synthesis	131
4.8	Experimental conditions for Batch and Continuous flow synthesis of NDI-Th-PDI-30 polymer with Optimized conditions	132
4.8.1	Synthesis of the NDI-Th-PDI-30 polymer by Batch synthesis	132
4.8.2	Synthesis of the NDI-Th-PDI-30 polymer by continuous flow	132
4.2	RESULT AND DISCUSSION	133
4.9.1	Synthesis and characterization	133
4.9.2	Photophysical Properties	138
4.9.3	Thermal Properties	139
4.10	Conclusion	141
4.11	References	143
CHAPTER 5		146-150
Conclusion and Future Prospective		
5.1	Conclusion	146
5.2	Future Prospective	149
	Abstract for indexing	151
	List of Publications	152
	List of Posters	153
	About the Author	155
	Copy of SCI Publication	156

CHAPTER 1

Introduction

1.1 Overview

The rising global population and economic expansion has resulted in an escalating global demand for energy. However, this demand is being met primarily by finite resources such as oil, coal, and gas, which are rapidly depleting. Awareness regarding the environmental impact of fossil fuels which causes environment pollution and global warming is increasing. To address this issue, there is a need for significant advancements in harnessing renewable energy sources such as wind and solar power.¹ Simultaneously, there is a necessity for the development of robust energy storage solutions, which are equally important for human well-being, industrial progress, and meeting the escalating energy demands of our growing world.^{2,3}

Conjugated polymers are a class of organic polymers, characterized by alternating single and double bonds along their backbone, possessing delocalized π -electrons, resulting in enhanced electrical conductivity and optical properties. These polymers have garnered significant attention across diverse fields owing to their numerous advantages, including structural and functional adaptability through molecular design, solution processability, lightweight nature, flexibility, diverse color options, simple synthesis, and low processing costs. Their unique electronic and optical properties make them promising materials for various applications, including Organic Photovoltaic Devices (OPVs), Light-Emitting Diodes (LEDs), Field-Effect Transistors (FETs), Sensors, Supercapacitors, Batteries, Biomedical Applications, Printed Electronics, Smart Textiles, and Water Purification.⁴ Despite the considerable potential exhibited by existing conjugated polymers, the synthesis of novel polymers and the study of existing ones remain essential for further progress in energy applications. By enabling the development and study of tailored materials with improved performance, addressing existing limitations, fostering innovation, and ensuring sustainability and cost-effectiveness in energy technologies, we can advance our understanding and create more efficient solutions.

The main goal of this thesis is to synthesize donor-acceptor conjugated polymers based on Rylene bisimides and evaluate their suitability as electrode materials for supercapacitors. Additionally, the thesis aims to employ efficient synthetic methods to develop these donor-acceptor conjugated polymers for energy applications, aiming for reduced reaction times, scalability, and reproducibility of molecular weight and polydispersity.

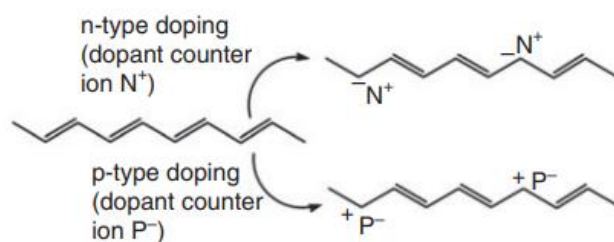
1.2 Organic Semiconductors

Organic semiconductors are comprised mainly of organic molecules or polymers that demonstrate semiconductor characteristics. In recent years, there has been notable interest in materials characterized by their distinctive properties, owing to their potential applications across a range of electronic devices. In contrast to traditional inorganic semiconductors such as silicon, organic semiconductors provide several advantages. These include flexibility, lightweight properties, cost-effective manufacturing processes (such as printing), and the potential for creating large-area and transparent devices.⁵

However, they typically have lower charge carrier mobilities and inferior electronic properties compared to their inorganic counterparts. Ongoing research in organic semiconductor development is mainly focused on improving their performance and stability for broader applications in electronics and optoelectronics. The conjugated polymer is superior organic semiconductor material as compared to small molecule owing to their cost-effective techniques, high mechanical flexibility, charge carrier mobility, etc. These organic semiconductors are primary classified in to three types like p-type, n-type and ambipolar.

1.2.1 P-Type Organic Semiconductors

Similar to inorganic semiconductors, organic semiconductors can also be doped to enhance their electronic properties. P-type organic semiconductors are characterized by an abundance of positive charge carriers, or "holes," which facilitate the movement of electrical current. The oxidizing agents used as an acceptor for extracting electrons from the polymer and make them positive charge species is depicted in **Scheme 1.1**.^{6,7} Because of the abundant π -electron density in conjugated polymers, various oxidizing agents have proven effective in this process. These materials are typically electron-rich, meaning they readily accept electrons to form holes. In p-type semiconductors, the electron affinity is low, indicating that the material has a weak tendency to accept electrons. These dopants create positively charged "holes" in the valence band of the polymer, increasing the concentration of positive charge carriers. This results in an increase in the overall conductivity of the material for positive charge carriers.



Scheme 1.1 The mechanism for doping process in conjugated polymer.⁷

The doping process may cause a change in the energy levels within the polymer matrix. Incorporating dopant molecules can specifically modify the energy levels within the valence band, facilitating electron transitions into the conduction band and generating holes within the valence band. P-type doping has the potential to substantially alter the electronic properties of the polymer, such as its energy levels, bandgap, and charge transport characteristics. These modifications are essential for tailoring the material's properties to suit specific applications, such as organic electronic devices. **Figure 1.1** illustrates some of the commonly used p-type conjugated polymers.

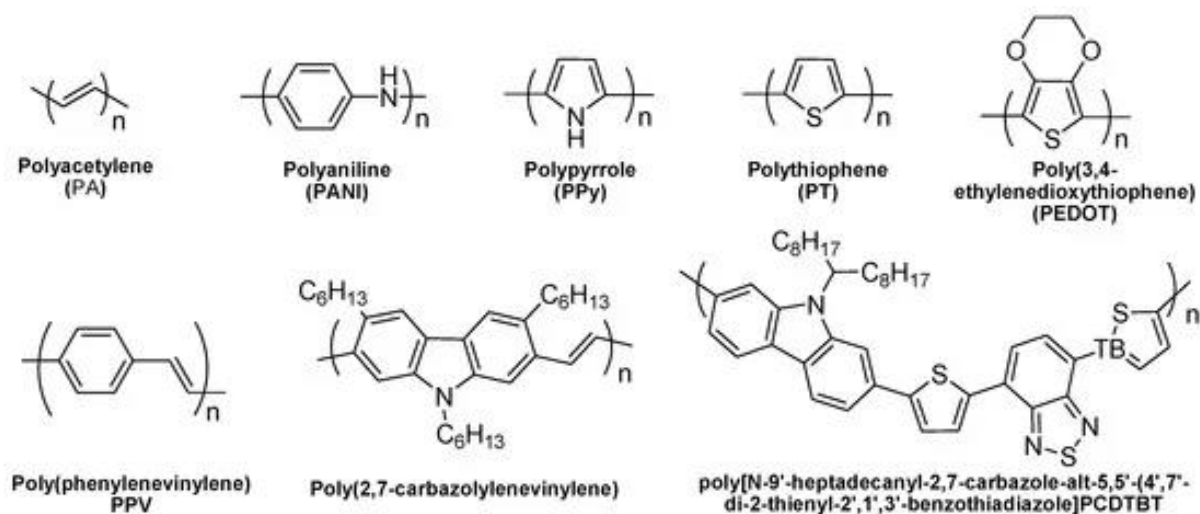


Figure 1.1 Common p-type semiconducting conjugated polymers.⁸

1.2.2 N-Type Organic Semiconductors

N-type organic semiconductors are materials that exhibit semiconducting behavior and are doped with electron-rich molecules or atoms, resulting in an excess of negative charge carriers (electrons) within the material, as shown in **Scheme 1.1**. This requirement arises because conjugated polymers inherently possess an abundance of π -electrons in their 2p_z orbitals. These

doping agents introduce additional electrons into the conjugated polymer chain, leading to an excess of negative charge carriers (electrons) and the formation of charged sites along the polymer chain. Finally, the conductivity of materials is shifted towards the n-type region. N-type organic semiconductors present several benefits, including solution processability, flexibility, and the potential for cost-effective fabrication, positioning them as promising contenders for future electronics. **Figure 1.2** illustrates some of the commonly used n-type polymers. These polymers are frequently employed in organic electronic applications due to their semiconducting properties and compatibility with n-type doping.

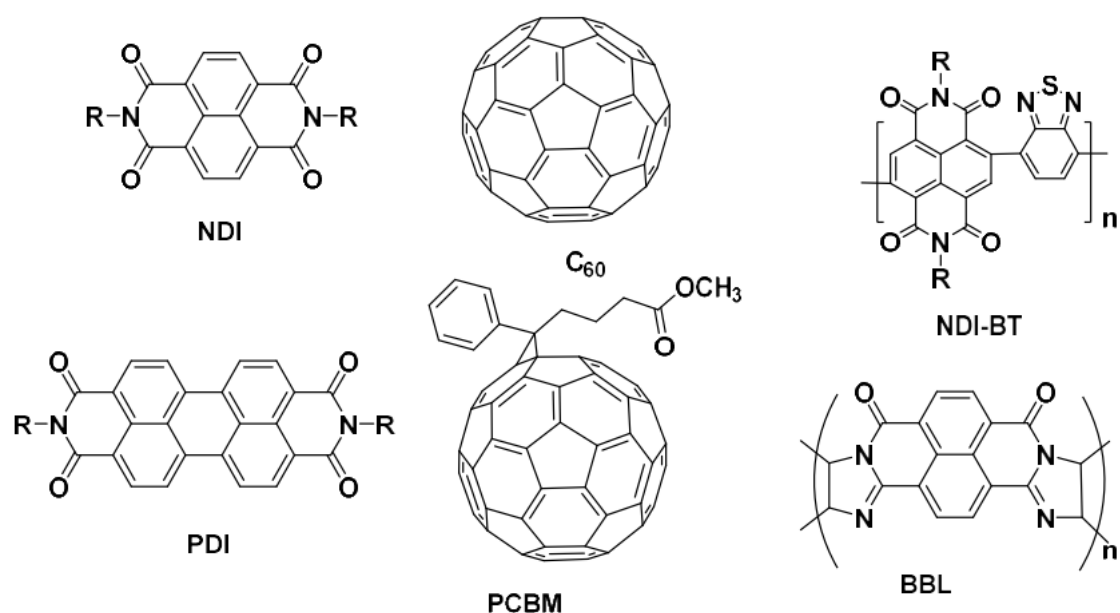


Figure 1.2 Examples of some n-type semiconducting conjugated polymers.^{9,10}

1.2.3 Donor-Acceptor Conjugated polymers

Donor-acceptor (D-A) conjugated polymers have emerged as a noteworthy category of semiconducting materials in the domain of organic electronics, attracting considerable interest owing to their distinctive optoelectronic characteristics. These polymers are characterized by alternating segments of donor and acceptor units along their backbone. The interplay between these donor and acceptor components promotes effective charge transport and allows for the customization of electronic properties, rendering them as promising candidates for a range of energy-related applications.

The polymer backbone typically consists of alternating donor and acceptor units, enabling extended π -conjugation for efficient charge transport. The donor and acceptor units have

distinct frontier molecular orbital energy levels. Typically, the donor unit has a lower-lying highest occupied molecular orbital (HOMO), which facilitates hole (positive charge) transport, while the acceptor unit has a higher-lying lowest unoccupied molecular orbital (LUMO), enabling electron (negative charge) transport. The precise configuration of the HOMO and LUMO significantly influences charge transport and device efficiency. It is feasible to adjust the electrical characteristics of these polymers via modifying the composition and chemical structure of the donor and acceptor units. This tunability allows for the adjustment of the polymer's optical and electronic properties, including its absorption spectrum and charge carrier mobility. The low-end gap is an exclusive behaviour of these polymers which is crucial for various applications such as photovoltaics, electrochromism. Also, in energy storage applications such as battery and supercapacitor, the narrow band gap significantly influences material conductivity and charge storage capacity. Overall, the narrow band gap of these polymers is essential for enabling efficient light absorption, emission, charge transport, and sensing across a widespread application in organic electronics and optoelectronics. The structure of commonly used semiconducting donor-acceptor conjugated polymers are demonstrated in **Figure 1.3**.

1.3 Application of Conjugated polymers

Conjugated polymers are utilized in a wide range of applications across diverse fields owing to their distinctive electronic and optical properties. These lightweight conductors hold immense potential, as their properties can be fine-tuned through modifications to the polymer structure, opening paths for tailored functionalities and versatile applications. The conjugated polymers find applications in various fields like Organic Field-Effect Transistors (OFETs), Organic Photovoltaics (OPVs), Organic Light-Emitting Diodes (OLEDs), Sensors and Biosensors, Energy Storage Devices, Electroluminescent Devices, Photodetectors and Biomedical Applications etc.⁴ Some of the main applications are described below,

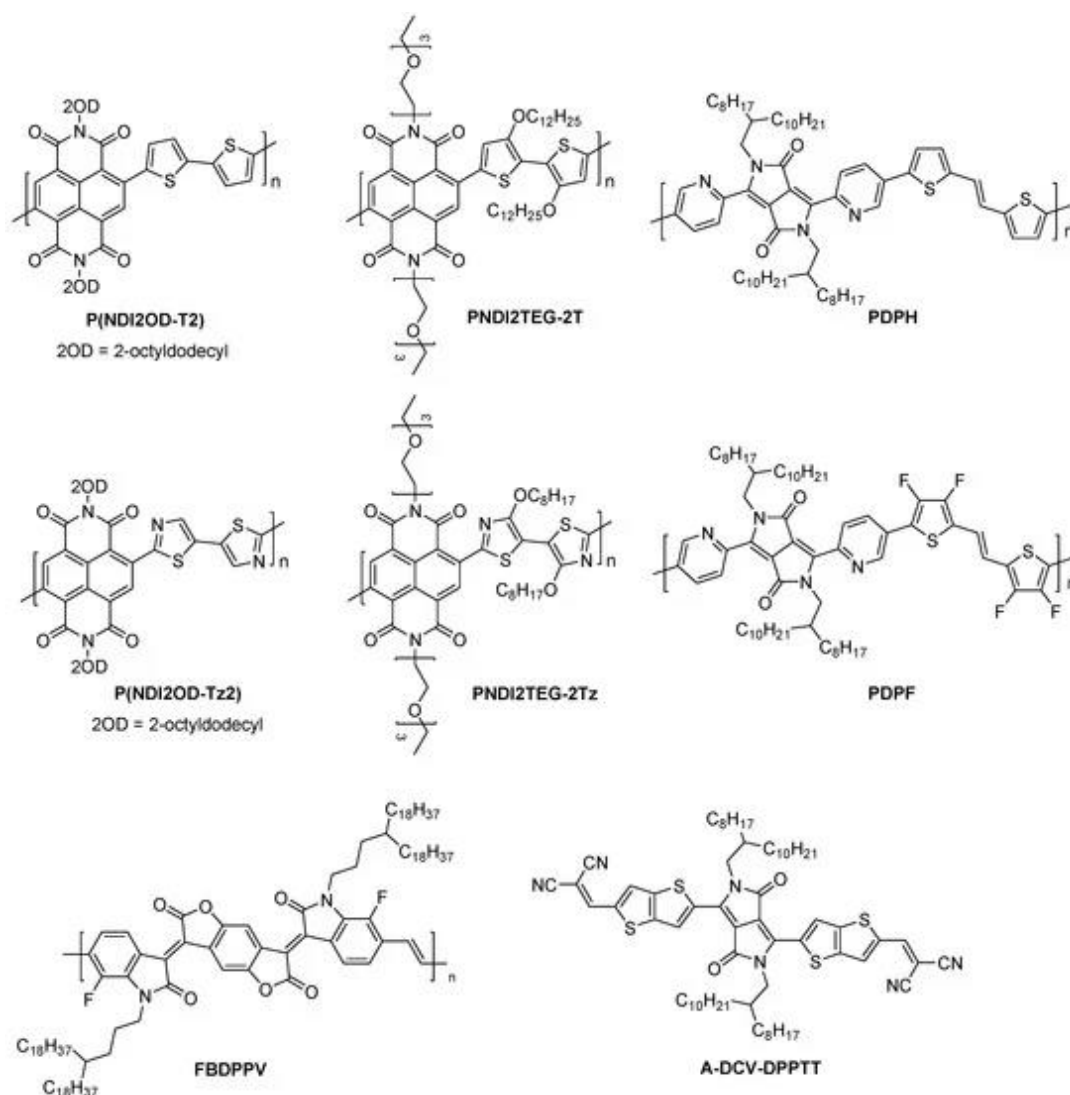


Figure 1.3 The structure of some commonly used semiconducting donor-acceptor conjugated polymers.⁸

1.3.1 Organic Light Emitting Diode (OLED)

Conjugated polymers have emerged as promising materials for OLED (Organic Light-Emitting Diode) applications due to their unique optoelectronic properties and processing advantages. The benefits of OLED displays and lighting systems emerge from the high efficiency and color tunability provided by these polymers. Numerous electronic displays, including televisions, mobile phones, and digital cameras, currently utilize organic semiconductors as their active components. Conjugated polymers offer notable advantages over their inorganic counterparts in OLED applications. These advantages include exceptional mechanical flexibility, lightweight characteristics, low voltage requirements, rapid switching speeds, and cost-

effectiveness. Such properties make them highly desirable for use in OLED technology, promising advancements in display and lighting applications. These attributes position organic semiconductors for substantial growth and continued advancements within the display technology industry. Organic Light-Emitting Diodes (OLEDs) operate based on the principle of electroluminescence (EL), wherein light is produced when an electric current is applied to an organic semiconductor material. In simpler terms, when electricity flows through the organic layer of the OLED, it emits light. **Figure 1.4** illustrates a basic OLED setup and provides an overview of how the device functions.

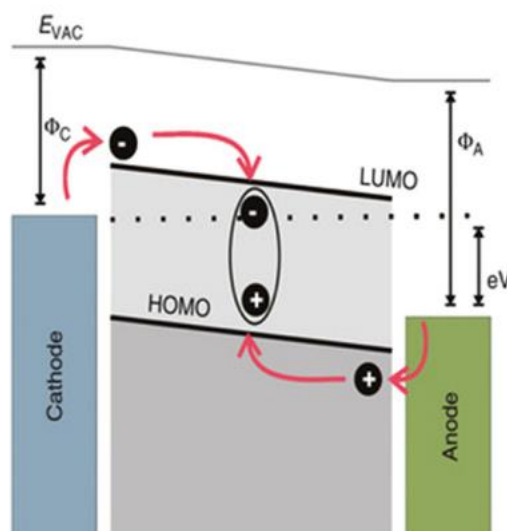


Figure. 1.4 A basic OLED setup and overview of the device functions.¹¹ Copyright © 2018 Elsevier Inc. All rights reserved.

An organic semiconductor is placed among two electrodes to make an OLED device. Applying a voltage causes the anode to inject holes into the organic layer and the cathode to inject electrons. These electrons and holes travel through the OLED towards its centre, jumping from molecule to molecule. Inside the OLED, they combine to form electronically excited states known as excitons.¹² This recombination process results in energy flow as light, a phenomenon known as electroluminescence. The intensity and colour of the emitted light depend on the materials used in the OLED and the applied voltage. Polymer OLEDs exhibit high efficiency, generating substantial light output with minimal power consumption.¹³ Poly(p-phenylene vinylene) (PPV) stands as the primary polymer employed in Polymer Light-Emitting Diodes (PLEDs).¹⁴ Furthermore, polythiophenes, polyphenylenes, polyfluorenes, and polyacetylenes find common usage in PLEDs as well.¹⁵

1.3.2 Organic Photovoltaics (OPV or solar cell)

Organic photovoltaics (OPV) are solar cells which use organic semiconducting materials to convert sunlight into electricity.¹⁶ The commonly used materials are typically carbon-based polymers or small molecules instead of traditional solar cells that use inorganic semiconductors like silicon.¹⁷ OPV cells operate on the principle of photovoltaic effect, where photons from sunlight are absorbed by the organic material, generating electron-hole pairs. These pairs then move through the cell, creating an electric current.¹⁸ Organic photovoltaics offer several advantages over conventional inorganic silicon based solar cells, such as flexibility, lightweight design, and potentially reduced manufacturing expenses.¹⁹ However, their efficiency and stability are areas of ongoing research and development. OPV technology holds promise for applications in portable electronics, building-integrated photovoltaics, and other solar energy harvesting systems.

The fundamental architecture of a solar cell consists of the photo-active layer, where the conversion of light into electricity occurs. This layer is made of a semiconductor material, which can be either organic/polymeric and situated in between the two electrodes as shown in **Figure 1.5 a-b**. The device structure of an organic solar cell (polymer solar cell or OPV) typically consists of several key components such as substrate, Transparent conductive layer, hole-transport layer, active layer, Electron Transport Layer, cathode, Encapsulation. In the active layer, a blend of donor and acceptor organic semiconducting materials facilitates the conversion of light energy into electrical energy. The donor absorbs photons, generating excitons, while the acceptor assists in charge separation and transport.

All-polymer solar cells exclusively employ polymers for both the electron donor and acceptor components, in contrast to conventional OPV devices. These devices utilize two different types of polymers: one serves as the electron donor (donor polymer), absorbing photons and generating electron-hole pairs upon exposure to sunlight, while the other acts as the electron acceptor (acceptor polymer), facilitating charge separation and transport. The interface between these two polymers is crucial for efficient charge transfer and ultimately the generation of electrical current. All-polymer solar cells offer several potential advantages over conventional OPV devices, including enhanced thermal stability, tunable electronic properties through chemical modification, and potentially lower manufacturing costs due to the compatibility of polymer-based materials with solution-based processing techniques. However, attaining high power conversion efficiencies and long-term stability poses a main challenge in

the advancement of all-polymer solar cells, and ongoing research efforts are focused on optimizing device architectures, polymer design, and fabrication processes to address these issues and unlock the full potential of this technology for renewable energy generation.

Thiophene-based conjugated polymer materials, such as poly(3-hexylthiophene) (P3HT), are frequently employed as p-type (donor) materials. Conversely, fullerene derivatives like PCBM are commonly utilized as n-type (acceptor) materials.²⁰ However, PCBM exhibits several limitations, including poor solubility, challenges with phase separation, and limited absorption.²¹ So, researchers are trying to replace this acceptor molecule with different donor-acceptor conjugated polymer or small molecules. The conjugated polymer or small molecule based on naphthalene and perylene are exclusively studied for their different properties. The donor-acceptor conjugated polymer P(NDI2OD-T2) was initially developed by the Fatchetti group and later commercialized under the name PolyeraActivInk N2200.²² This polymer displayed remarkably high electron mobilities of approximately $0.85 \text{ cm}^2/\text{Vs}$ in organic field-effect transistors (OFET). Various research groups have extensively investigated this moiety, exploring different donor moieties, processing parameters such as solvents and temperature, and varying donor/acceptor weight combinations.

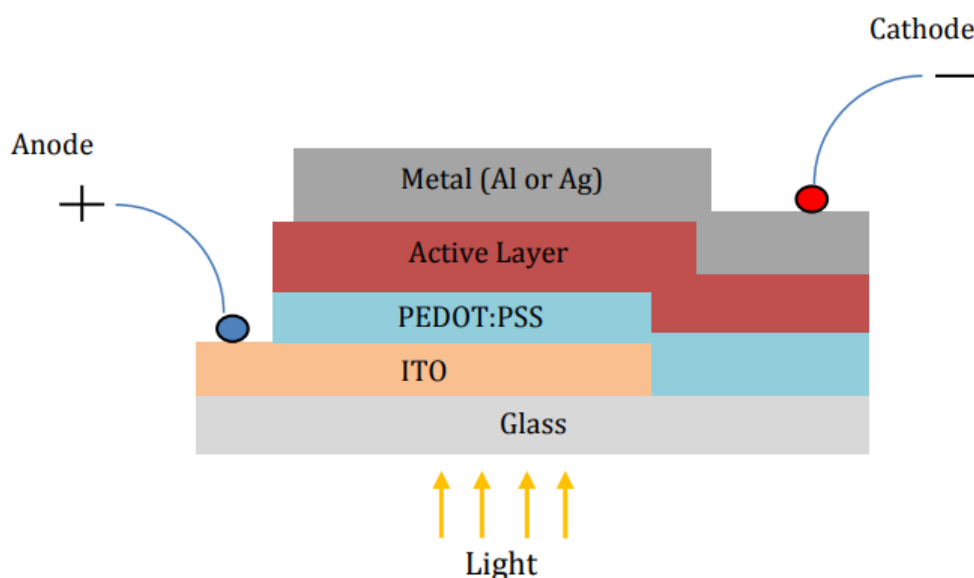


Figure 1.5a: Organic solar cell device structure.¹⁸

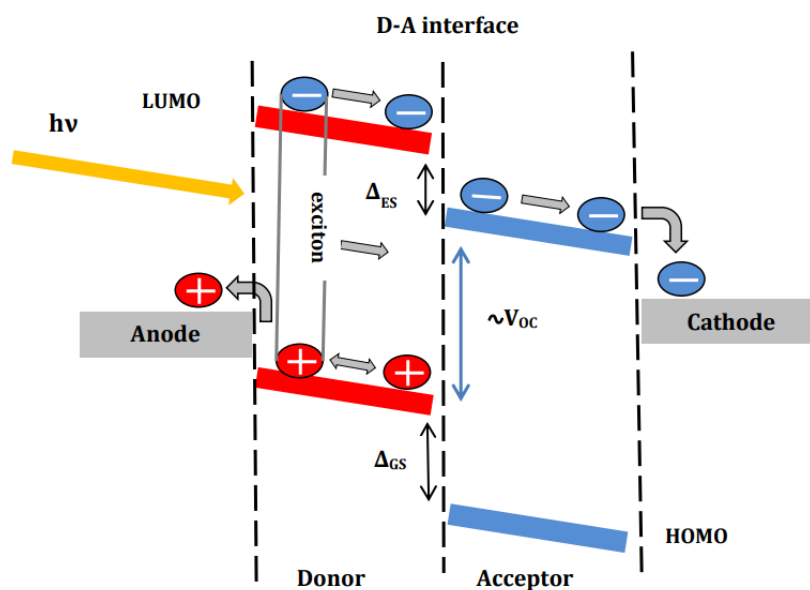


Figure 1.5b: Schematic diagram of operating principles in organic solar cells.¹⁸

1.4 Energy Storage: Supercapacitor

Energy storage is the essential process of storing energy, which plays a vital role in modern energy systems. It involves capturing excess energy produced from sources like solar, wind, or grid power during periods of excess production or low demand. Electrochemical energy storage systems (EES) are witnessing significant growth across various scales, from microbatteries used in smart cards to large-scale batteries for electric vehicles and warehouse batteries. Despite notable advancement, there is a clear need for future energy storage solutions that offer higher performance, greater versatility, smaller size, lighter weight, and, most importantly improved economic viability.²³

There are various methods of energy storage, each with its own advantages, disadvantages, and applications. The battery and supercapacitor are crucial and common energy storage technologies. The electrode materials serve as important components of these energy storage devices and perform an important function in determining their overall efficiency.²⁴ Traditionally, in these devices metal-based inorganic compounds are used as electrode materials such as Li, Co, Fe, Sn, and Mn etc. The organic materials have outstanding prospects to replace current energy storage devices due to its advanced property and capabilities, including flexibility, lightweight nature, cost-effectiveness, environmental friendliness, and suitability for various device designs. While advancements have been made in organic

electrode materials for energy storage, significant challenges remain to be addressed before achieving widespread commercialization on a large scale.²⁵

1.4.1 Battery

Rechargeable batteries are essential for their ability to provide reversible electrochemical energy storage and conversion.²⁶ Batteries store energy as chemical energy and convert it into electrical energy upon release. Typical batteries comprise two electrodes, namely the anode and cathode, connected to each other, along with an electrolyte and separator. Among the all-rechargeable batteries, lithium-ion batteries (LIBs) have received significant attention.²⁷ Since their commercialization by Sony in 1991, LIBs have quickly become the dominant choice in the market for movable electric devices.²⁸ The fundamental operating principle of a Li-ion battery is depicted in **Figure 1.6.** and charging discharging mechanism are discussed here, when an external electrical current is given to a lithium-ion battery, lithium ions travel from the positive electrode towards the negative electrode during the charging process. This causes the anode to become lithium-enriched by storing energy. On the other hand, while discharging, the lithium ions that have been stored move back through the electrolyte from the anode to the cathode, producing an electrical current that can be used to power external devices. As a result, electrical power that has been stored is released. One significant gain of lithium-ion batteries is that they provide high energy density as compared with other commercialized batteries. However, the Li-ion batteries have some issues such as abundance of Li metal,²⁹ dropping capacity upon repetitive charging-discharging cycles, life time,³⁰ cost-effectiveness and efficiencies etc.

Battery devices also suffers from slow charging, low power delivery rates, and decreasing capacity over time.³¹ Consequently, there's a rising demand for energy storage innovations that offer rapid energy delivery, affordability, sustainability, and stability during repeated use.³²

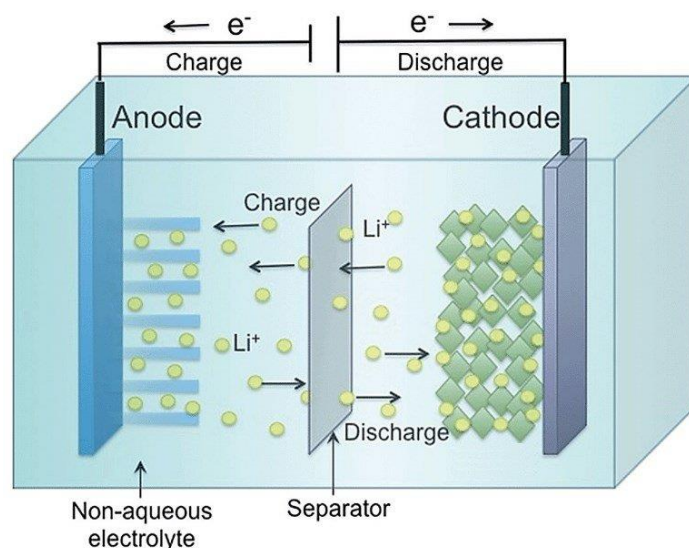


Figure 1.6 The principle of the lithium-ion battery (LiB) involves the insertion of lithium ions (depicted as yellow spheres) into the matrices of both the anode and cathode during charging and discharging, respectively.³³ © 2016 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

1.4.2 Supercapacitor

A supercapacitor (SC) also known as electrical capacitor (EC) is a high-capacity capacitor with higher capacitance values and can store 1000 times more electrical energy than other capacitors. The supercapacitors are placed between electrolytic capacitors and rechargeable batteries in terms of their energy storage capacity.³⁴ The disparity in energy density and power density among batteries, conventional capacitors, and supercapacitors is illustrated by the Ragone Plot, as depicted in Figure 1.10.³⁵

Supercapacitors present numerous compensations over traditional batteries, such as high-power density, rapid charging and discharging rates, sustained energy supply, extended cycle life, adaptability to varying operating temperatures, and environmental sustainability.^{3,36} Supercapacitors find frequent use in scenarios demanding sudden bursts of high power, such as in hybrid vehicles, renewable energy setups, and portable electronics. Nonetheless, their energy density tends to be lower compared to batteries, which makes them less optimal for prolonged energy storage purposes. Researchers are actively engaged in efforts to boost the energy density and overall performance of supercapacitors, aiming to broaden their utility across diverse domain.

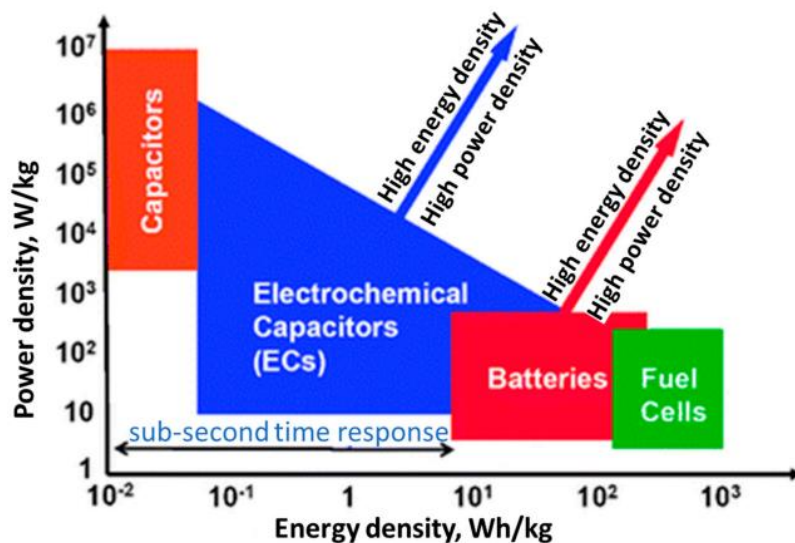


Figure 1.7 The Ragone plot illustrates the correlation between power and energy density energy storage devices.³⁵

The electrode are central components of supercapacitor and its performance is mainly depending upon electrode. The impact of electrode material on supercapacitor performance are detailed here:

- Specific Capacitance:** It measure the energy stored by a supercapacitor.
- Electrochemical Stability:** Electrode materials must exhibit good electrochemical cycle stability without undergoing significant degradation. Materials that maintain their structural integrity and performance over many cycles contribute to the long-term durability and reliability of the supercapacitor.
- Conductivity:** Maximizing electrical conductivity in supercapacitor electrodes enables rapid charge and discharge, enhancing power density.
- Surface Area and Porosity:** Increased surface area enhances the electrode-electrolyte interface, resulting in higher capacitance and improved energy storage performance by providing a large number of active sites.
- Ion Accessibility:** Effective ion accessibility is crucial for enabling rapid ion transport between the electrolyte and the electrode surface during charge and discharge processes. Electrode materials with open pore structures and interconnected pathways promote efficient ion diffusion, leading to faster kinetics and improved supercapacitor performance.
- Environmental Stability:** Electrode materials should maintain their performance under various environmental conditions, including temperature extremes and exposure to moisture or corrosive agents. Materials with good environmental stability ensure the longevity and reliability of the supercapacitor in real-world

applications. g) **Cost and Scalability:** Materials that are abundant, inexpensive, and compatible with scalable manufacturing processes are desirable for widespread adoption of supercapacitors in various applications.

By carefully selecting and optimizing electrode materials based on these criteria, researchers can enhance the performance of supercapacitors and unlock their full potential for energy storage applications.

Conventional capacitors consist of two conductive plates which separates by a dielectric layer as revealed in **Figure 1.8**. When a voltage is provided across the capacitor's terminals, electric charges gather on the conductive plates, establishing an electric field between them. The presence of the dielectric material between the plates blocks the flow of current while permitting the electric field to persist.

Capacitance (C) is used calculated using following formulae,

$$C = \frac{Q}{V}$$

Where, Q = Charge, and V = Voltage.

The capacitance of a capacitor, measured in farads (F), represents its ability to store electrical charge.

It is influenced by variables such as the surface area of the plates, the spacing between them, and the characteristics of the dielectric material. The capacitance of a system rises as the surface area of the plates expands and declines as the separation between them increases.³⁷

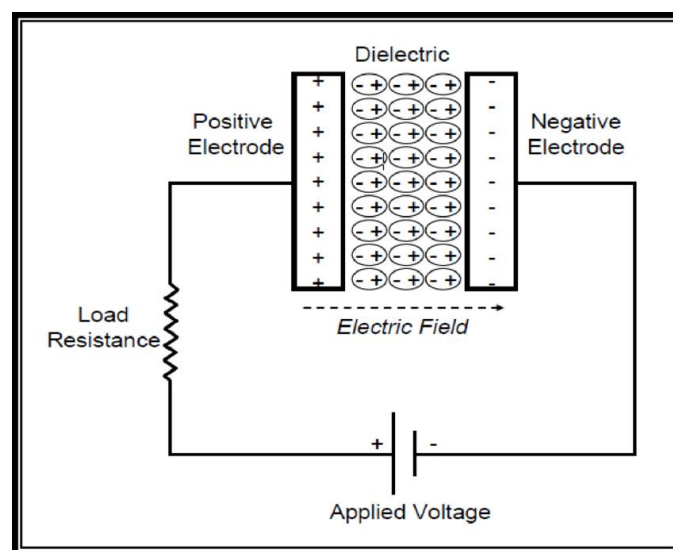


Figure 1.8 Schematic of a conventional capacitor.³⁸

1.4.3 Types of Supercapacitors

Supercapacitors have the capability to reach higher capacitance compared to conventional capacitors and operate based on the same principles as conventional capacitors. On the basis of mechanism, the supercapacitor is further divided into three types as depicted in **Figure 1.9**,

- a) EDLC
- b) Psuedocapacitors
- c) Hybrid Capacitors

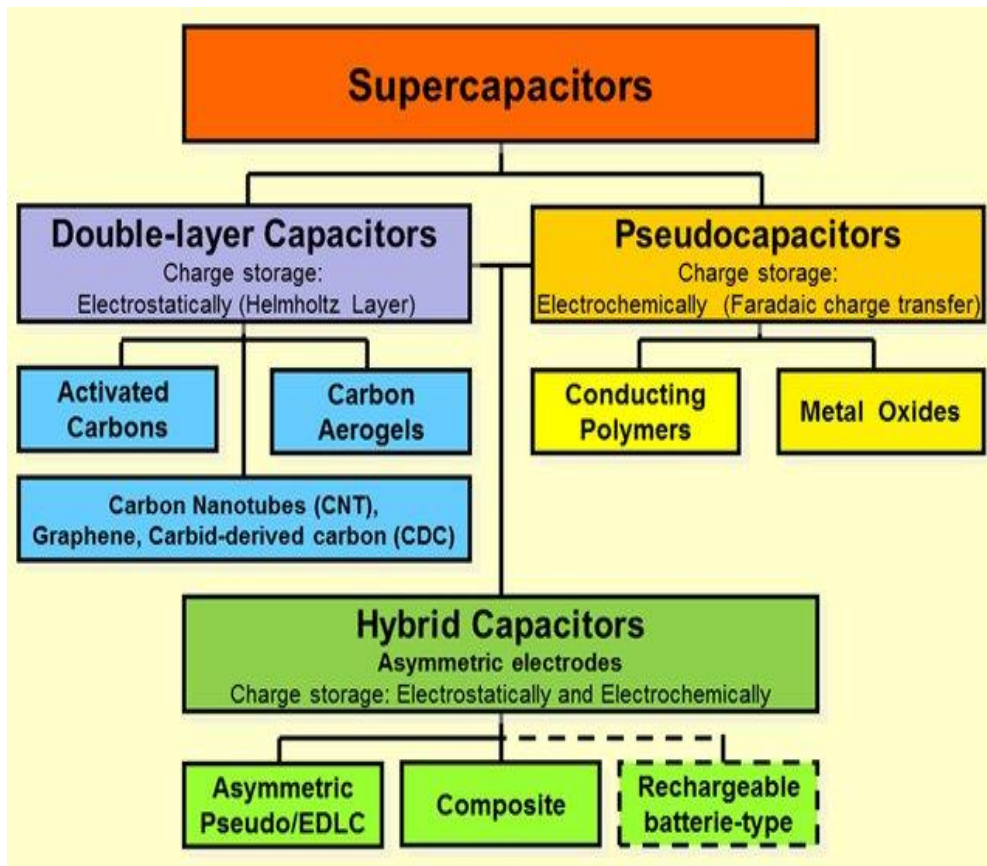


Figure 1.9 Classification of supercapacitors.³⁹

a) Electrochemical double-layer capacitors (EDLCs)

EDLC stands for Electric Double-Layer Capacitor that uses a double-layer capacitance mechanism for energy storage. In EDLCs, porous electrodes separated by an electrolyte accumulate electric charges at their interfaces upon voltage application, forming double layers. These double layers create capacitance, allowing the EDLC to store electrical energy. EDLCs are known for their excellent power density, quick charging and discharging, and long cycle life. They are commonly used in applications requiring burst power delivery, such as in hybrid

vehicles, renewable energy systems, and portable electronics. The commonly used electrode materials in EDLCs are activated carbon, carbon aerogel, carbon nanotube and graphene, etc. High conductivity and large surface area are crucial factors for achieving high capacitance in electrodes. Consequently, carbon-based materials possessing large surface areas are extensively employed as active substances in EDLCs.⁴⁰ The charging and discharging mechanism of EDLCs are given in **Figure 1.10**.

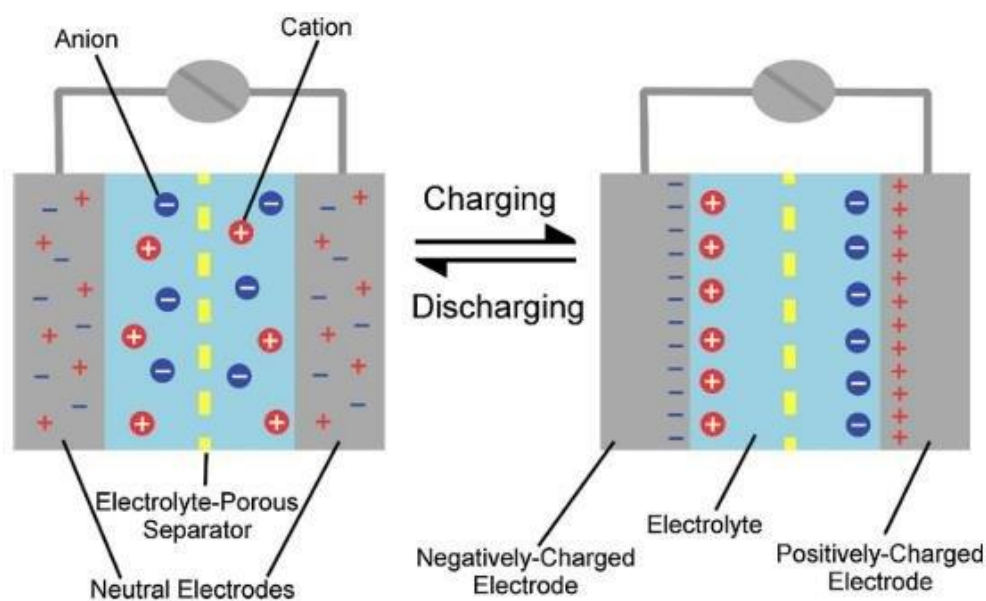


Figure 1.10 EDLCs Charging-discharging mechanism.⁴¹ Copyright © 2016, IEEE.

b) Pseudocapacitors

Pseudocapacitors combine the energy storage features of both capacitors and batteries. Unlike traditional capacitors, which store energy through electrostatic charge separation, pseudocapacitors store energy through quick and reversible faradaic redox reactions at the electrode-electrolyte interface. This allows for higher energy densities than supercapacitors while maintaining their characteristic fast charging and discharging rates. Pseudocapacitors often use transition metal oxides, conducting polymers, or other materials with high surface area and redox activity as electrode materials. They are commonly used in applications such as in portable electronics, electric vehicles, and grid-scale energy storage systems.

Pseudocapacitors store energy by redox reaction and through electron transfer at the electrode-electrolyte interface. The mechanism of pseudocapacitance involves several processes, including electrosorption, redox reactions, and intercalation processes. These mechanisms collectively contribute to the storage of electrical energy in pseudocapacitors and demonstrated

in **Figure 1.11**.⁴² Two common types of electrode materials utilized for storing charge in pseudocapacitors are metal oxides and conducting polymers.

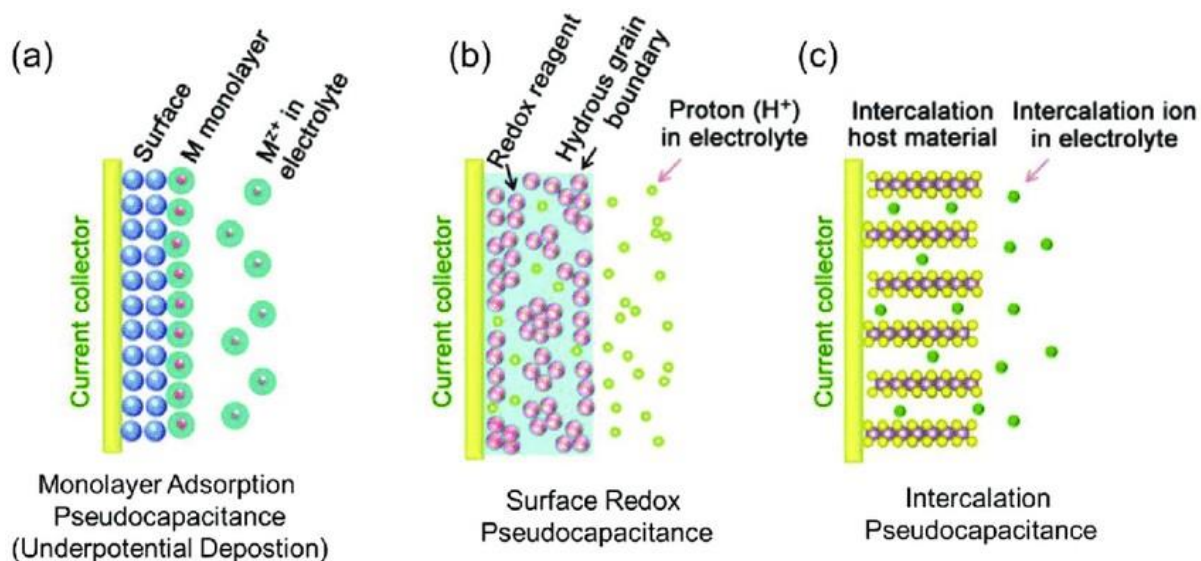


Figure 1.11 Various reversible redox processes contribute to pseudocapacitance including: (a) monolayer adsorption (b) surface redox, and (c) intercalation pseudocapacitance.⁴³

i) Metal Oxides

Different metal oxides such as Fe_2O_3 , MoO_3 , Co_2O_3 , MnO_2 , RuO_2 , NiO , V_2O_5 , CuO , etc., have been identified as electrode materials for pseudocapacitors owing to their excellent conductivity.⁴⁴ The ability to exhibit multiple valence states and undergo reversible redox reactions, these materials are well-suited for various electrochemical applications. However, their low conductivities result in lower electrochemical potentials. Ruthenium oxide is the focus of much research due to its superior capacitance compared to other metal oxides and having highest specific capacitances.⁴⁵ Nevertheless, the practical application of this approach is hindered by its low flexibility and conductivity, rare materials, high cost and environmental harm.³⁷

ii) Conducting polymers

Conductive polymers are commonly employed as electrode materials in pseudocapacitors owing to their outstanding redox characteristics, high specific capacitance, and swift charge-discharge rates.³⁷ The combination of high charge density and cost-effectiveness makes conducting polymers an attractive choice for various energy storage devices, including pseudocapacitors.

Among the most extensively researched conducting polymers for incorporation into supercapacitor devices are polyaniline, polypyrrole (PPy), poly(3,4-ethylenedioxythiophene) (PEDOT), and various derivatives of polythiophene. These materials offer tunable electronic conductivity and can attain high levels of doping when paired with the appropriate counterion.^{25,46}

In conjugated polymers, energy storage and release are facilitated through redox reactions. During oxidation, ions are incorporated into the conducting polymer backbone, while during reduction (de-doping), ions migrate back into the bulk electrolyte. As a result, the charging process within the conducting polymer-based electrode occurs throughout the bulk material, rather than solely on the electrode surface. This feature contributes to the observed high specific capacitances in such electrodes.

c) Hybrid Supercapacitors

A hybrid supercapacitor combines features of both traditional supercapacitors and batteries.⁴⁷ It typically consists of two electrodes, one with a high surface area like EDLC and the other with a high capacitance resulting from fast redox reactions (pseudocapacitance). It involves the charge storage electrostatically and electrochemically.

Unlike electric double-layer capacitors (EDLCs), hybrid systems offer both high specific capacitance and improved specific energy. These systems demonstrate superior power density and cycle stability, which are typically limiting factors for pseudocapacitors. Hybrid supercapacitors and their corresponding electrodes are categorized into various types based on the materials utilized in their fabrication. Asymmetric hybrid supercapacitor electrodes consist of one electrode utilizing electrochemical double-layer capacitance (EDLC) and another electrode employing pseudocapacitance.⁴⁸ Battery-type hybrid supercapacitor electrodes consist of one electrode from a battery and one from a supercapacitor. These hybrids aim to meet the demand for both high power from batteries and high energy from supercapacitors. By combining a high energy density battery with fast recharging times and the outstanding power density and cycle life of a supercapacitor, they offer a balanced solution. Another type of hybrid electrode used in supercapacitors is the composite electrode, created by combining conducting polymers, metal oxides, and carbon-based materials.

These materials provide a capacitive charged layer (electric double layer) along with a high surface area backbone, enhancing contact between the electrolyte and pseudocapacitive

materials deposited on them. Hybrid supercapacitors can be categorized as symmetric or asymmetric based on their configurations. In symmetric hybrid supercapacitors, the electrodes consist of two similar materials, incorporating both pseudocapacitive and electrochemical double-layer capacitance (EDLC) properties. Conversely, asymmetric hybrid supercapacitors are made up of two electrodes from dissimilar materials. The working mechanism of hybrid supercapacitors are illustrated in **Figure 1.12**. In this demonstration, charge storage mechanism is EDLC type generated from an electrode made up of activated carbon and pseudocapacitive type, which originates from another Lithium oxide electrode.

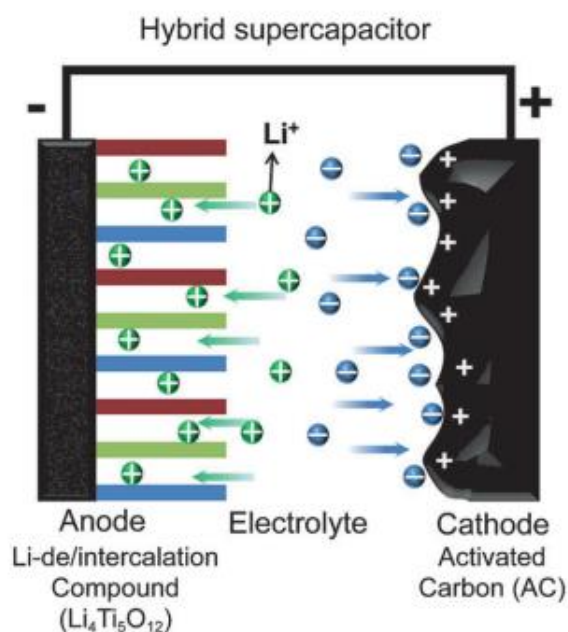


Figure 1.12 Hybrid Supercapacitor.⁴⁹ Copyright © 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

1.4.4 Conjugated Polymer as Electrode material for supercapacitors.

The first conductive polymer polyacetylene was discovered in the 1970s⁵⁰ Since this discovery, conducting polymers (CPs) have seen swift advancement across a spectrum of applications, thanks to their unique physical and chemical attributes. Among these applications, conjugated polymers show promise as electrode materials owing to their high conductivity, capacitance, ease of synthesis, and environmentally friendly characteristics.^{27,51}

Conjugated polymers hold significant promise due to their ability to achieve high charge densities while being cost-effective to produce, especially when compared to expensive metal

oxides.⁵¹ Supercapacitors are classified into four different types based on the conducting polymers used and device configuration.^{46b,52,53} Type I supercapacitors- It is being symmetric with p-type polymers electrodes. However, the operating voltage window ranges from 0.5 to 0.75 V in aqueous electrolytes which results in low energy density. In contrast, asymmetric type II devices- It use distinct p-type polymers as electrode. This setup extends the working potential window of device. As a result, Type II devices exhibit a broader voltage window and higher energy density compared to Type I.⁵⁴ Moving on to Type III supercapacitors, which are symmetric uses both n-type or donor-acceptor conjugated polymers. Type III provides high voltage and energy density as compared to Type I and II due to the use of D-A polymers⁵³ Lastly, Type IV supercapacitors involve an asymmetric setup like Type II, offering enhanced performance in terms of voltage window and energy density.⁵⁵

Among the frequently employed conjugated polymers for supercapacitor electrodes are polyaniline, poly(3,4-ethylenedioxythiophene), and polypyrrole. These materials, are characterized by their electron-rich nature, exhibit favorable charge-storage properties, making them popular choices in supercapacitor applications.⁴⁶ The conjugated polymers store the energy by redox reaction process - n-type doping and p-type doping as discussed in **Section 1.2**.

Although the conducting polymers exhibit higher charge storage capacities compared to carbon materials (EDLCs).⁵⁶ The carbon materials such as carbon nanotubes, graphene, activated carbons, and carbon aerogel etc., offer superior stability, excellent electrical conductivity, and longer cycle life. The conducting polymers mixed with these carbon materials to use as electrode material offers several advantages. These include enhanced mechanical stability, heightened conductivity, and increased surface area. Consequently, such composites result in improved charge retention and enhanced capacitive behavior.⁵⁷ The most common polymers and their composites (**Figure 1.13**) utilized for Supercapacitor electrode are described below,

I. PolyAniline (PANI)

Polyaniline (PANI) has garnered significant attention as a conducting polymer, particularly for its potential as an electrode material in supercapacitors. It offers notable attributes including high specific capacitance, excellent electrical conductivity, electrochemical stability, tunable properties, flexibility, processability, environmental compatibility, and multiple redox states. Polyaniline (PANI) is a widely studied conducting polymer with promising applications as an

electrode material in supercapacitors such as high specific capacitance, high electrical conductivity, electrochemical stability, tunable properties, flexibility, processability, environmental compatibility and multiple redox states.^{24a,58} The electrochemical performance of PANi nanostructures depends upon morphology, so synthesis of PANI by efficient method plays a crucial role. Polyaniline (PANi) can be synthesized relatively easily through chemical or electrochemical polymerization methods. Among Various polymerization techniques,⁵⁹ interfacial polymerization stands out for the synthesis of PANi nanofibers as this is a relatively straightforward and cost-effective method.

Sivakkumar and colleagues⁶⁰ fabricated PANI nanofibers using the interfacial polymerization method and utilized as electrode in supercapacitor and exhibited a capacitance of 554 F g⁻¹ (1.0 A g⁻¹). However, PANI showed lower experimental capacitance as compared to its theoretical capacitance value of 2000 F g⁻¹.⁶¹ The polyaniline composites are extensively studied with different carbon material such as carbon nanotube, carbon nanofibers, carbon spheres or particles, graphene, graphene oxide (GO) and reduced GO. K. Wang et al.⁶² showcased polyaniline (PANI) nanowires grown on an Au electrode through electropolymerization. These nanowires were then utilized as electrodes in a supercapacitor with 1M HClO₄ as the electrolyte, achieving a capacitance of 950 F g⁻¹ (1 A g⁻¹). J. Wu and colleagues⁶³ developed PANI/rGO composites and exhibits notable performance, attributed to favorable morphology aiding electrolyte diffusion and electron transport. S. Kurungot et al.⁶⁴ developed a PANI–Toray paper through *in-situ* electropolymerization and this electrode material exhibited a specific capacitance (Cs) of 1335 F g⁻¹ (10 A g⁻¹) in a solid-state symmetric supercapacitor operating. It also showed good cycle stability and average energy and power density. The polyaniline graphene nanorod composite synthesized via *in-situ* electropolymerization showed the synergistic effect between PANI and graphene.⁶⁵ The PANI/graphene composites synthesized in-situ demonstrate a significant capacitance of 763 F g⁻¹ at 1 A g⁻¹, outperforming both graphene paper (180 F g⁻¹) and pristine PANI (520 F g⁻¹). Many research investigations have delved into employing polyaniline composites that integrate *in-situ* additions of carbon nanotubes or graphene as electrode materials in supercapacitors.⁶⁶ These nanocomposites have shown enhanced charge-storage properties and stability compared to pristine polyaniline.

II. Polypyrrole (PPy)

Polypyrrole (PPy) is another significant conducting polymer that has generated interest as one of the most promising materials due to its array of unique advantages. These include excellent conductivity, straightforward synthesis methods, environmental friendliness, and cost-effectiveness. Consequently, PPy finds applications across various fields, including supercapacitors, batteries and fuel cells.^{67,68}

Dubal and coworkers⁶⁹ synthesized a polypyrrole (PPy) with various nanostructures of on stainless steel substrates, aiming at their utilization in supercapacitor (SC) applications. Among the array of nanostructures investigated, the PPy nanosheets displayed the most remarkable performance of C_s to be 586 F g^{-1} (2 mV s^{-1}) surpassing the performance of other nanostructures. In general, the polypyrrole demonstrated pseudocapacitive performances lower than their theoretically anticipated values and exhibited poor stability. Thus, PPy is used with conducting material to increase the specific capacitance and cycle stability. An et al.⁷⁰ synthesized a polypyrrole composite with SWCNTs as electrodes, achieving a specific capacitance of 265 F/g , surpassing pristine PPy and SWCNTs. Meanwhile, Wu et al.⁷¹ synthesized polypyrrole (PPy) and graphene oxide (GO) based 3D core shell nanomaterial using an in-situ surface-initiated polymerization approach and achieved capacitance of up to 370 F/g (0.5 A/g), with 4000 cycling stability.

Similarly, the *in-situ* polymerization of polypyrrole with CNTS, RGO, copper sulfide (CuS), and molybdenum disulfide (MoS₂) demonstrated improved charge-storage performance compared to pristine polypyrrole.^{70,72} Recently, Smirnov et al. reported the *in-situ* synthesis of polypyrrole in the presence of cellulose nanofibers grown over graphene, resulted high specific capacitance (810 F g^{-1}) than externally mixed sample (371 F g^{-1}).

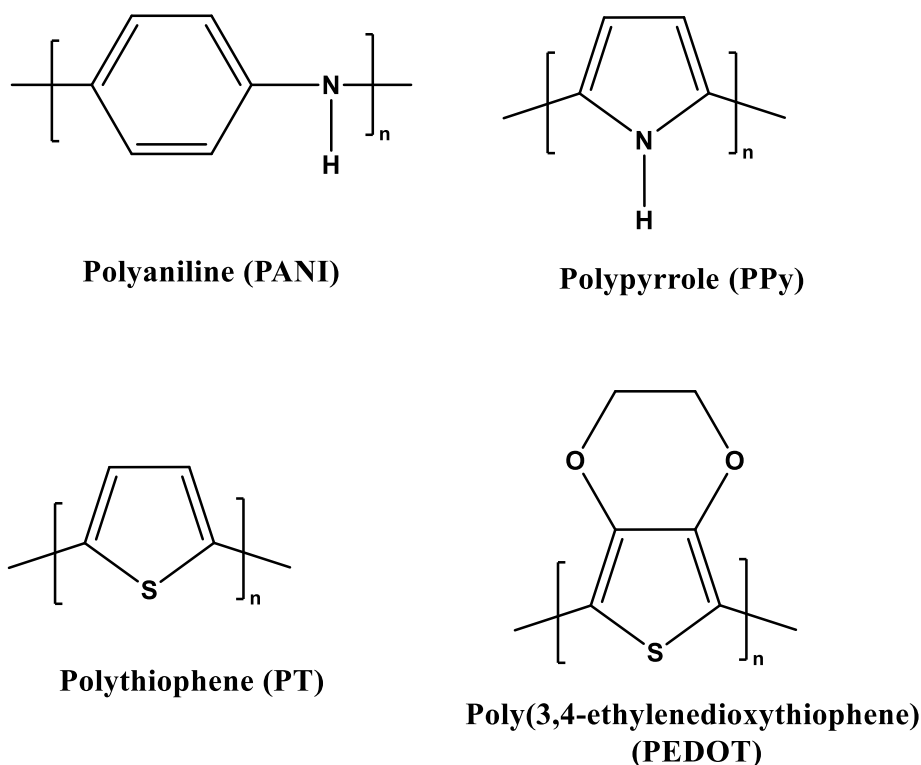


Figure 1.13 The structures of some of the commonly used p-type conjugated polymers.

III. Polythiophene (PTh) and its derivatives

These conducting polymers offer high electrical conductivity, good electrochemical stability, and the ability to undergo reversible redox reactions, making them suitable candidates for energy storage applications.^{3,51,74} Additionally, their tunable properties and ease of synthesis allow for customization to meet specific performance requirements in supercapacitor devices. Overall, polythiophene and its derivatives show promise in contributing to the development of efficient and high-performance supercapacitors.⁷⁵

Laforge and colleagues successfully synthesized polythiophene and investigated as an electrode material in supercapacitors. They achieved a notable capacity of 260 F/g, demonstrating promising electrochemical performance. Moreover, the polythiophene electrode exhibited excellent cycle stability and maintained its capacitance over 500 cycles.⁷⁶ Gnanakan and colleagues studied, PTh-tartaric acid nanoparticles showed a higher specific capacitance than Pure PTh nanoparticles.⁷⁷ Numerous researchers have focused on the development of composite electrodes by blending polythiophene (PTh) with carbon materials. The objective is to create composites that demonstrate enhanced supercapacitor performance compared to individual components. Fu and colleagues⁷⁸ fabricated a polythiophene/multi-walled carbon

nanotube composite through electrochemical methods. The composite electrode displayed superior capacitive properties compared to individual components, namely MWCNT and pristine polythiophene. Xu and colleagues.⁷⁹ Xu et al. synthesized poly(2-(thiophen-2-yl)furan) via electropolymerization, achieving a specific capacitance of 392.0 F g^{-1} at 5 A g^{-1} with limited stability. The operated with broad potential range of 2.0 V by using for both cathode and anode electrode.⁸⁰ For instance, PEDOT synthesized via electropolymerization on a graphite sheet showed 126.5 F g^{-1} capacitance when utilized in symmetrical (type I) supercapacitors.⁸¹ In recent years, the literature concerning PEDOT has expanded rapidly, driven by its exceptionally desirable properties.⁸²

Nevertheless, conductive polymers have a limitation in that they can only operate within a rigid potential window, operating beyond these ranges can lead to degradation of the CPs and it restricts their wide range of applications. Therefore, selecting an appropriate potential window is crucial to ensure the longevity and effectiveness of CP-based systems. The p-type conjugated polymers are commonly used with aqueous electrolytes.

The use of an aqueous electrolyte presents numerous advantages, such as lower resistance and higher ionic concentration, which are desirable for energy storage (ES) devices to achieve increased capacitance. Additionally, aqueous electrolytes offer benefits in terms of lower cost and environmental friendliness. However, a notable drawback of this electrolyte is its limited voltage window of 1.2 V. This constrained voltage range adversely impacts the energy density and power density, both critical properties of supercapacitors. One of the primary limitations of supercapacitors, particularly for practical applications, is their relatively lower energy storage capacity compared to batteries.

A slight increase in voltage can significantly enhance energy density. P-type conjugated polymers are often paired with aqueous electrolytes, limiting their voltage window to 1.2 V, while n-type or donor-acceptor conjugated polymers offer potential for broader voltage ranges, enabling energy storage in both positive and negative electrodes.

These donor-acceptor (n-type) conjugated polymers are essential in advancing the field of high-energy supercapacitors. The organic electrolytes demonstrate stability in operation at higher operating voltages, reaching up to 3.5 V. Therefore, investigating donor-acceptor polymers as electrode materials in conjunction with organic electrolytes is crucial for the advancement of high-energy supercapacitors. Despite their benefits, organic electrolytes face challenges such as low ionic conductivity, resulting in increased internal resistance, suboptimal electrode-

electrolyte interaction, and elevated operational expenses, ultimately leading to diminished electrochemical performance. Additionally, polymer electrodes with rigid structures struggle to establish effective contact with electrolytes.⁸³ Improving the conductivity of electrode materials and optimizing the electrode-electrolyte interface is crucial to minimize electrolyte resistance in supercapacitors using organic electrolytes, as restricted counter-anion diffusion and low conductivity may limit the electrochemical reaction to the electrode surface, leaving much of the polymer material unreacted.³

Consequently, it is observed that the donor-acceptor polymers exhibited expressively low performance than theoretical results.⁸⁴ Recently, Researchers have been trying to address this problem by synthesizing an electrode material suitable structural modification as described in next **Section 1.4.4 IV**.

IV. Donor-acceptor (n-type) conjugated polymers

The donor-acceptor conjugated polymers are efficiently and well explored in the field of organic photovoltaics. More recently, these polymers have gained attention as electrode materials in energy storage devices, offering several advantages over expensive metal oxides and carbon materials.^{52,80b,85,86} These polymers are widely employed in optoelectronic applications owing to their favorable characteristics, such as high charge carrier mobilities, straightforward processability, broad absorption across the entire visible spectrum, lightweight nature, and facile synthesis.^{87,88}

The utilization of donor-acceptor polymers as electrode material for supercapacitors is due to their ability to enhance efficiency. The donor-acceptor polymers with low bandgap are efficient materials to store energy in both positive and negative electrodes, obtaining a higher operating voltage window.^{53,89} However, there are only few reports of the n-type (donor-acceptor) polymers utilized as electrode material for energy storage devices. Mostly, these polymers are used as electrode material for Type III (symmetric), Type IV (asymmetric) or Hybrid supercapacitor device as discussed in **Section 1.4.4**. The donor-acceptor polymers offer several advantages over p-type polymers as electrode materials for supercapacitors like compatible with organic electrolytes, operates with wider potential window which further leads to enhance high energy density of supercapacitor device. Despite their promise, donor-acceptor polymers

face several challenges as electrode materials for supercapacitors such as low electrical conductivity, low cycle stability, and optimization of electrode/electrolyte interfaces.

In recent studies, researchers have been trying to address this problem by synthesizing electrode materials with suitable structural modifications. A few such reports are presented in this section. John R. Reynolds and colleagues published a study introducing a novel P((BEDOT-*il*)) donor-acceptor polymer derived from EDOT and Isoindigo.⁵³ This type III device operated in high voltage window of 2.25 V but low cycle stability (50 % lost after 100 cycles). Seferos and co-authors⁸⁹ synthesized donor-acceptor polymers P(DEQ) and P(DDDBT) and incorporated them into Type III supercapacitors. Both polymers were employed in supercapacitors with notably wide voltage windows of 2.5 V, surpassing those of PEDOT used in Type I devices. This study proved that the impact of acceptor group on stability and conductivity of donor-acceptor polymers. The P(DDDBT) donor acceptor polymer having more acceptor units showed good performance compared to P(DEQ), but the performance of the device itself was poor and diminished with cycling.

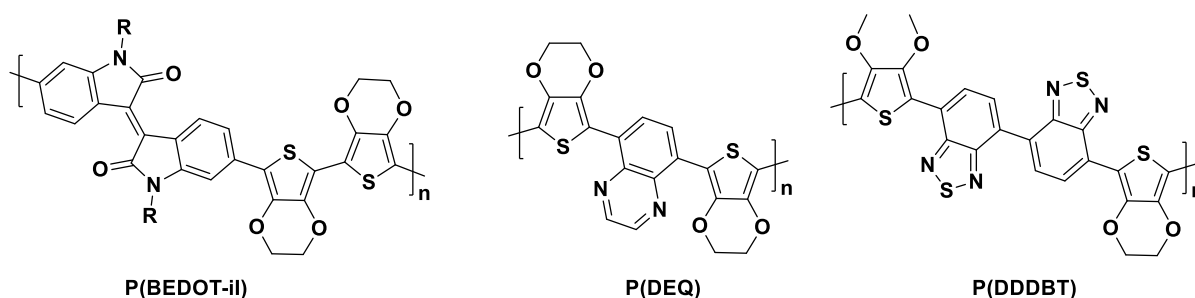


Figure 1.14 Chemical structure of P((BEDOT-*il*)), P(DEQ) and P(DDDBT) polymers.

In 2015, Unalan et al.⁹⁰ synthesized donor-acceptor P(DTBT) polymers and sprayed it over the SWCNT layer and utilized as electrode for electrochromic supercapacitor. The SWCNT/P(DTBT) showed the improved capacitance of 112 F g⁻¹ at 1 Ag⁻¹ compared to SWCNT. It showed exceptional cycle stability of 12500 cycles with 85 % retention and operated with low voltage window of -0.3 to 1.5 V. Luscombe et al.³² synthesized three n-type hyperbranched donor-acceptor polymers from triphenylamine (TPA) and naphthalene diimide (NDI) monomer with varying thiophene spacers for application as cathode material of supercapacitor. The polymers were synthesized with controllable pore sizes and surface area to enhance the diffusion rates of solvents and electrolytes. However, both symmetric and asymmetric supercapacitor devices were assembled with a voltage limit of 2.0 V. These devices

exhibited moderate capacitance of 0.5 and 22 F g⁻¹, respectively. Impressively, they demonstrated cycling stability over 500 cycles with 90% retention of capacitance.

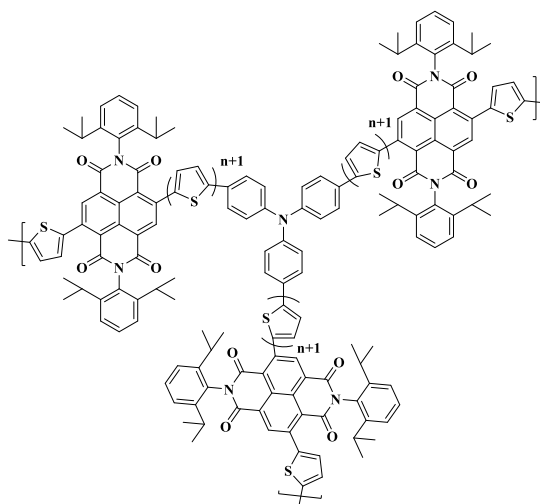


Figure 1.15 Structure of N-type hyperbranched donor-acceptor polymer based on triphenylamine (TPA) and naphthalene diimide (NDI) monomer.

In another study, Hong Meng et al.⁹¹ synthesized porous PBOTT-BTD donor-acceptor polymer and spray-coated it over flexible ITO/PET substrate to form a film. Further, PBOTT-BTD polymer used in positive electrode asymmetric device with PEDOT as a negative electrode in 1.4 V potential windows which showed capacitance of 21 F g⁻¹. The D-A polymer exhibited improvement of capacitance as compared to PDEBT polymer in three-electrode configuration but was unable to achieve a high potential range and good cycle stability which can be attributed to its high internal resistance.

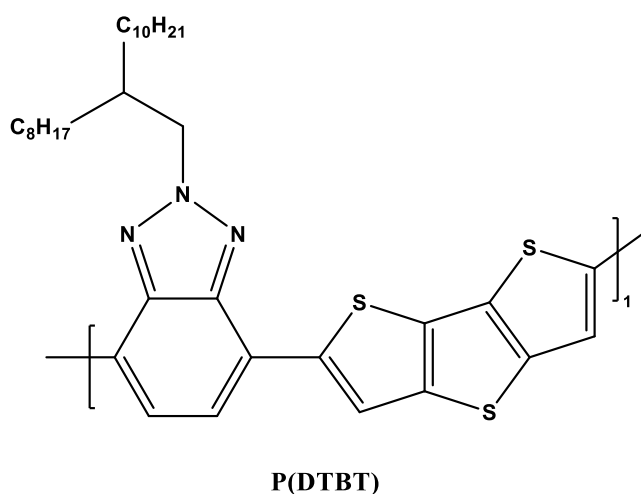


Figure 1.16 Chemical structure of P(DTBT) polymer.

Recently, Cheng Zhang et al.⁹² synthesized donor-acceptor conjugated polymers using anthraquinone and nitrobenzene acceptors with EDOT-carbazole-EDOT as donor and applied them as electrode materials for supercapacitor. The investigation focused on incorporating electron-withdrawing groups into conducting polymers and analyzing their influence on hole injection, subsequently impacting crucial electrochemical properties like capacitance and cycling stability. However, despite these efforts, the polymers yielded lower capacitance values. Their stability reduced after 500 cycles with very less retention of active material.

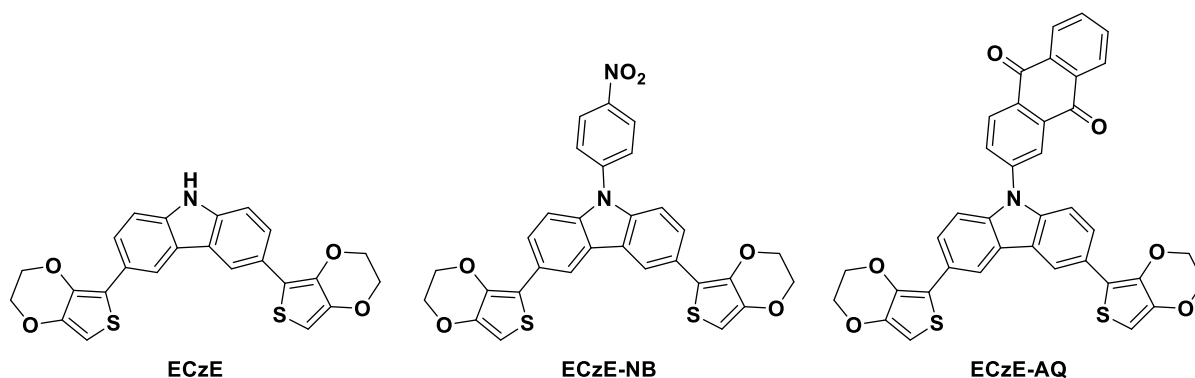


Figure1.17 The structure of ECzE, ECzE-NB and ECzE-AQ.

Our research team synthesized donor-acceptor polymers via direct heteroarylation polymerization (DHAP), incorporating naphthalenediimide (NDI) and thiophene-terminated phenylenevinylene, and evaluated their performance in supercapacitors.⁵² The polymer composite, designated as P-2, exhibited a specific capacitance of 124 F g^{-1} at 0.5 A g^{-1} , coupled with excellent stability over 5000 cycles. Furthermore, a type III symmetric supercapacitor (SC) was assembled utilizing carbon nanotubes and the polymer composite as electrodes, demonstrating a capacitance of 40 F g^{-1} at 0.5 A g^{-1} when operated with 1.0 V in an aqueous electrolyte. In another study conducted by our research group,⁸⁶ the charge storage capacity of rylene-based donor-acceptor alternating and random polymers was examined. The random copolymer exhibited lower capacitance compared to the alternating polymers. Specifically, the perylene-based alternating polymer P(PDI-alt-BDT) demonstrated a high specific capacitance.

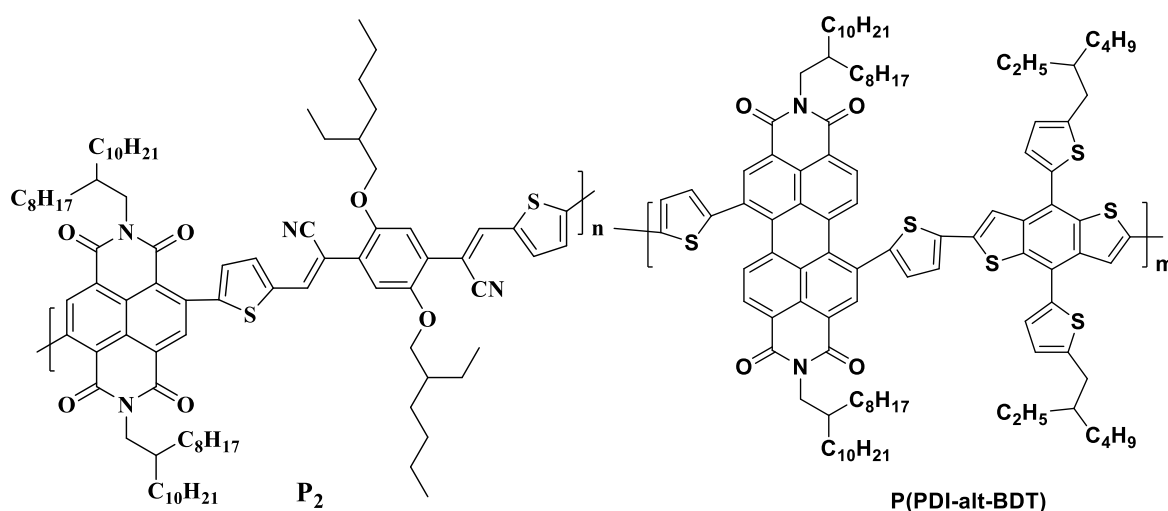


Figure 1.18 The structure P-2 polymer based on naphthalene diimide (NDI) acceptor and thiophene-terminated phenylenevinylene donor and P(PDI-alt-BDT) alternate polymer.^{52,86}

Despite numerous efforts to enhance the electrochemical performance, the donor-acceptor polymers presented here exhibited limitations including low capacitance, high equivalent series resistance, low energy density, and poor cycle stability. Hence, there is a critical need for designing and synthesizing electrode materials with high surface area and large pore size to attain improved performance in supercapacitor devices. The structure of common donor acceptor conjugated polymer used as electrode material in supercapacitor are shown in **Figure 1.14-1.18**.

1.5 Synthesis of Donor-acceptor conjugated polymer

As we already discussed in **Section 1.2.3**, Donor-acceptor conjugated polymers find applications in a diverse array of fields including organic electronics, optoelectronics, photovoltaics, sensors, batteries, and supercapacitors. Despite their potential, the synthesis of conjugated polymers poses challenges such as lengthy reaction times, scalability issues, and reproducibility of molecular weight. Their synthesis allows for the customization of materials to meet the specific requirements of each application. These conjugated polymers exhibit advantages in terms of low cost, good conductivity, flexibility, rich colour variations, simple synthetic procedure, and controllable structure.⁹³

Consequently, the array of synthetic techniques for generating conducting polymers continues to expand. Apart from electrochemical or chemical,⁹⁴ oxidative polymerizations,⁹⁵ transition metal-catalyzed cross-coupling reactions offer a notably potent approach for forming Csp²-

Csp² and Csp-Csp² bonds.⁹⁶ Transition-metal catalysts, particularly those based on nickel or palladium complexes, are frequently utilized in synthetic processes. Palladium-catalyzed cross-coupling reactions are especially prominent for conjugated polymers synthesis. These reactions include the Heck,⁹⁷ Negishi,⁹⁸ Stille,⁹⁹ and Suzuki coupling methods.¹⁰⁰ In 2010, the Nobel Prize was awarded to Heck, Negishi, and Suzuki in recognition of their groundbreaking contributions to the development of cross-coupling reactions.¹⁰¹

Donor-acceptor conjugated polymers are often synthesized using Stille and Suzuki polymerization methods, both of which are outlined below.

1.5.1 Suzuki Polymerization

The Suzuki polymerization, a variant of the Suzuki coupling reaction, is recognized as a potent method for synthesizing conjugated polymers. This technique involves the polymerization reaction of aryl boronic esters or boronic acids with aryl halides (commonly bromides or iodides) in the presence of a palladium catalyst. The molecular structures of the monomers used in the Suzuki cross-coupling reaction are illustrated in **Figure 1.19**. The reaction proceeds through transmetalation, wherein the boron atom of the boronic ester coordinates with the palladium catalyst, followed by oxidative addition and reductive elimination steps. These processes result in the creation of carbon-carbon bonds among the monomers. Overall, the Suzuki polymerization serves as a versatile and extensively utilized technique for synthesizing conjugated polymers, enabling the development of advanced materials with tailored electronic, optical, and mechanical properties.

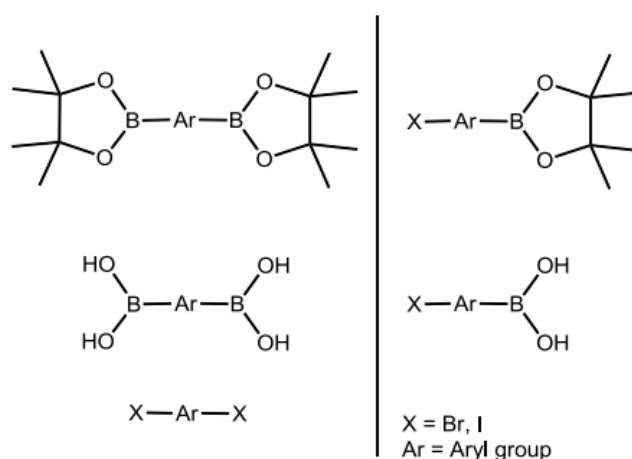


Figure 1.19 The structure of monomers used in Suzuki coupling.

1.5.2 Stille Polymerization

The Migita-Kosugi-Stille coupling reaction, also known as the Stille reaction, stands as a pivotal method for fabricating conjugated polymers.¹⁰² Notably, it has demonstrated the capability to yield polymers of exceptionally high molecular weight with minimal defects.¹⁰³ In this polymerization technique, organostannane compounds react with aryl or vinyl halides (typically bromides or iodides) with the help of palladium catalyst to form polymer backbone.

The mechanism of Stille reactions is elucidated in **Figure 1.20**. Initially, the palladium catalyst ($\text{Pd}(0)\text{L}_2$) undergoes oxidative addition upon reacting with an aryl halide, resulting in the formation of an organopalladium (II) complex. Subsequently, transmetalation takes place, wherein the aryltin compound participates, leading to the formation of a biarylated palladium species. Following this, the biarylated palladium species undergoes trans/cis isomerization. Ultimately, reductive elimination takes place, generating a biaryl product ($\text{R-R}'$) and restoring the palladium (0) species, thus concluding the catalytic cycle.¹⁰⁴

The Stille polymerization method presents numerous advantages, such as operating under mild reaction conditions, exhibiting high tolerance towards various functional groups, and enabling the production of polymers with precisely controlled molecular weights and structures. Additionally, the reaction is known for its ability to generate polymers with high molecular weights and low defect densities. In summary, Stille polymerization stands as a versatile and extensively utilized technique for synthesizing conjugated polymers, providing avenues for the creation of advanced materials with customized electronic, optical, and mechanical properties.

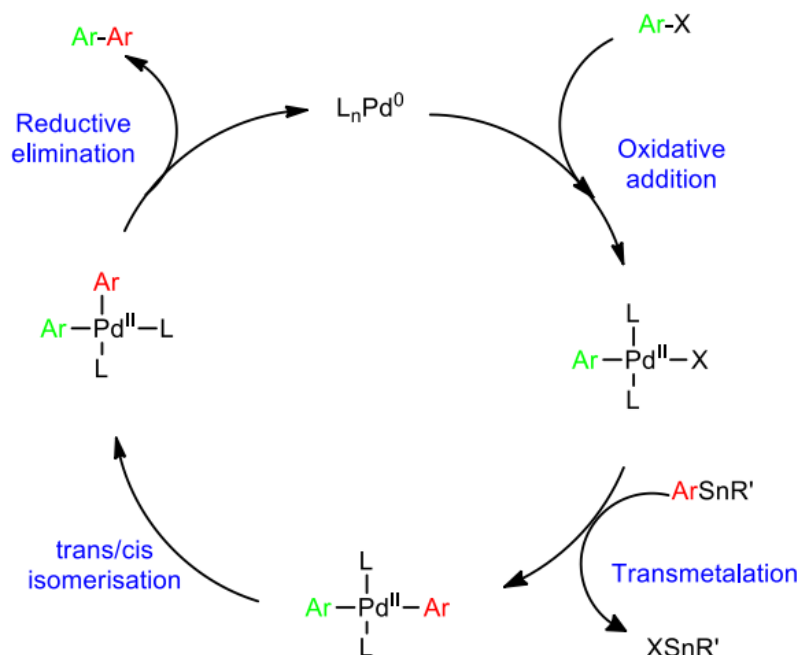


Figure 1.20 Schematic of Stille coupling reaction using Palladium (Pd 0) as catalyst.¹⁰⁵

1.5.3 Batch polymerizations and its limitation: Most commonly, the conjugated polymers are synthesized by conventional batch synthesis. The batch polymerization reactions have some limitations in terms of long reaction times, non-scalable approach due to variability in molecular weight, and polydispersity in every batch. These variation in molar mass and dispersity shows further impact on the low and variable performance of polymer material when it is used in energy applications. This inconsistency can have significant implications for the performance and reliability of the polymers in various applications, as outlined below,

- Physical Properties:** The polymers with different molecular weights can exhibit distinct physical properties such as mechanical strength, flexibility, and viscosity. Batch-to-batch variation in molecular weight may lead to inconsistencies in these properties, affecting the material's suitability for specific applications.
- Optical Properties:** Molecular weight and dispersity of conjugated polymers can influence light absorption, emission, and charge transport properties. Variations in molecular weight from batch to batch may result in differences in device performance, affecting efficiency and stability.
- Electrical Conductivity:** For conducting polymers used in electronic devices or energy storage applications, molecular weight can impact electrical conductivity. Batch-to-

batch variation in molecular weight may lead to differences in charge carrier mobility and conductivity, affecting device performance and efficiency.

- d) **Processing and Compatibility:** Polymers with different molecular weights may require adjustments in processing conditions such as solubility, viscosity, and film-forming properties. Incompatibility between batches due to molecular weight variations can result in processing challenges and inconsistencies in device fabrication.
- e) **Stability and Reliability:** In applications requiring long-term stability and reliability, such as energy storage devices or biomedical implants, batch-to-batch variation in molecular weight can affect material degradation rates, mechanical integrity, and device lifetime.

The impact of different batch to batch molecular weight and polydispersity are described here using few examples, Bumjoon J. Kim et al.¹⁰⁶ synthesized a donor polymer, PPDT2FBT with M_n of 12, 24, and 40 kg mol⁻¹, used for PSC in combination with P(NDI2OD-T2) electron acceptor polymer. This exhibited varying power conversion efficiencies (PCEs) 3.78%, 4.18%, and 5.03% for the electron donor PPDT2FBT polymers with molecular weights of 12, 24, and 40 kg/mol, respectively. This research highlights the substantial impact of varying polymer molecular weights on the efficiency of solar cells. In another study, Alex K. Y. Jen et al.¹⁰⁷ demonstrated Organic Field-Effect Transistors (OFETs) using a donor-acceptor PIDSe-DFBT polymer with three different number average molecular weights: 30.1, 46.3, and 61.8 kg/mol. They observed that the polymer with the highest molecular weight exhibited superior performance in terms of both electron mobility and hole mobility. Later, Sunghun Cho and colleagues¹⁰⁸ demonstrated two-electrode symmetric supercapacitors utilizing PPy:PSS electrodes with varying molecular weights (M_w) of Poly(4-styrenesulfonate) (PSS). The molecular weights of PSS used in the supercapacitors were 1000 kg/mol, 200 kg/mol, and 70 kg/mol. Capacitance values of the PPy:PSS supercapacitor were measured as 25.3, 13.0, and 109.5 F g⁻¹ at 0.05 A g⁻¹, respectively. This study underscores the significant influence of polymer molecular weight on the energy storage performance of supercapacitors.

1.5.4 Microwave Polymerization

As described in **Section 1.2**, the organic semiconductors or conjugated polymers are showing great interest in a variety of application. These conjugated polymers are commonly used batch polymerization which is simple but having some limitations. Recently, the microwave-

assisted synthesis of conjugated polymer has gained better interest. The Microwave polymerization is the prominent approach to overcome the limitation of batch polymerizations and offers several advantages including shorter reaction times, higher reaction yields, and improved control over the polymerization process.¹⁰⁹ Microwave-assisted polymerization of conjugated polymers is a technique where microwave radiation is utilized to facilitate the synthesis of these polymers. In this method, the reaction mixture containing the monomers and any necessary catalysts or initiators is exposed to microwave irradiation. Microwave irradiation heats the reaction mixture rapidly and uniformly, leading to faster and more efficient polymerization reactions. The general microwave reaction set up are given in **Figure 1.21**. Additionally, microwave-assisted polymerization allows for the synthesis of conjugated polymers with tailored properties, making it a valuable tool in materials science and polymer chemistry.



Figure. 1.21 The general microwave reaction set up.

Microwave-assisted polymerization enables precise control over reaction conditions such as temperature and reaction rate. This control allows researchers to tailor the properties of the synthesized polymers to meet the specific requirements of different applications, such as desired molecular weight, dispersity, and optoelectronic properties. Polymers synthesized using microwave-assisted polymerization may exhibit improved performance characteristics, such as higher charge carrier mobility, improved light absorption, and better charge transport properties. Microwave-enhanced polymerization offers scalability for large-scale production of conjugated polymers, rendering it suitable for industrial manufacturing and application. The shorter reaction times and higher reaction yields offered by this method contribute to increased

efficiency and reduced manufacturing costs. Overall, microwave-assisted polymerization holds promise as a valuable tool for synthesizing polymers tailored for use in different applications, offering advantages in terms of speed, purity, control over properties, device performance, scalability, and efficiency.

1.5.5 Continuous Flow Polymerization

Overall, batch-to-batch variation in molecular weight can introduce uncertainties and inconsistencies in polymer performance, impacting the reliability, efficiency, and functionality of materials in various applications. Minimizing this variation through improved process control, quality assurance measures, and optimization of polymerization conditions is essential for ensuring consistent and reliable performance in real-world applications. This research aims to address this problem by investigating the synthesis of donor-acceptor conjugated polymers for energy applications using a continuous flow method.¹¹⁰ By implementing continuous flow polymerization as an alternative approach and adopting best practices in polymer synthesis and manufacturing, it is possible to mitigate batch-to-batch variations in conjugated polymers and ensure consistent product quality for commercial applications. Continuous flow polymerization is a method of polymer synthesis where reactants are continuously fed into a reaction system and polymerization occurs in a continuous manner as the reaction mixture flows through a reactor. The simple schematic for continuous flow polymerization given in **Figure 1.25**. The continuous flow polymerization offers several advantages over traditional batch methods, including improved control, scalability, efficiency, less reaction time, proper heat transfer and safety.

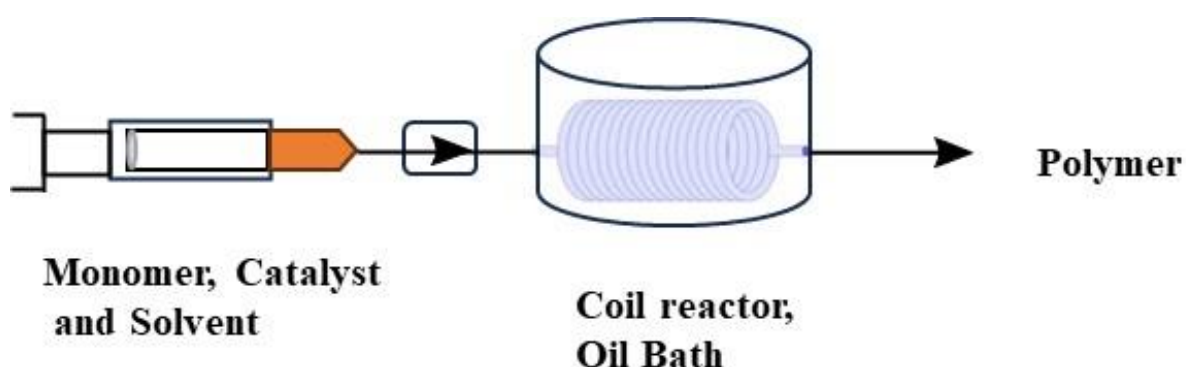


Figure 1.22 Schematic representation of continuous flow polymerization.

Implementing continuous flow polymerization methods can provide better control over reaction conditions and enhance consistency in polymer properties compared to traditional batch processes. Continuous flow systems enable precise regulation of reactant flow rates, reaction temperatures, and residence times, resulting in more uniform polymerization and reduced variability between batches.

1.6 Aim of The Thesis

A detailed literature survey was carried out about the role of conjugated polymer in various energy related applications such as energy generation and energy storage. Particularly, the donor-acceptor conjugated polymers are efficient material which plays an important role in application in organic light emitting diode (OLED), organic polymer solar cell, battery and supercapacitor. Introduction also highlighted the significance of supercapacitors in energy storage devices and the advancements that are necessary for supercapacitors. In supercapacitor, p-type conjugated polymers are commonly used as electrodes which limits the high energy density due to operation in low potential window. In this view, donor-acceptor conjugated polymers are efficient materials to obtain a higher operating voltage window. However, donor-acceptor conjugated polymer suffers from limitations such as high equivalent series resistance, low capacitance, cycle stability. So, there is a need to develop an efficient electrode material.

Although, the donor-acceptor conjugated polymers exhibited a valuable role in different energy applications. The synthesis of conjugated polymers remains a challenge for commercial purpose and reproducing the device-level performance in different energy applications. These conjugated polymers are most commonly synthesized by conventional batch synthesis which has limitations in terms of time taking reactions, non-scalable approach due to variation in molecular weight, and polydispersity in different batches. However, these issues can be tackled by using an efficient synthetic method such as the continuous flow synthesis.

The aim of this thesis is to synthesize suitable donor-acceptor conjugated polymers for application as efficient supercapacitor electrodes. In chapter 2, the P(PDI2OD-T2) donor-acceptor conjugated polymer and its composites with multiwalled carbon nanotubes (MWCNT) were synthesized. The polymer/MWCNT composites were synthesized by *in-situ* polymerization approach within very short reaction time. This *in-situ* strategy further provides the utilization of a synthetic method to fine-tune the morphology, surface area, and porosity of

materials to achieve better electrochemical properties of polymeric supercapacitor electrodes. Further, the symmetric supercapacitor devices fabricated using polymer composite exhibited excellent capacitance and stability. Finally, the quasi-solid device was demonstrated that exhibited an impressive power density and energy density indicating its practical viability for real-world applications. In chapter 3, the naphthalene-based P(NDI2OD-T2) donor-acceptor conjugated polymer and their *in-situ* synthesized composites were utilized as electrode material. The asymmetric hybrid supercapacitor demonstrated using a P(NDI2OD-T2) polymer/MWCNT composites achieved high capacity along with better cycle stability. This research focused on achieving precise control over polymer properties, including molecular weight, and chemical structure, surface area, morphology to optimize the performance of the resulting polymers in supercapacitor energy storage applications.

Conjugated polymers are attractive and promising materials for several applications relating to energy. These conjugated polymers are most commonly synthesized by conventional batch synthesis which has limitations in terms of long reaction times, non-scalable approach due to batch-to-batch variation in molecular weight, and polydispersity. In the last chapter, this problem was addressed by investigating the synthesis of donor-acceptor conjugated polymers for energy applications using a continuous flow method. The P(NDI2OD-T2) is well known polymer for different energy related application and NDI-Th-PDI-30 donor-acceptor polymers are efficient acceptor polymer for organic polymer solar cell which are studied from our group. So, these two polymers were chosen for optimization of synthetic strategy. The study also focused on optimizing the synthesis of these polymers in batch, microwave, and continuous-flow synthetic methods. Additionally, the thesis aims to investigate the scalability, efficiency, and reproducibility of continuous flow polymerization for synthesizing conjugated polymers tailored for energy applications, with the ultimate goal of contributing to the development of high-performance and sustainable energy applications.

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CHAPTER 2

**Enhanced High-Voltage Symmetric
Supercapacitor Electrodes via In-situ Synthesized
Multiwalled Carbon Nanotube-Doped
Perylenebisimide based Donor-Acceptor
Conjugate Polymer P(PDI2OD-T2)**

2.1 INTRODUCTION

Supercapacitors (SC) have demonstrated significant ability in the energy storage field because of high power density, stability of devices, excellent reversibility, and quick charging/discharging capabilities.¹⁻⁵ The electrode materials are the central components of these energy storage devices and perform an important function in determining their overall efficiency.⁶⁻⁷ In Energy-storing devices, the conjugated polymers are commonly used as prominent electrode materials due to several advantages as compared to costly metal oxide and carbon materials.⁸⁻¹³ The conjugated polymers exhibit advantages in terms of low cost, good conductivity, flexibility, rich color variations, simple synthetic procedure, and controllable structure.^{8,14-16} Energy density is one of the key parameters for developing efficient supercapacitor devices and meeting the needs of various applications of energy storage. However, the supercapacitor's energy density [$E = \frac{1}{2} CV^2$] is directly dependent upon the specific capacitance C and to the square of the operating voltage.¹⁷⁻¹⁸ The energy density of the device is significantly enhanced by even a slight voltage rise. In general, for energy storage applications, electron-rich or p-type conjugated polymers are used with aqueous electrolytes which limit their voltage window.¹⁹⁻²⁰ The donor-acceptor conjugated polymers are efficient materials to obtain a higher operating voltage window by storing energy in both positive and negative electrodes. Their application in combination with organic electrolytes is an important aspect of developing a high-energy supercapacitor.^{17,21}

The use of organic electrolytes offers a higher voltage window,²² however it has limitations such as limited ionic conductivity, higher internal resistance, and poor electrode|electrolyte interaction. A polymer electrode having a rigid structure offers poor contact with electrolytes, low counter-anion diffusion, and low conductivity due to the unexposed surface of the electrode, all of which lowers the performance.^{4,23} Consequently, it is observed that the donor-acceptor conjugated polymers show a significantly low performance compared to the theoretically predicted results.²⁴ In recent studies, researchers have been trying to address this problem by synthesizing electrode materials with suitable structural modifications. A few such reports are presented in this section. Luscombe et al. synthesized a series of three hyperbranched donor-acceptor polymers from triphenylamine (TPA) and naphthalene diimide (NDI) monomers with varying thiophene spacers for application as cathode material of supercapacitor.²⁵ In another work, Hong Meng et.al described the preparation of porous P(DEBT/TETPA) copolymer electrode where TETPA possessed a tetrahedral structure to

induce porosity and DEBT performed as a carrier.²⁶ Recently, Cheng Zhang et al. synthesized donor-acceptor conjugated polymers using anthraquinone and nitrobenzene acceptors with EDOT-carbazole-EDOT donor and applied them as electrode materials for supercapacitor.²⁷ This study explored the effect of incorporation of electron-withdrawing groups into conducting polymers and its impact on hole injection, which in turn affects key electrochemical properties such as capacitance and cycling stability. Despite these approaches, so far, the donor-acceptor polymers suffer from poor energy density, large equivalent series resistance, limited capacitance, and restricted cyclability.^{17,21,28} Therefore, the development and synthesis of electrode materials that increase surface area and expose the reaction centres is crucial for enhancing the performance of supercapacitors.²⁹

One of the approaches for enhancing the surface area of the polymers is to mix porous conducting carbon based additives like graphene, CNTs, carbon nanofiber, and carbon black with conjugated polymers.³⁰⁻³⁶ Carbon nanotubes (CNTs), a class of conducting carbon materials, are distinguished by their exceptional properties including high electrical conductivity, extensive surface area, robust thermal stability, and notable flexibility.³⁷ Different strategies have been exploited to develop composites of conjugated polymers with singled walled carbon nanotubes (SWCNT) and multiwalled carbon nanotubes (MWCNT).³⁸ Among these approaches, the *in-situ* synthesis has been reported to be effective for p-type polymers, for example polypyrrole,³⁹⁻⁴¹ poly(3-hexylthiophene),⁴² PEDOT,⁴³ Polythiophene,⁴⁴ polyaniline⁴⁵⁻⁴⁹ etc. It has been shown that *in-situ* mixing of CNT with conjugated polymers exhibits better electrochemical performance as compared to external mixing of pristine polymer and neat CNT due to their uniform mixing, high surface area, better morphology control, and improved conductivity in the former case.

Herein, we present the first report of a perylenebisimide based donor-acceptor π -conjugated polymer P(PDI2OD-T2) and its *in-situ* composite with MWCNT, which exhibited potential application as both positive and negative electrode material for supercapacitor application. The P(PDI2OD-T2) or poly{[N,N'-bis(2-octyldodecyl)-3,4,9,10-perylenedicarboximide-(1,7&1,6)-diyl]-alt-5,5'-(2,2'-bithiophene)} donor-acceptor conjugated polymer and its *in-situ* composites with MWCNT was synthesized by a modified Stille polymerization reaction within a short interval of time (two hours), where it is normally reported to take long reaction times of 12 to 72 hours.⁵⁰⁻⁵² The composites of P(PDI2OD-T2) polymer have been synthesized through the *in-situ* incorporation of different weight percentage of multiwalled carbon nanotubes (MWCNTs) such as 25 % (P-1), and 33.0 % (P-2) during the

polymerization. The *in-situ* addition of the MWCNT serves a dual role in offering a high surface area, wide pore distribution, and exposure of the active reaction centres of the polymer which indeed improves the movement of electrolyte ions at the electrode|electrolyte interface. The electrochemical performance of the pristine polymer P-0 and polymer composites (P-1 and P-2) were investigated in a conventional three-electrode arrangement in the organic electrolytic solution. The *in-situ* generated polymer composite (P-2) showed higher specific capacitance than the pristine polymer. Furthermore, the *in-situ* prepared composite polymer P-2 was explored for both positive as well as negative electrodes with symmetric supercapacitor device (SC) which was able to achieve high operating voltage (3.1 V). Additionally, a solid-state (flexible) device has been efficiently demonstrated using P-2 polymer, which showcased equally good performance with a high-voltage window. The synthesis of polymer/MWCNT composites by *in-situ* polymerization with MWCNT and its electrochemical characterization are schematically summarized in **Figure 2.1**.

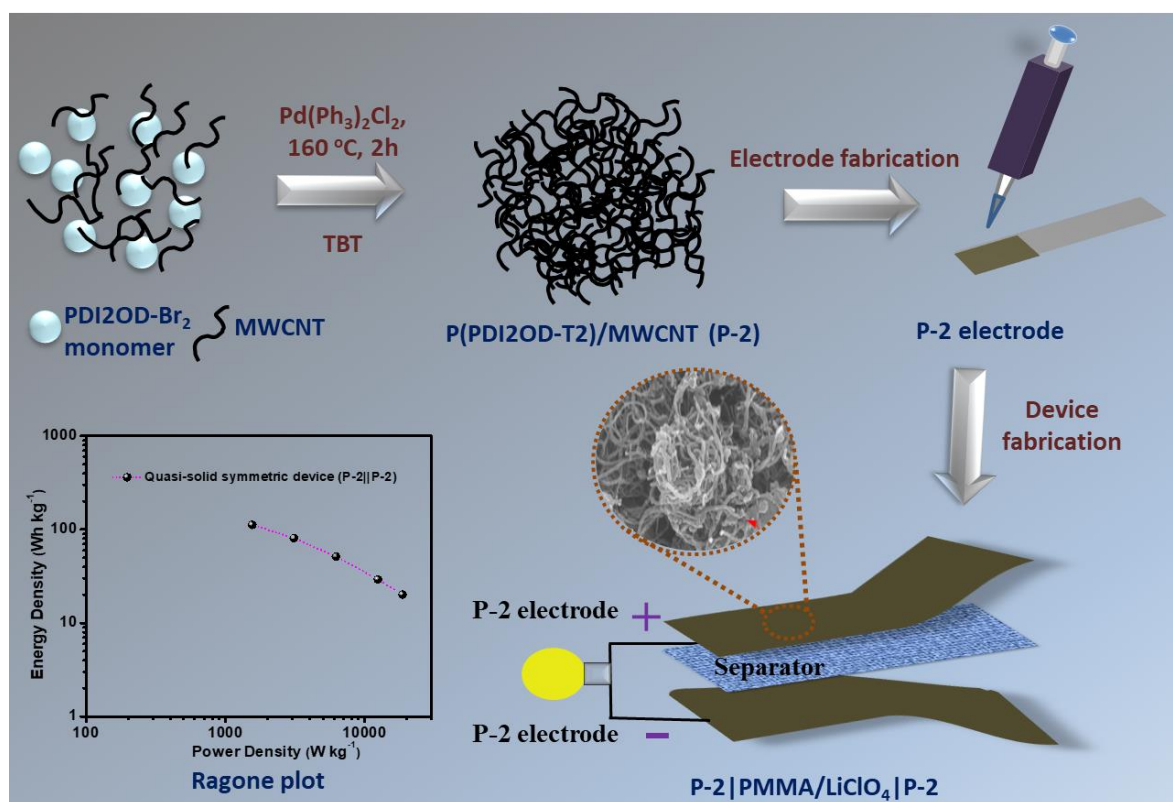


Figure 2.1. Schematic diagram summarizing the *in-situ* polymerization of P(NDI2OD-T2) with MWCNTs along with their electrochemical analysis in quasi-solid state symmetric supercapacitor device.

2.2 EXPERIMENTAL SECTION

2.2.1 Material

The following substances were purchased from TCI chemicals and used without purification: 3,4,9,10-Perylenetetracarboxylic dianhydride (PTCDA), 2-octyl-1-dodecanol, triphenylphosphine, Potassium phthalimide, molecular bromine (Br₂), hydrazine hydrate, and Iodine (I₂). 5,5'-bis(trimethylstannyl)-2,2'-bithiophene, bis(triphenylphosphine)palladium (II) dichloride (Pd(Ph₃)₂Cl₂), methanol, dichloromethane, chloroform, deuterated chloroform, acetone, glacial acetic acid, sulphuric acid (H₂SO₄), propylene carbonate (PC), multiwalled carbon nanotube (MWCNT), lithium perchlorate (LiClO₄), polymethyl methacrylate (PMMA), celgard (polypropylene), polyvinylidene fluoride (PVDF), and N-methyl pyrrolidone (NMP) were bought from Sigma-Aldrich and utilized directly. The solvent 4-tertiary butyl toluene, N,N-Dimethylformamide (DMF), and 1,2,4-trichlorobenzene were purchased from Sigma-Aldrich and dried before using.

2.2.2 Measurements

¹H and ¹³C NMR spectra for monomer and polymers were checked in deuterated chloroform solvent where TMS was used as the reference on a Bruker 200 and 400 MHz NMR spectrophotometer. The molecular weight of polymers was measured by Gel Permeation Chromatography (GPC) using a high-temperature Agilent PL-GPC 220 system equipped with an RI detector. The solvent 1,2,4-trichlorobenzene (TCB) was used as the eluent at a flow rate of 1 mL/min at 140 °C. About 2 mg sample was dissolved in 2 mL of TCB and filtered with a 0.45 mm PVDF filter. The UV-Vis absorption spectra of polymers were measured using a Perkin Elmer lambda-35 UV/Vis spectrometer with deuterium and tungsten lamps as sources. A Perkin Elmer STA (Simultaneous Thermal Analyzer) 6000 thermogravimetric analyzer was used to perform TGA (thermogravimetric analysis). The samples were heated from 50 to 700 °C at a rate of 10 °C/min under a nitrogen atmosphere. The HR-TEM images were taken using a JEOL JEM-F200 HR-TEM device. The FE-SEM images were captured by FEI NOVASEM 450 FE-SEM instrument.

2.2.3 Sample Preparation

UV-vis absorption measurements were taken in solution state by dissolving the polymer in chloroform at various concentrations. The solution was prepared in chloroform at a concentration of 1 mg / 50 mL to calculate the concentration of MWCNTs in polymer composites (C-X). For FE-SEM and HR-TEM sample preparation, methanol was used as

solvent to dispersed the polymer sample (1 mg polymer in 2 mL methanol). After that, the dispersion was drop-casted over mica for SEM and copper grid for TEM analysis.

2.2.4 BET Experimental Setup.

Using the Quantachrome Quadrasorb SI Analyzer (automatic surface area and pore size analyzer), the pore size distribution and nitrogen adsorption/desorption isotherms of MWCNT, P-0, and P-2 composite polymers were evaluated at 77 K. The surface area of the samples was measured with the Brunauer-Emmett-Teller (BET) method, with nitrogen as the adsorption gas and at 77 K bath temperature. The pore size distribution plots were produced using Density Functional Theory (DFT) at 77 K on carbon with N₂ as the model (slit pore, NLDFT equilibrium model).

2.2.5 Electrode preparation for three electrode studies

Carbon fiber paper was used as a support or current collector for the active material. A homogenous slurry was made by dispersing 4.75 mg of the desired sample (P-1, P-2) and 0.25 mg Polyvinylidene fluoride (PVDF) binder in 500 μ L of N-methyl pyrrolidone (NMP). The slurry was sonicated for 4-6 hours for better dispersion of the material and 100 μ L of this slurry was cast over a piece of carbon fiber paper to achieve 1 mg / cm² loading. However, the P-0 electrode has been prepared by using an 80:15:5 ratio active material (pristine polymer P-0), multi-walled carbon nanotubes, and PVDF with a similar process of slurry preparation and coating. After that the electrodes were allowed to dry overnight in an oven at 60 °C.

2.2.6 Flexible Electrode for device

The flexible electrode was supported over flexible scotch grofoil tape. A slurry of the active material was prepared in the above-mentioned ratio in 200 μ L of NMP. The homogeneously dispersed slurry was cast over peeled grafoil scotch in a 2 cm² area to get an active material loading of 0.64 mg cm⁻² (P-2 electrode). The coated electrode was dried overnight in the oven at 60 °C. This electrode was further used for quasi-solid state device fabrication and electrochemical characterizations.

2.2.7 Quasi Electrolyte Preparation

Non-aqueous quasi-solid polymer electrolyte was prepared for solid-state flexible supercapacitor device fabrication. For gel formation, 1.6 g polymethyl methacrylate (PMMA) was dissolved in 5 mL of 3 M LiClO₄ in propylene carbonate (PC) and heated at 115°C with constant stirring for 1h.

2.2.8 Electrochemical Measurements.

The BioLogic VMP3 instrument was used to conduct all electrochemical tests. The three-electrode cells were assembled using carbon fiber paper coated with the active material as the working electrode, a platinum mesh as the counter electrode, and Ag/Ag⁺ as the reference electrode in 1M LiClO₄/PC electrolyte. The potential window was set at -0.2 to -1.4 V vs. Ag/Ag⁺. The cyclic voltammetry (CV) was measured at a scan rate of 5, 10, 20, 50, and 100 mV s⁻¹. For the computation of capacitance, galvanostatic charge-discharge measurements were performed at current densities of 0.5, 1, and 2.5 A g⁻¹. The device-level performance and the electrochemical characterization of the liquid organic and non-aqueous quasi-solid device were also measured with the same instrument as used for the three-electrode system. The electrochemical studies of the device were performed in the potential window of 0.2 to 3.3 V.

2.2.9 Flexible Device Fabrication

The electrode supported over a thin layer of grafoil-peeled scotch tape was coated with a thin layer of quasi-solid (PMMA-LiClO₄) electrolyte. The separator cell guard membrane (polypropylene) was weighted with a thin electrolyte layer and the device was assembled and packed with the help of transparent scotch tape. This symmetric device was used for the studies as a supercapacitor as well as a flexible supercapacitor.

2.3 Synthesis of Monomers and polymers

2.3.1 Synthesis of Monomers

The detailed synthetic procedures and characterization for monomers are outlined below.

a) Synthesis of 2-octyl decyl bromide (A1)

Triphenylphosphine (43.02 g, 164.04 mmol) was carefully added to a dry two-necked round bottom flask containing 250 ml of anhydrous dichloromethane. Then it was allowed to stir for 15 minutes under nitrogen purging. The molecular bromine (26.21 gm, 164.04 mmole) was added dropwise via a dropping addition funnel. Following this, 2-octyl 1-dodecanol (48.97 g, 164.04 mmol) was introduced via a dropping funnel within a 30-minute duration. The blend underwent stirring at ambient temperature under a nitrogen atmosphere overnight. Upon completion, the mixture was transferred to a separating funnel and washed with sodium thiosulfate (Na₂S₂O₃) until the yellowish color disappeared. The organic layer underwent extraction and subsequent evaporation, resulting in the formation of a white solid compound. Further purification was achieved by washing the solid with n-hexane using a Buchner funnel,

followed by vacuum drying. Finally, purification was achieved by column chromatography using petroleum ether. The yield obtained was 82.0%. The ^1H NMR spectrum (200 MHz, CDCl_3) displayed peaks at δ ppm: 3.46-3.43 (d, 2H), 1.57-1.54 (m, 1H), 1.27 (m, 32H), and 0.91-0.85 (t, 6H).

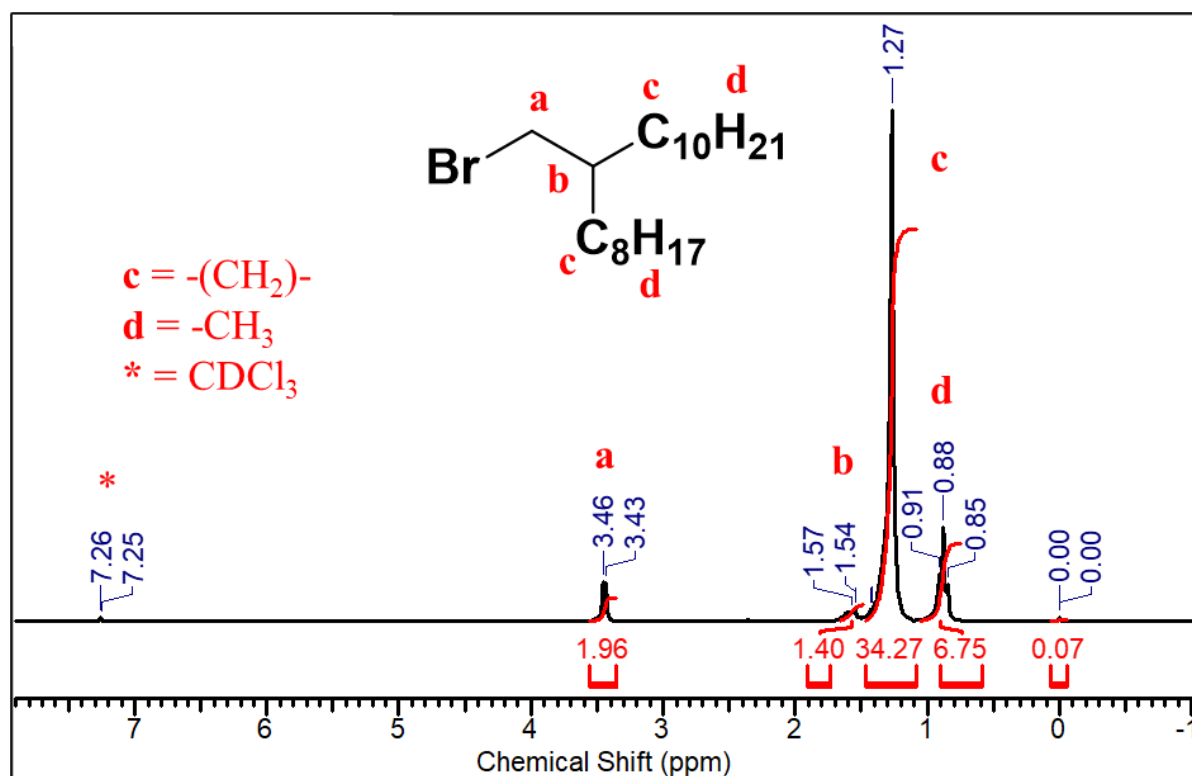


Figure 2.2 ^1H NMR spectrum of 2-octyl 1-dodecyl bromide (CDCl_3)

b) Synthesis of 2-(2-octyldodecyl)isoindoline-1,3-dione (A2)

In a dry round-bottom flask, a quantity of potassium phthalimide weighing 30.95 g (corresponding to 167.10 mmol) was mixed with 150 ml of dry dimethylformamide (DMF) under a nitrogen atmosphere. The resultant blend was subjected to stirring at 90°C for a duration of 1 hour. Following this, 2-octyl 1-dodecyl bromide (54.906 g, 151.91 mmol) was introduced gradually into the reaction mixture. The reaction was permitted to continue for a period of 24 hours at 90°C . Once the reaction concluded, the mixture was cooled to room temperature and subsequently poured into one liter of water. Dichloromethane served as the extraction solvent, and the merged organic layer underwent successive washings with 0.2 N KOH, saturated NH_4Cl , and was then dried using anhydrous Na_2SO_4 . The solvent was removed under reduced pressure by evaporation. The obtained product underwent purification through column chromatography, employing a blend of petroleum ether and ethyl acetate. The yield obtained was 75.7%. The ^1H NMR spectrum (200 MHz, CDCl_3) exhibited peaks at δ ppm:

7.85-7.83 (d, 2H), 7.72-7.69 (dd, 2H), 3.59-3.59 (d, 2H), 1.68 (m, 1H), 1.24 (m, 32H), and 0.88-0.84 (t, 6H).

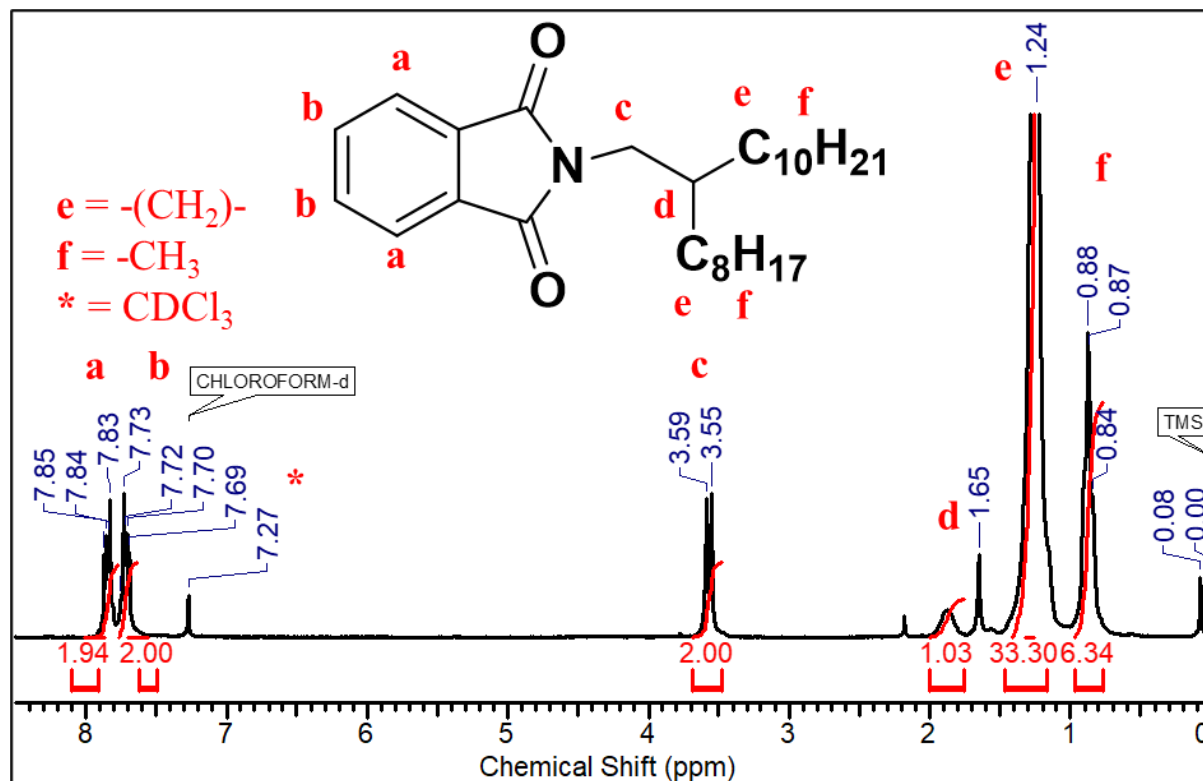
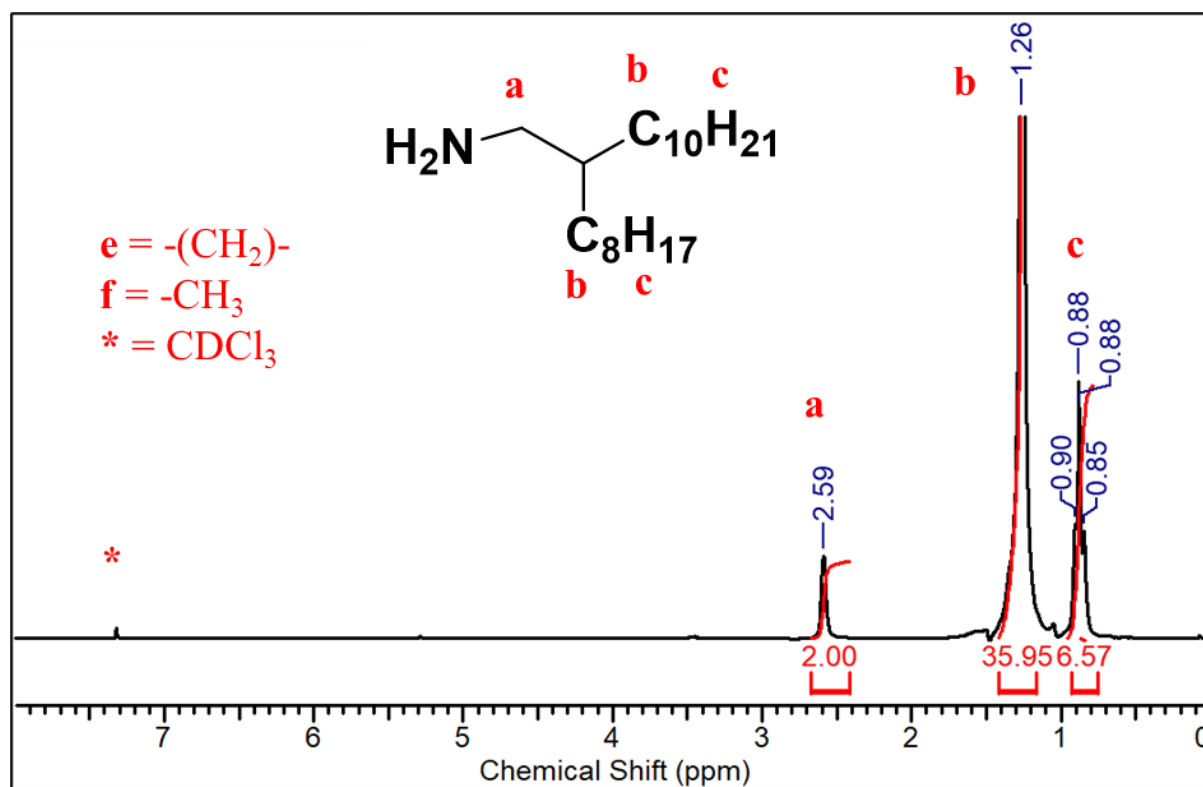
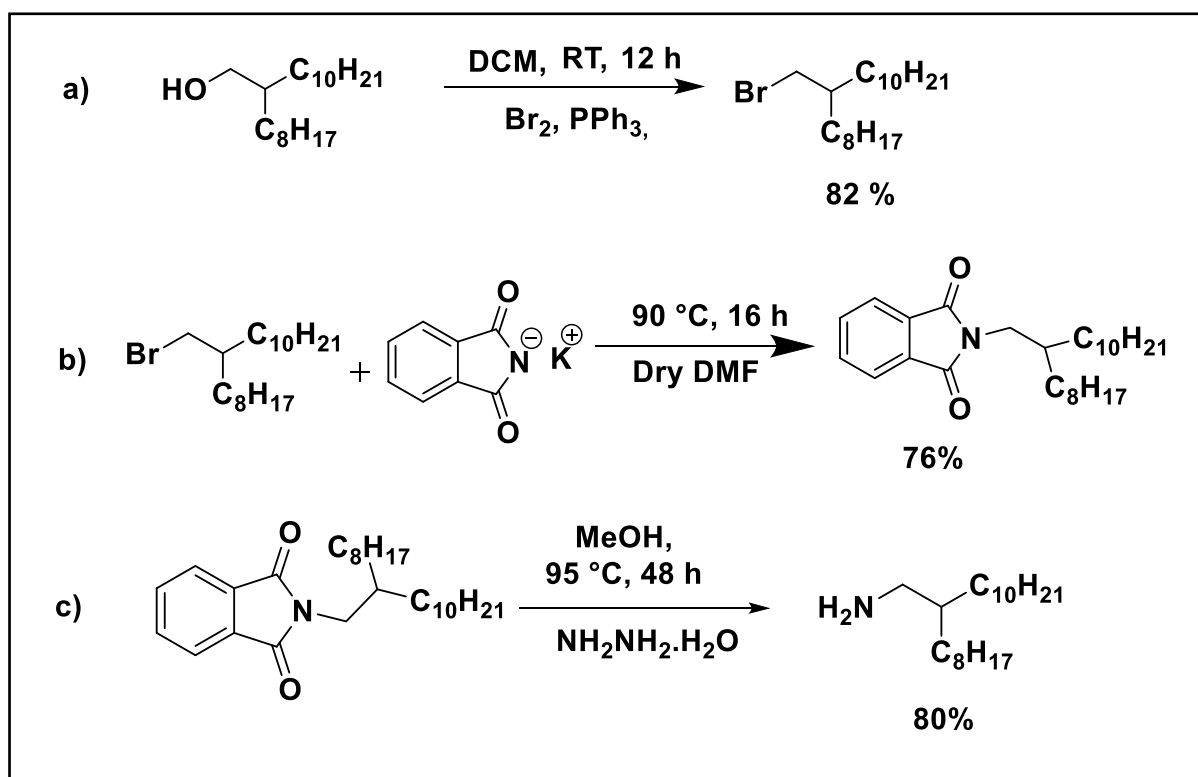


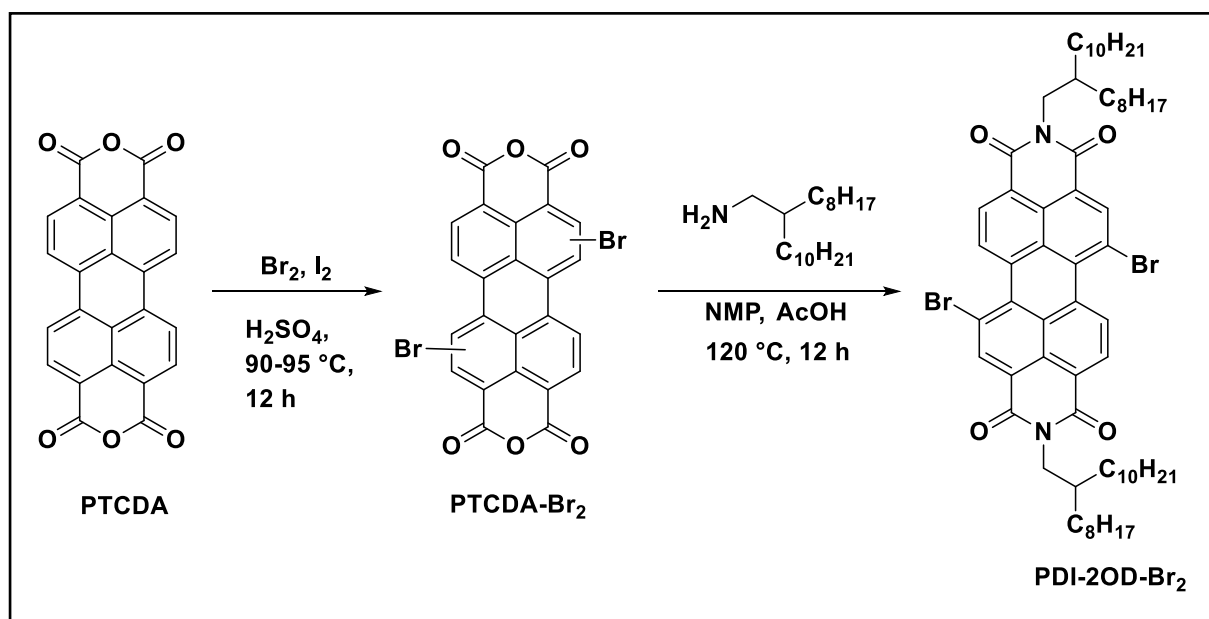
Figure 2.3 ¹H NMR spectrum of 2-(2-octyldodecyl)isoindoline-1,3-dione (CDCl₃).

c) Synthesis of 2-octyldodecan-1-amine (A3)

In a dry round-bottom flask, a mixture of 2-(2-octyl dodecyl)isoindoline-1,3-dione (A2) weighing 24.0 g (equivalent to 56.2 mmol) and hydrazine hydrate weighing 8.44 g (equal to 168.61 mmol) was prepared, followed by the introduction of dry methanol (250 ml). Under a nitrogen atmosphere, the reaction mixture was stirred at 95°C for a duration of 48 hours, with continuous monitoring conducted using thin-layer chromatography (TLC). Once the reaction reached completion, methanol was eliminated using a rotary evaporator, and the remaining residue was dissolved in 100 ml of dichloromethane (DCM). The mixture underwent washing with a 10% potassium hydroxide solution and extraction with DCM. Subsequently, the combined organic layer was subjected to washing with brine (a concentrated sodium chloride solution), followed by drying over anhydrous sodium sulfate. After concentration using a rotary evaporator, the final product was obtained. The yield achieved was 80.5%. The ¹H NMR spectrum (200 MHz, CDCl₃) displayed peaks at δ ppm: 2.59 (d, 2H), 1.54 (m, 1H), 1.26 (m, 32H), and 0.90-0.85 (t, 6H).

Figure 2.4 ^1H NMR spectrum of 2-octyldodecan-1-amine (CDCl_3).

Scheme 2.1 Synthesis of 2-octyldodecan-1-amine.

d) Synthesis of PDI2OD-Br₂Scheme 2.2 Synthesis of PDI2OD-Br₂ monomer

Initially, 3,4,9,10-Perylenetetracarboxylic dianhydride (PTCDA) (5 g, 12.74 mmol) was stirred with 100 ml of sulfuric acid. Following this, 250 milligrams of iodine were poured, and allowed for heating at 90°C for 2 hours. Elemental bromine was then added dropwise, and the reaction mixture was further heated at 95°C overnight with continuous stirring. The resulting mixture was slowly added to ice water, causing precipitation of a product which was subsequently filtered and washed with methanol and water. The product mixture underwent vacuum drying at 120°C for 24 hours. Purification of the brominated PTCDA (Br-PTCDA) was difficult due to its poor solubility. Hence, crude brominated PTCDA was directly subjected to imidization.⁵³

The crude 1,7-Dibromo-3,4,9,10-perylenetetracarboxylic acid dianhydride (3.0 g, 5.453 mmol) was introduced into a 250 ml two-neck round bottom flask equipped with a magnetic stirring bar. Following this, glacial acetic acid (20 mL) and N-methyl pyrrolidine (60 mL) were added to the flask and purged with argon. The reaction mixture underwent stirring and was heated to 60°C for 20 minutes to ensure a uniform dispersion. Following the addition of 2-octyl-1-dodecylamine (2.867 g, 16.359 mmol), the reaction mixture was heated at 120°C for 12 hours while continuously stirring. Subsequently, the mixture was cooled to room temperature and combined with 500 mL of water. Following two hours of stirring, the water mixture underwent vacuum filtration using a Buchner funnel. The resulting residue was carefully washed with

water and subjected to vacuum drying. The crude product was purified using column chromatography, employing solvent systems of pet ether/ethyl acetate (1:6) and pet ether/dichloromethane (50:50). Finally, yielded the pure red colored substance (Yield = 29%). The ^1H NMR spectrum (400 MHz, CDCl_3) exhibited peaks at δ ppm: 9.50-9.48 (d, 2H), 8.93 (s, 2H), 8.71-8.69 (d, 2H), 4.16-4.14 (d, 4H), 2.06 (m, 2H), 1.27-1.23 (m, 64H), and 0.87-0.84 (m, 12H). The ^{13}C NMR spectrum, recorded in 100 MHz CDCl_3 , displayed signals at δ ppm: 163.24, 162.75, 138.08, 132.98, 130.08, 129.27, 126.99, 123.16, 122.75, 120.79, 44.85, 36.62, 31.68, 30.01, 29.63, 29.57, 29.29, 26.47, 22.66, and 14.10. The MALDI-TOF analysis showed a molecular weight of (1111.21) m/z: 1112.904.

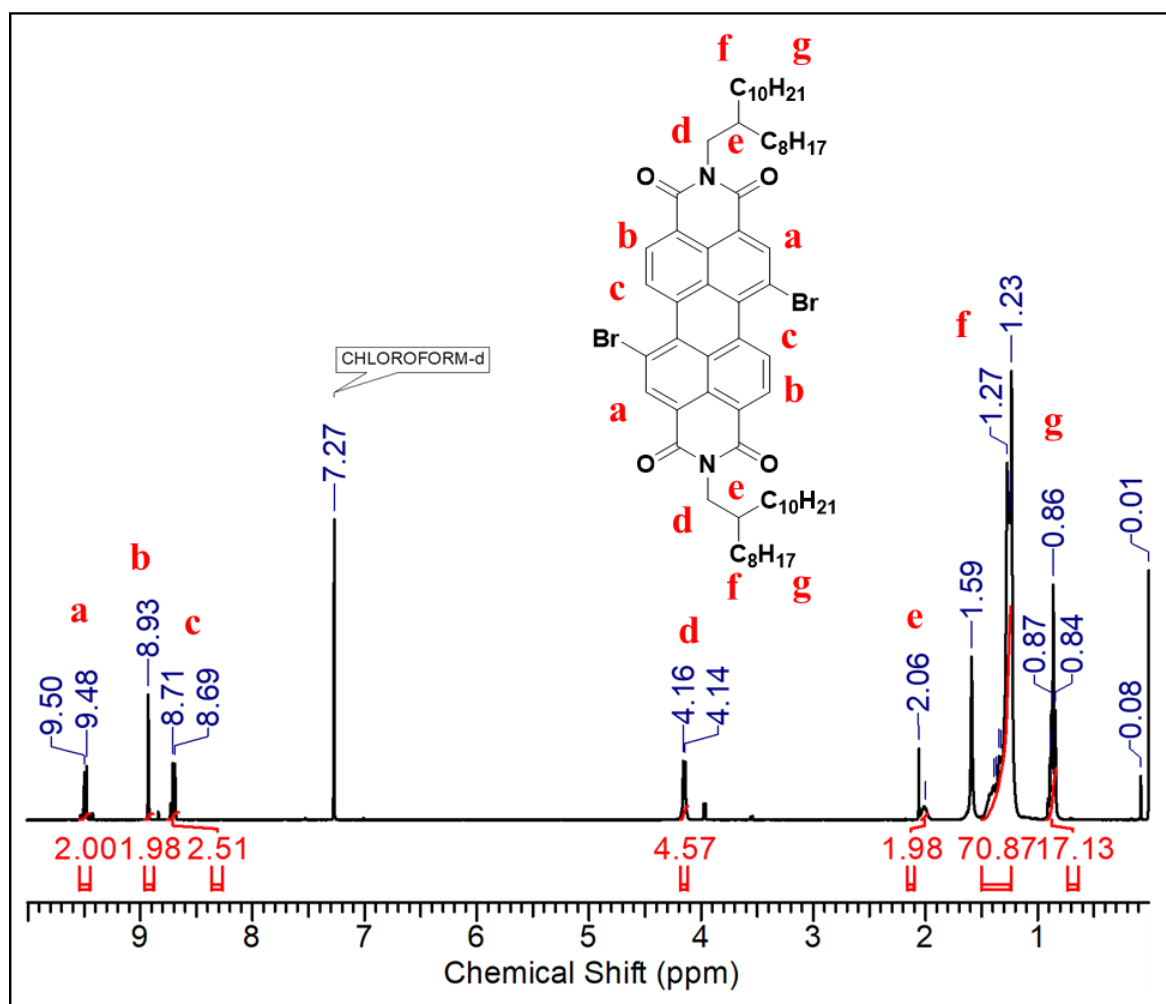


Figure 2.5 ^1H NMR spectrum of monomer PDI2OD-Br₂

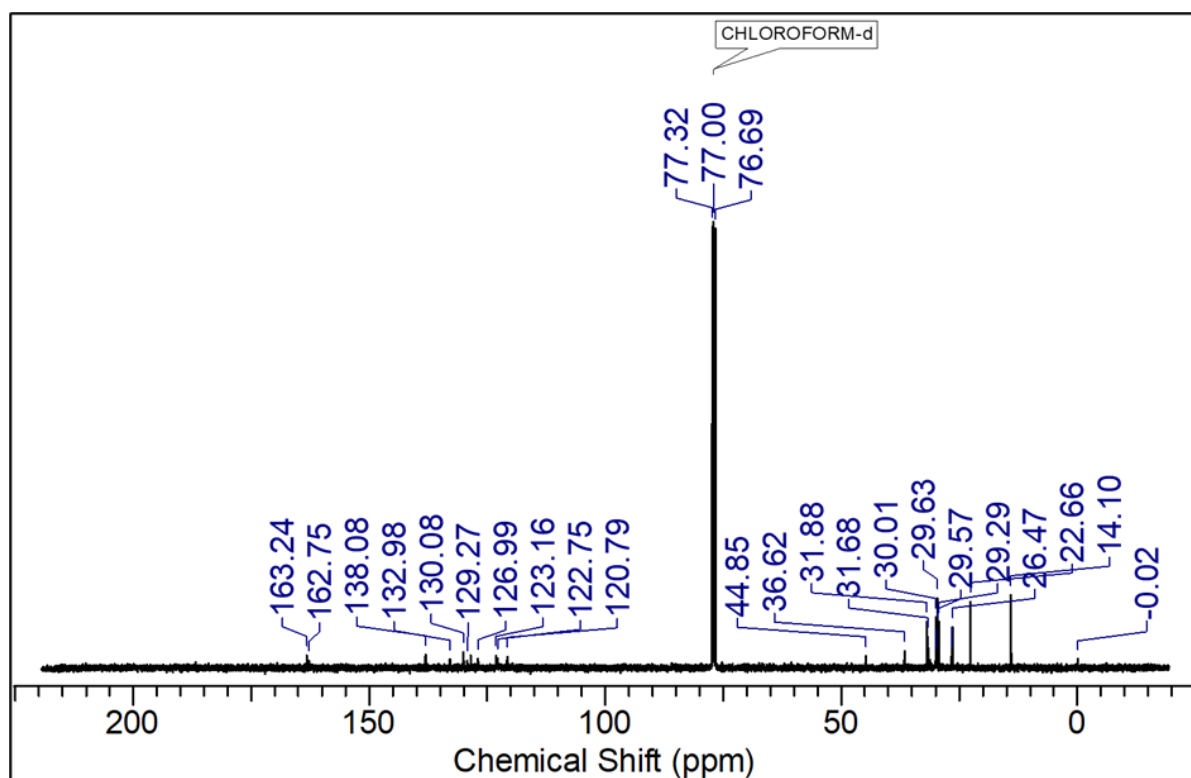


Figure 2.6 ^{13}C NMR spectrum of monomer PDI2OD-Br₂

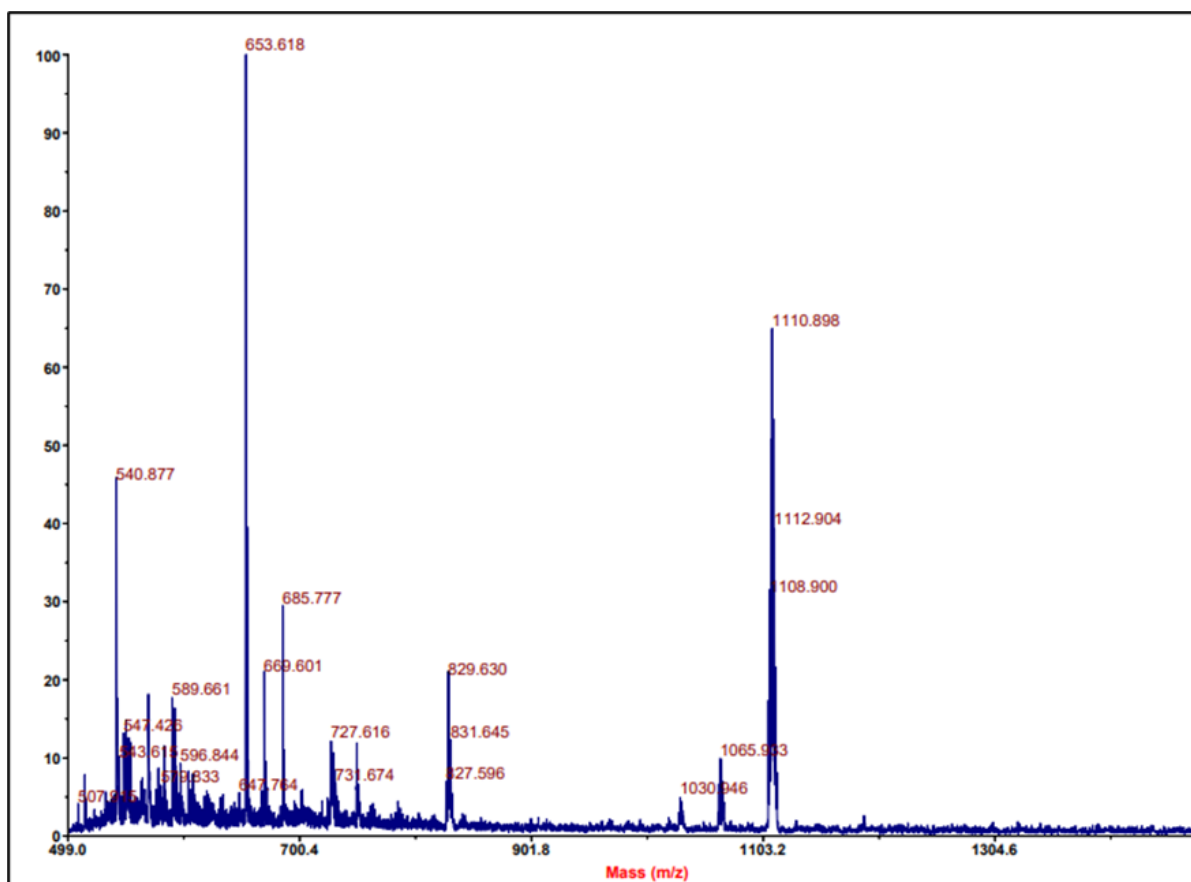
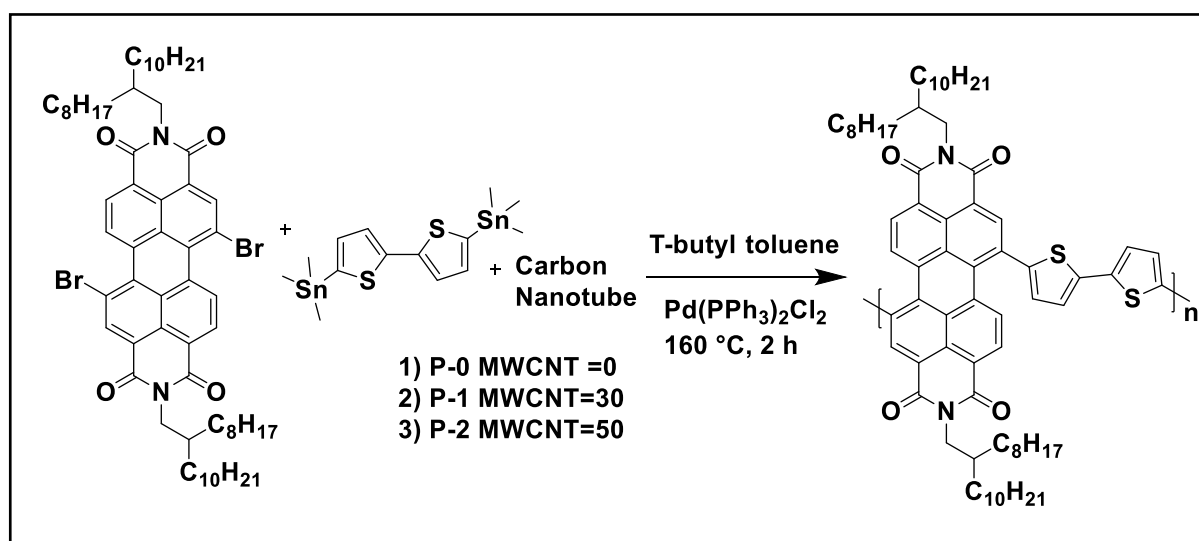


Figure 2.7 MALDI-TOF spectrum for PDI2OD-Br₂ monomer.

2.3.2 Synthesis of P(PDI2OD-T2) Polymer and their composite polymers with MWCNT by Stille Coupling Approach

2.3.2.a Synthesis of P(PDI2OD-T2) (P-0)

The synthetic scheme for monomer PDI2OD-Br₂, and characterization are described in **Section 2.3.1**. The PDI2OD-Br₂ (200 mg, 0.179 mmole) and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (88 mg, 0.179 mmol) monomers were added to the Schlenk tube which was equipped with a stirring magnet. Dry 4-ter-butyl toluene solvent (10 ml) was poured to the reaction mixture and subjected to nitrogen purging at ambient temperature for 30 minutes. Under nitrogen environment, 6.53 mg (0.009308 mmole) of bis(triphenylphosphine) palladium (II) dichloride (Pd(PPh₃)₂Cl₂) were added into aforesaid solution and again purged with nitrogen for 30 minutes; the Schlenk tube was then moved to oil bath and allowed to heat for 2 hours at 160 °C with continuous stirring. After completion of polymerization, the reaction mixture was cooled to ambient temperature and the polymer were dissolved in chloroform and reprecipitated using methanol followed by filtration over Büchner funnel. To purify the polymers the Soxhlet extraction was done with the help of methanol for 24 hours followed with acetone. Finally, the polymer was subsequently dried at 60 °C in a vacuum oven. Yield (142 mg, 85 %). ¹H NMR spectrum (400 MHz, CDCl₃) δ ppm: 8.75–8.74 (br, 2H aromatic), 8.41 (br, 4H aromatic) 7.32–7.24 (br, 4H), 4.14–4.13 (br, 4H), 2.02 (br, 2H), 1.34–1.22 (br, 64H), 0.85–0.82 (br, 12 H). Mn:17100, Mw: 31600, Đ_M:1.8.



Scheme 2.3 Synthesis of P(PDI2OD-T2) (P-0) polymer and their composites with MWCNTs P-1 and P-2 (C-X).

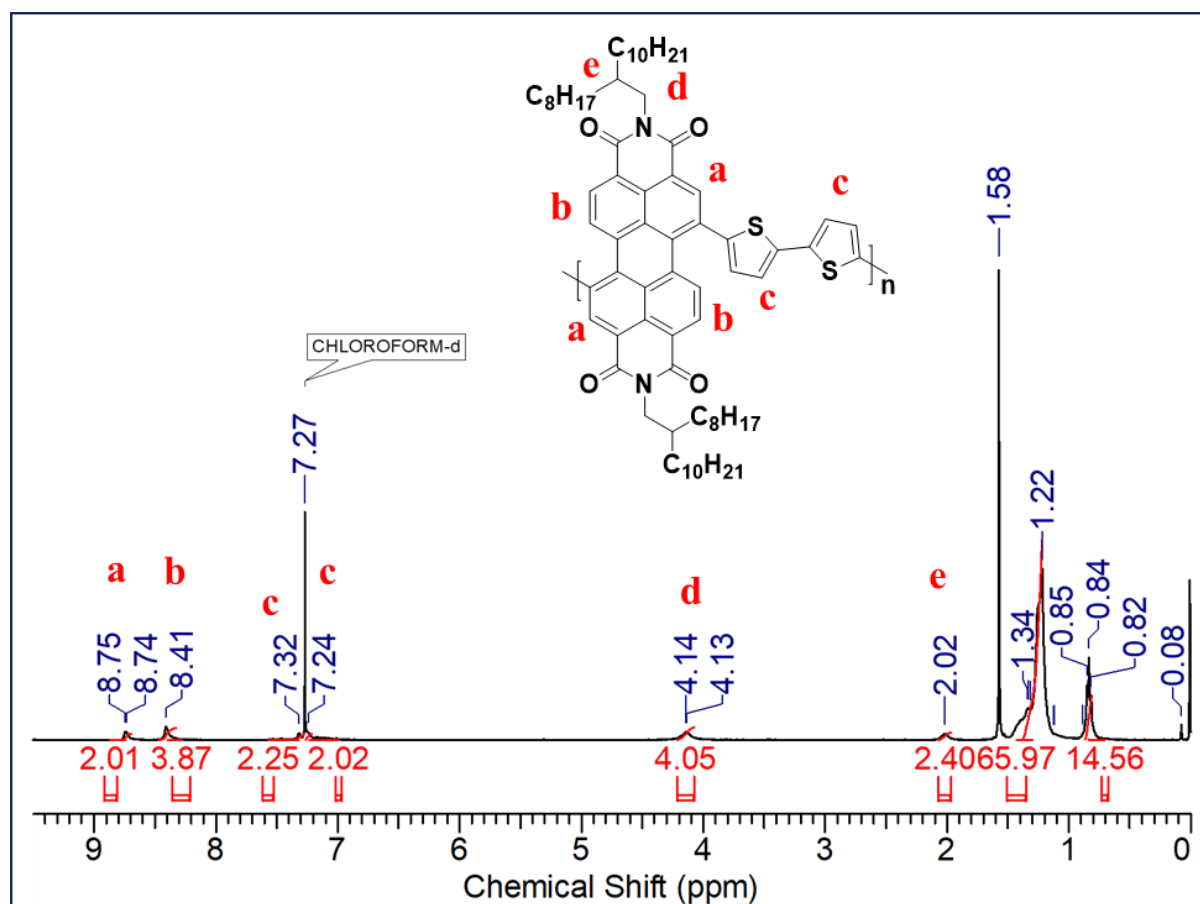


Figure 2.8 ^1H NMR spectrum of P(PDI2OD-T2) P-0 Polymer.

2.3.2.b Synthesis of Polymer Composite C-X. (P-1 and P-2)

The composite polymer synthesis follows the similar synthetic procedure as mentioned above for P(PDI2OD-T2) (P-0) polymer with the exception that multiwalled carbon nanotube (MWCNT) was added with the monomer by *in-situ* method to obtain polymer MWCNT composites. The detailed synthesis is given below.

i) Synthesis of Polymer composites P-1

The identical quantities of monomers, catalyst, and solvents were utilized as described in the **Section 2.3.2.a** and 60 mg of MWCNTs were added to the Schlenk tube which was equipped with a stirring magnet. After that the steps followed were similar as mentioned for P(PDI2OD-T2) (P-0) polymer (**Section 2.3.2.a**). For workup, the reaction mixture was brought to ambient temperature, and precipitated in methanol (chloroform dissolution was avoided in order to preserve the MWCNT-incorporated polymeric networks produced by the *in-situ* polymerization). Yield (250 mg – 60 mg MWCNTs = 190 mg, 95 %). ^1H NMR spectrum (400 MHz, CDCl_3) δ ppm: 8.75 (br, 2H aromatic), 8.41 (br, 4H aromatic) 7.32-7.24 (br, 4H), 4.14

(br, 4H), 2.02 (br, 2H), 1.34-1.12 (br, 64H), 0.85-0.82 (br, 12 H). Mn: 12500, Mw: 19600, Đ_M:1.5.

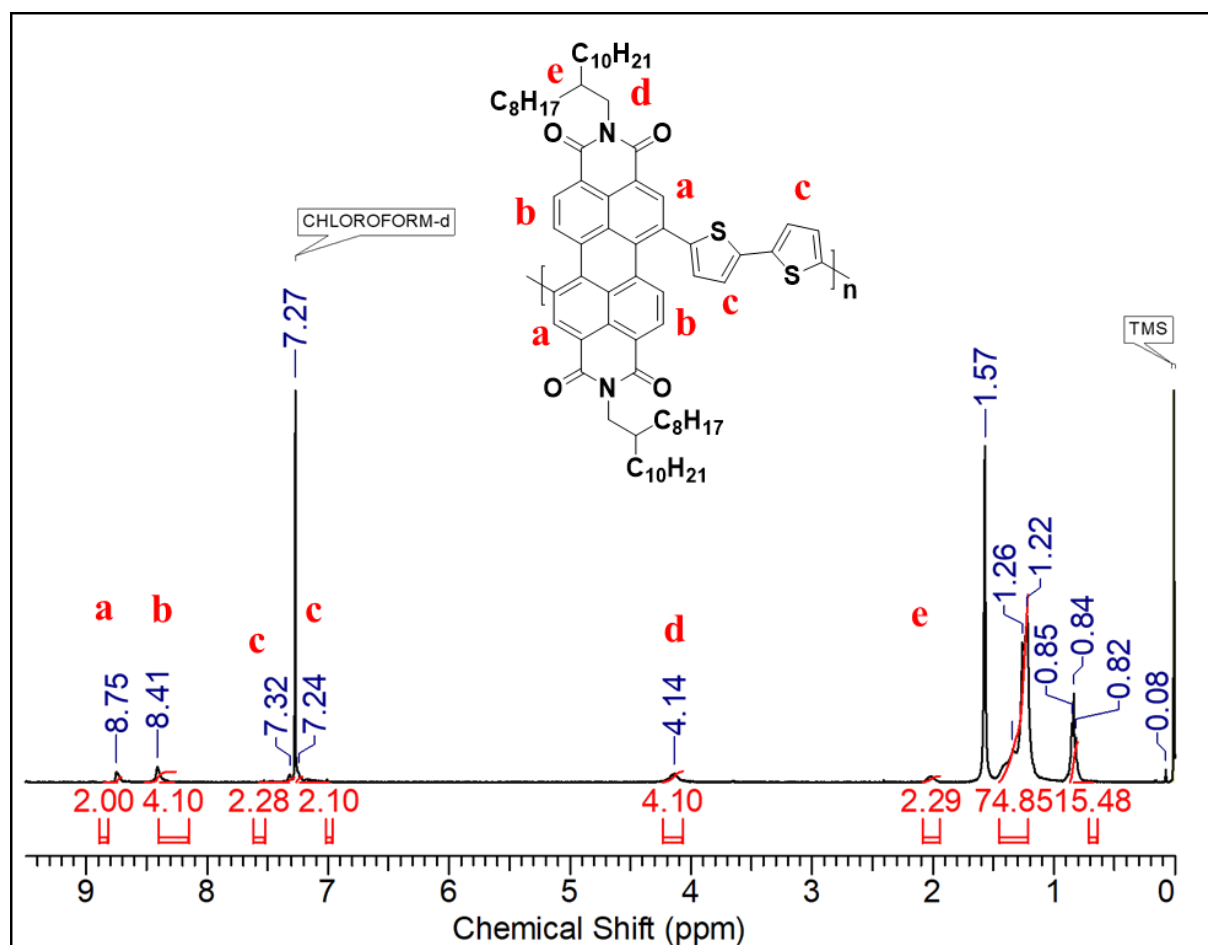


Figure 2.9 ¹H NMR spectrum of P-1 Polymer.

ii) Synthesis of Polymer composites P-2

The identical quantities of monomers, catalyst, and solvents were utilized as described in the **Section 2.3.2.a** and 100 mg of MWCNTs were added to the Schlenk tube which was equipped with a stirring magnet. Then followed the same procedure as given for P-0 and P-1 polymer (**Section 2.3.2.a and Section 2.3.2.b.i**) Yield (270 mg – 100 mg MWCNTs = 171 mg, 86 %). ¹H NMR spectrum (400 MHz, CDCl₃) δ ppm: 8.74 (br, 2H aromatic), 8.41 (br, 4H aromatic) 7.32-7.24 (br, 4H), 4.14 (br, 4H), 2.02 (br, 2H), 1.34-1.22 (br, 64H), 0.85-0.82 (br, 12 H). Mn: 20400, Mw: 28400, Đ_M:1.4.

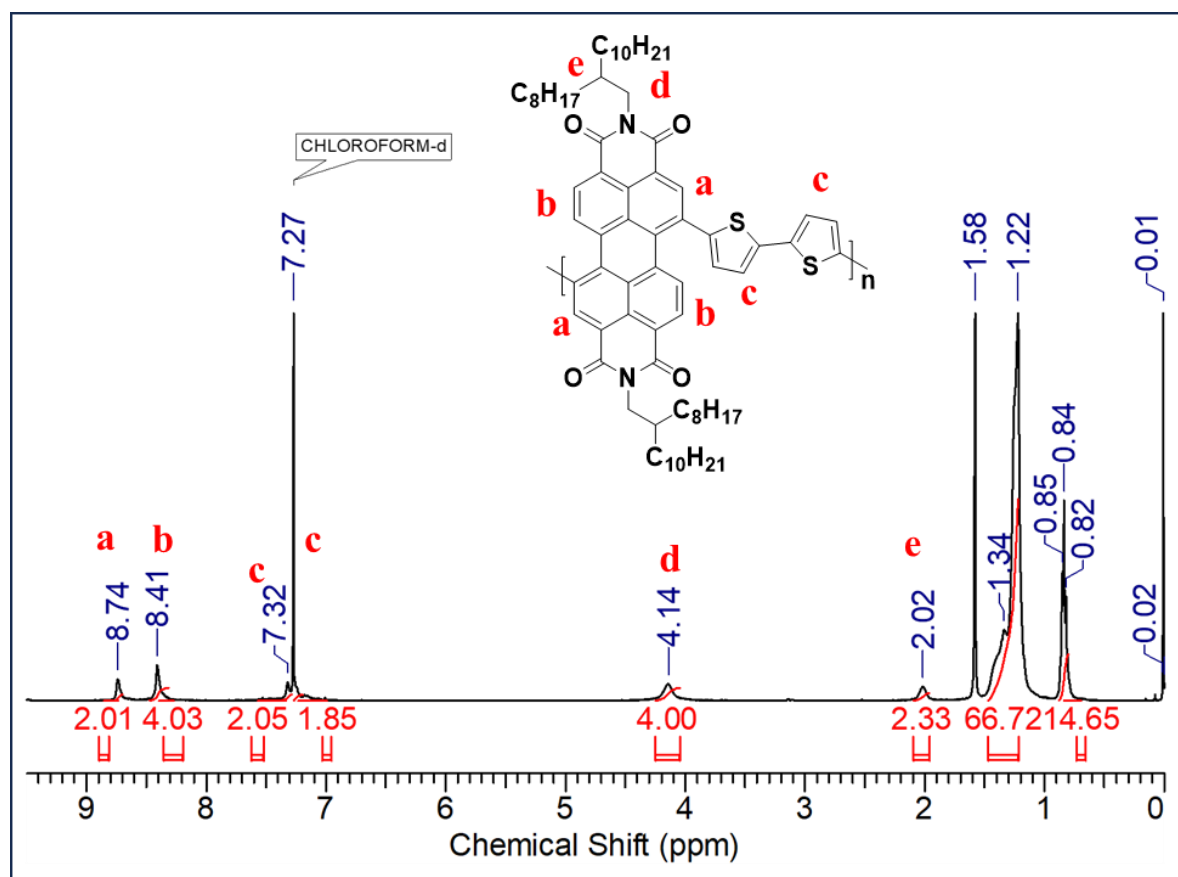


Figure 2.10 ^1H NMR spectrum of P-2 Polymer.

2.4 Results and Discussion

2.4.1 Synthesis and Characterization

PDI2OD-Br₂ was synthesized by brominating 3,4,9,10-Perylenetetracarboxylic dianhydride, followed by imidization with 2-octyl-1-dodecylamine. The synthetic scheme and procedure of monomer PDI2OD-Br₂ are described in **Section 2.3.1**. The structural characterization of monomer PDI2OD-Br₂ by ^1H , ^{13}C NMR spectroscopy and MALDI-TOF spectrum are given in **Figures 2.5, 2.6 and 2.7**. **Scheme 2.3** shows the synthesis of P(PDI2OD-T2) (P-0) polymer and its *in-situ* synthesized composites (P-1 and P-2) with MWCNT.

Stille polymerization was used to synthesize the P(PDI2OD-T2) (P-0) polymer and its composites with MWCNT (P-1 and P-2). The P(PDI2OD-T2) polymer is commonly synthesized by Stille or Suzuki polymerization and it requires around 12-72 hours of reaction time.⁵⁰⁻⁵² The polymerization is usually carried out in toluene at a temperature of around 90 °C for 72 h resulting in moderate molecular weights of ~ 50000. In this work, we have adopted some modifications in the reaction conditions like the use of high boiling solvent 4-ter-butyl toluene and also conducting the polymerization at a higher temperature of 160 °C. Interestingly,

the polymerization was completed in a very short time of two hours. Here, PDI2OD-Br₂ monomer was reacted with 5,5'-bis(trimethylstannyl)-2,2'-bithiophene at 160 °C and Pd(Ph₃)₂Cl₂ catalyst has been utilized with 4-tertiary-butyl toluene as the high boiling solvent which yielded the P(PDI2OD-T2) polymer within two hours of reaction time. In this chapter, the pristine P(PDI2OD-T2) polymer is named as P-0. The polymer composites P-1 and P-2 were polymerized with *in-situ* inclusion of different doses of MWCNT like 60 and 100 mg along with the monomers respectively. The polymers were precipitated directly in methanol (rather than the typical approach of dissolution of polymer in chloroform and reprecipitation in to methanol) to prevent the loss of MWCNTs that were incorporated by *in-situ* polymerization. Using methanol and acetone solvents, polymer P-0 and their composites were purified by Soxhlet extraction. The probable weight percentage of MWCNT as feed weight percent incorporation in polymer composites P-1 and P-2 were determined (the amount of MWCNT in feed divided by total yield) to be 23.0 % and 36.9 %, respectively.

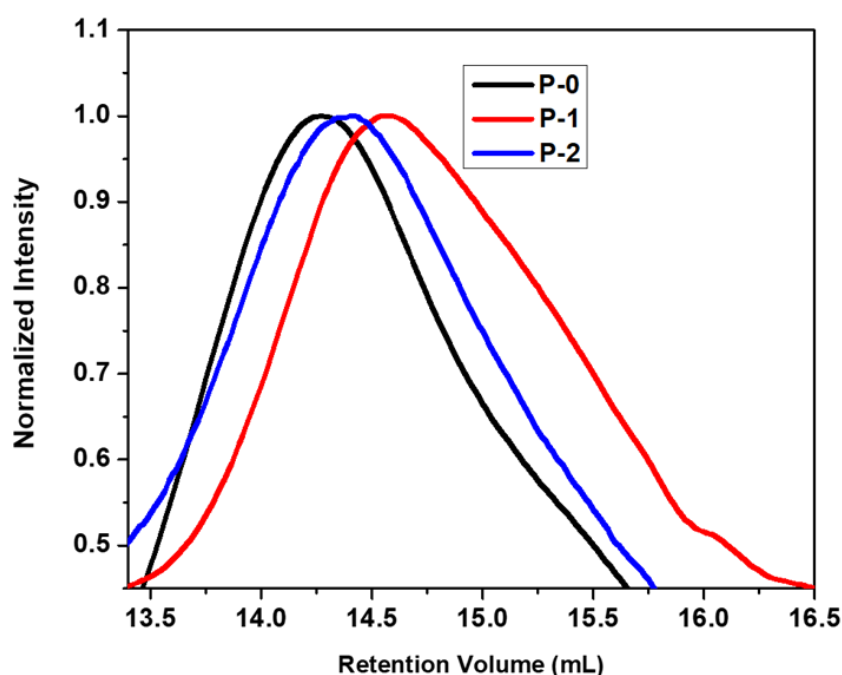


Figure 2.11 Gel permeation chromatogram (GPC) of P(PDI2OD-T2) (P-0), P-1 and P-2 Polymer.

The polymers were soluble in chloroform, 1,2,4-Trichlorobenzene, and insoluble in DMF and THF. ¹H NMR spectroscopy was used to confirm the structure of the polymers, which are given in **Figures 2.8-2.10**. The polymer solution in chloroform was filtered first with filter paper and then polytetrafluoroethylene (PTFE) filter to remove the MWCNTs and the MWCNT-free

polymer samples were used for ^1H NMR spectroscopy and GPC analysis. The molecular weights, along with the polydispersity (Đ), of the polymers were determined using Gel Permeation Chromatography (GPC) with 1,2,4-Trichlorobenzene as the eluent at 140 °C. The chromatogram is shown in **Figure 2.11**. The number average molecular weight for polymers ranged from M_n 12500 to 20500 Kg mol^{-1} and dispersity (Đ) from 1.4 to 1.8 as shown in **Table 2.1**.

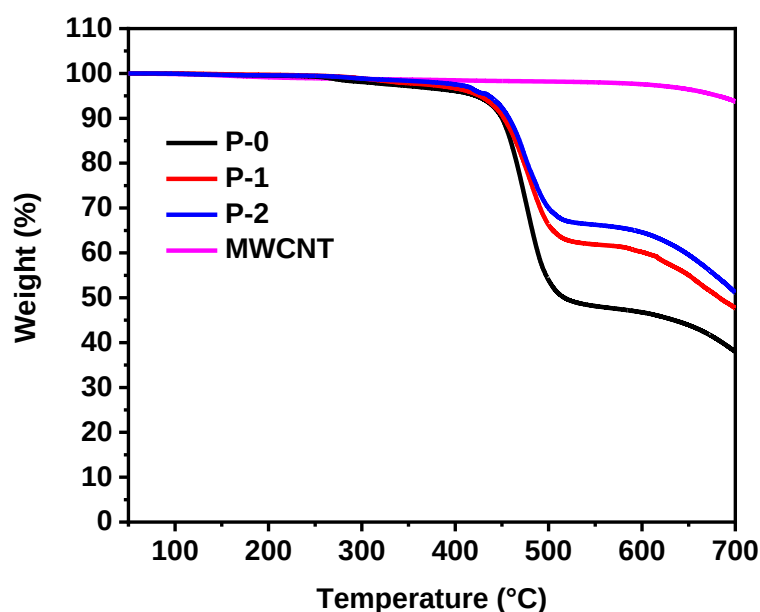


Figure 2.12. Thermogravimetric analysis recorded for P-0, MWCNT, and P-1 and P-2 samples.

Thermogravimetric analysis (TGA) in a nitrogen environment was used for determining thermal properties of the polymer and composites. The TGA curves in **Figure 2.2** demonstrated high thermal stability of the polymers up to 400 °C. The following formula was utilized to calculate the percent incorporating of MWCNT for composite samples from the TGA curves.⁵⁴

% of MWCNT incorporated

$$= \% \text{ remaining pristine MWCNT} - \left(\frac{\% \text{ loss of composite}}{\% \text{ loss of Pure polymer}} \times 100 \right)$$

Table 2.1 Polymerization yield, molecular weights and MWCNT % incorporation determined by feed, TGA and UV-Vis spectroscopic analysis for polymer P-0 and its composites P-1 and P-2.

Sr. No	Polymer	M_n^x (Kg mol ⁻¹)	M_w^x (Kg mol ⁻¹)	$\bar{D}_M^y$	% Yield	% weight of MWCNT in feed ^z	% weight of MWCNT from TGA	% Weight of MWCNT from absorption spectroscopy ^d
1.	P-0	17.2	31.5	1.8	85	0	0	0
2.	P-1	12.5	19.5	1.5	90	23.1	24.8	26.0
3.	P-2	20.5	28.5	1.4	86	36.9	33.0	35.8

^x M_n and M_w measured with GPC where eluent is 1,2,4-Trichlorobenzene and PS is standards;

^y $\bar{D}_M$ is the polydispersity; ^z MWCNT incorporation in feed determined based on the overall yield.

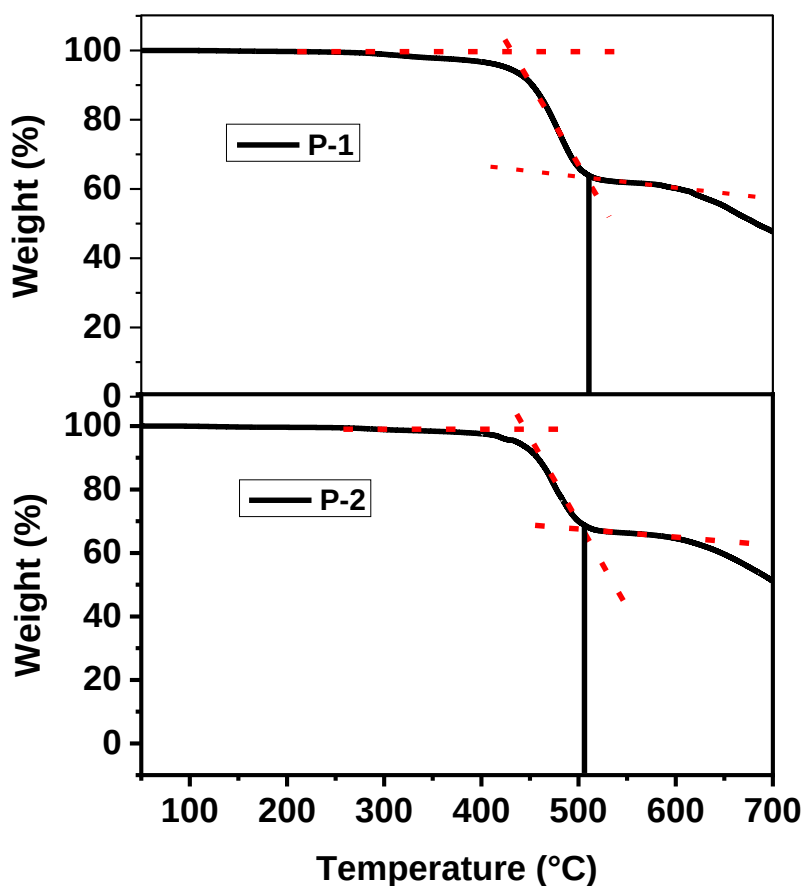


Figure 2.13 TGA curves of the polymer composites (P-1 and P-2).

As illustrated in **Figure 2.13**, the loss of mass has been calculated by measuring the vertical separation between the two tangent lines formed on the weight loss plot. The percent of pristine MWCNT that remained was 97.61 %, while 50.31 % of pristine polymer (P-0) was lost. The MWCNT incorporation percentage was calculated to be 24.8, and 33.0 percent for the composites P-1, and P-2, respectively. The percentage of MWCNTs in polymer composites was also calculated by using absorption spectroscopy. The absorption spectra for the polymers were recorded in chloroform and given in **Figure 2.14**. The absorption band between the 300 nm to 430 nm indicates the π - π^* transition. The band between 430 nm to 535 nm and 535 nm to 720 nm corresponds to the S0-S2 and S0-S1 electronic transitions respectively.⁵⁰ Using the Beer-Lambert Law, the molar extinction coefficient (ϵ) for polymer P-0 was calculated as $31931 \text{ L M}^{-1}\text{cm}^{-1}$ based on absorption spectra of P-0 recorded at different concentrations in chloroform solvent (**Figure 2.15**). The percentage of polymer and MWCNT in polymer composites was calculated with the help of the molar extinction coefficient (ϵ) and the detailed calculations are described in **Section 2.4.2**. The percentage of MWCNT in polymer composite P-1 and P-2 were determined to be 26 and 35.8 % respectively. The percentage MWCNT incorporation calculated from UV-Vis absorption spectra matched very well with the feed ratio and percentage MWCNT calculated from TGA are given in **Table 2.1**.

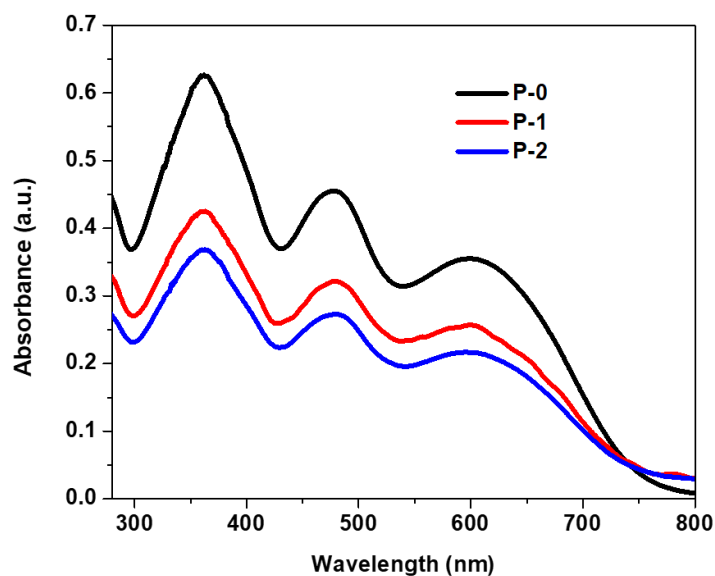


Figure 2.14 UV-Vis Absorption spectrum for the P-0, P-1, and P-2 polymers measured in chloroform solvent.

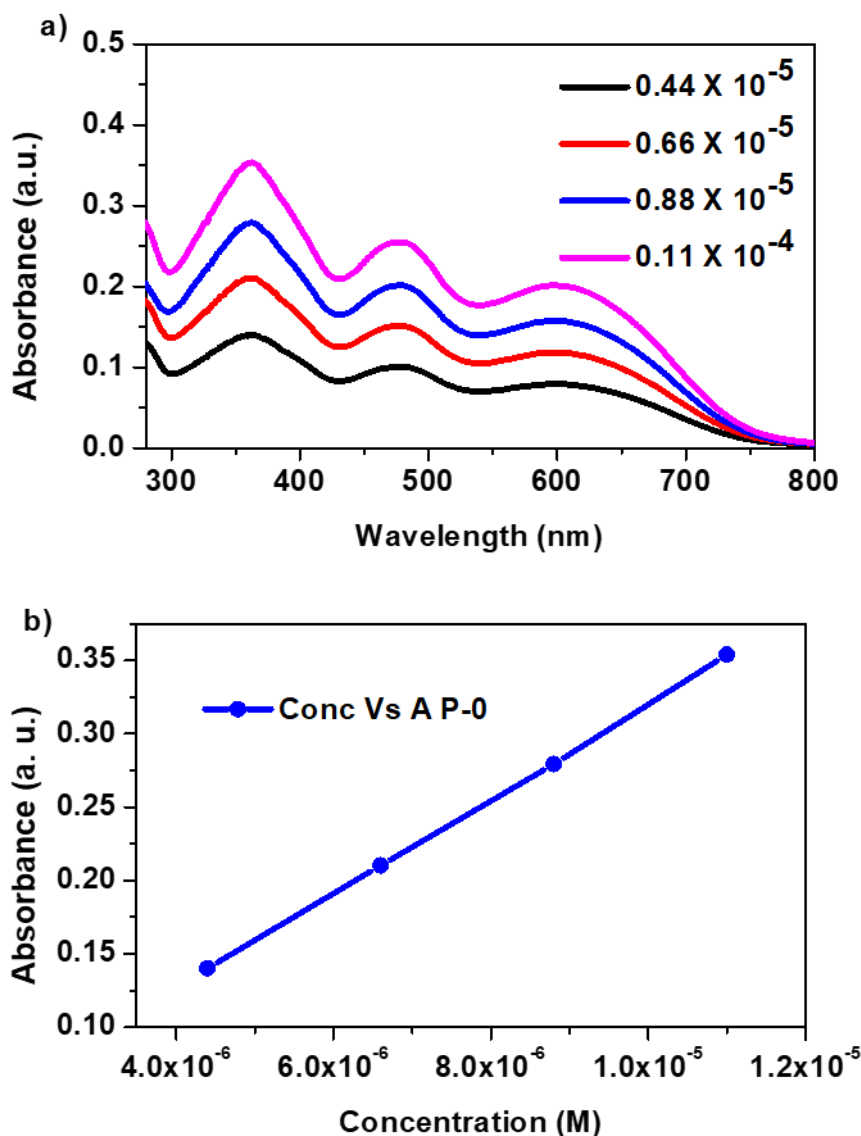


Figure 2.15 UV-vis absorption spectra for P-0 or P(PDI2OD-T2) polymer a) at different concentrations b) Absorption vs concentration plot of P-0 polymer.

2.4.2 Calculation for percentage of MWCNTs in polymer composites determined using absorption spectroscopy

The molar absorptivity coefficient for P(PDI2OD-T2) or P-0 polymer was determined to be $31931.7 \text{ L M}^{-1} \text{ cm}^{-1}$ at a wavelength of 362 nm using Lambert-Beers law, where A is Absorbance is equal to molar absorptivity coefficient (ϵ) $\times$ concentration (c) $\times$ path length (l).

The calculation for obtaining the concentration of polymer in the composites is shown below.

➤ **P-0** $C=A/\epsilon$ $A=0.6268$; $C=0.6268/31931.7=1.9598 \times 10^{-5} \text{ M}$

1 M = 1113.67 gm of Polymer (repeating unit mass) = $1.9598 \times 10^{-5} \times 1113.67 = 0.02182$ gm, for 1000 ml solution.

As 1 mg polymer was dissolved in 50 ml of chloroform: $(0.02182 \times 50) / 1000 = 1.09 \times 10^{-3}$ g = 1 mg

➤ **P-1** A = 0.4245;

$C = 0.4245 / 31931.7 = 1.6927 \times 10^{-5}$ M = $1.3293 \times 10^{-5} \times 1113.67 = 0.01480$ gm.

In 50 ml: $(0.01480 \times 50) / 1000 = 7.40 \times 10^{-4}$ g = 0.740 mg

Amount of CNT = 1mg – 0.740 mg polymer = 0.26 mg CNT

➤ **P-2** A = 0.3682;

$C = 0.3682 / 31931.7 = 1.1530 \times 10^{-5}$ M = $1.1530 \times 10^{-5} \times 1113.67 = 0.01284$ gm.

In 50 ml: $(0.01284 \times 50) / 1000 = 0.642$ mg

Amount of CNT = 1mg – 0.642mg polymer = 35.8 mg CNT.

Based on these calculations, the percentage of polymer and Multi-Walled Carbon Nanotubes (MWCNT) in the composite polymers P-1 and P-2 were determined to be 26% and 35.8% respectively, using the molar absorptivity coefficient (ϵ).

2.4.3 Morphology.

The FE-SEM and HR-TEM techniques were studied to determine the morphology of all-polymer samples and MWCNT. **Figure 2.16a** shows that P-0 polymer exhibited a spherical morphology with interconnected nature of spherical particles of varying diameters for the spheres (**Figure 2.17a**). On the other hand, the MWCNT exhibited entangled tubular morphology (**Figure 2.16b**) with a highly porous interconnected network of carbon tubes (**Figure 2.16b**). A uniform dispersion and wrapping of MWCNT over polymer was observed for P-1 and P-2 with an enhancement of porous network (**Figure 2.16c-d**). The FE-SEM images show better interaction of the polymer with MWCNT during the *in-situ* polymerization reaction as shown in **Figure 2.16**. Compared with P-1, the composite P-2 showed well-wrapped structure with MWCNT along with very good porous architecture. This uniform networking of the MWCNT over composite polymers is expected to enable the exposure of active sites and act as a direct pathway for electron transport. The FE-SEM images at a higher magnification of 5 μ m are given in **Figure 2.17**. This also indicates the maximum contact of MWCNT with polymer where no bulk growth was observed.

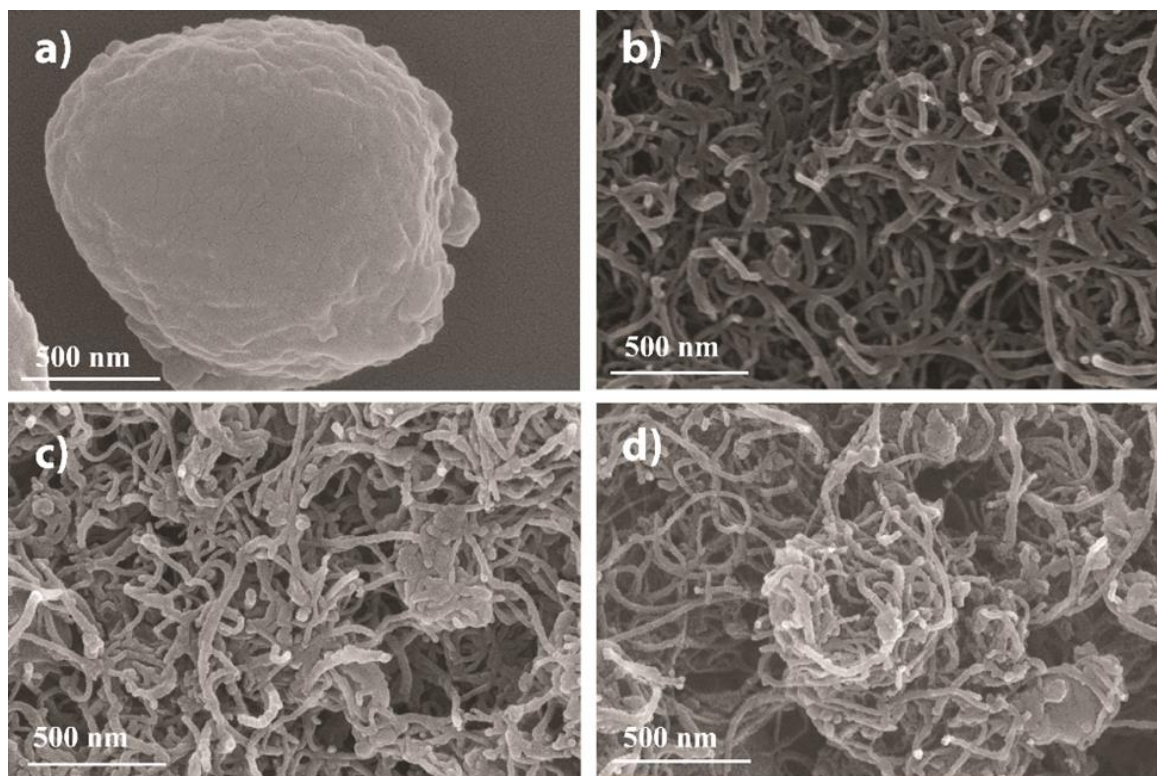


Figure 2.16 FE-SEM images of (a) P-0, (b) neat MWCNTs, (c) P-1, and (d) P-2 at a resolution of 500 nm.

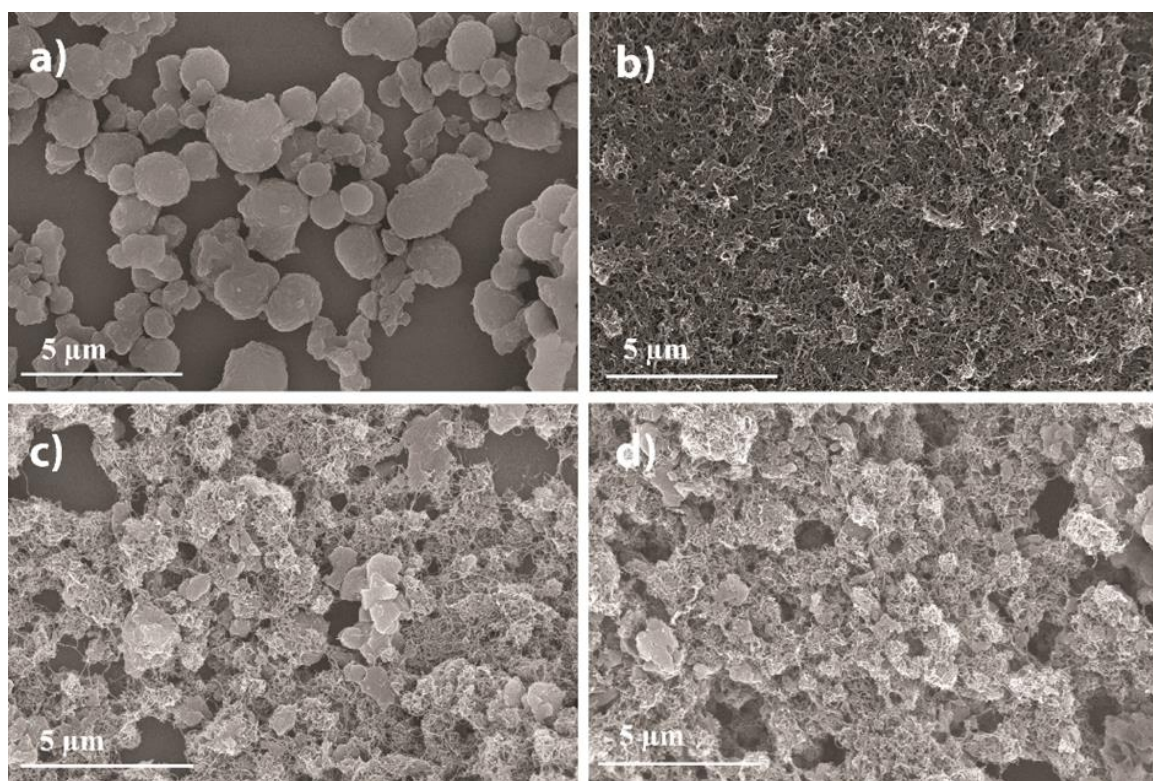


Figure 2.17. FE-SEM images of (a) pristine P-0, (b) neat MWCNTs, (c) P-1, and (d) P-2 at 5 μm.

The samples were also studied by HR-TEM. Neat polymer P-0 polymer (**Figure 2.18a**) and MWCNT (**Figure 2.18b**) showed spherical and tubular morphology respectively, which confirmed the observation from FE-SEM (**Figure 2.16a and 2.16b**). **Figure 2.18c and 2.18d** showed the overall increase in the diameter of MWCNT with polymer layer spread on the surface of MWCNT. HR-TEM images confirm the lack of unwanted agglomeration and presence of homogeneous distribution in *in-situ* synthesized samples. The FE-SEM and HR-TEM images prove the uniform polymeric network with MWCNT and the absence of bulk networks resulted by the *in-situ* polymerization method. This is expected to enhance the electrochemical performance for the composites.

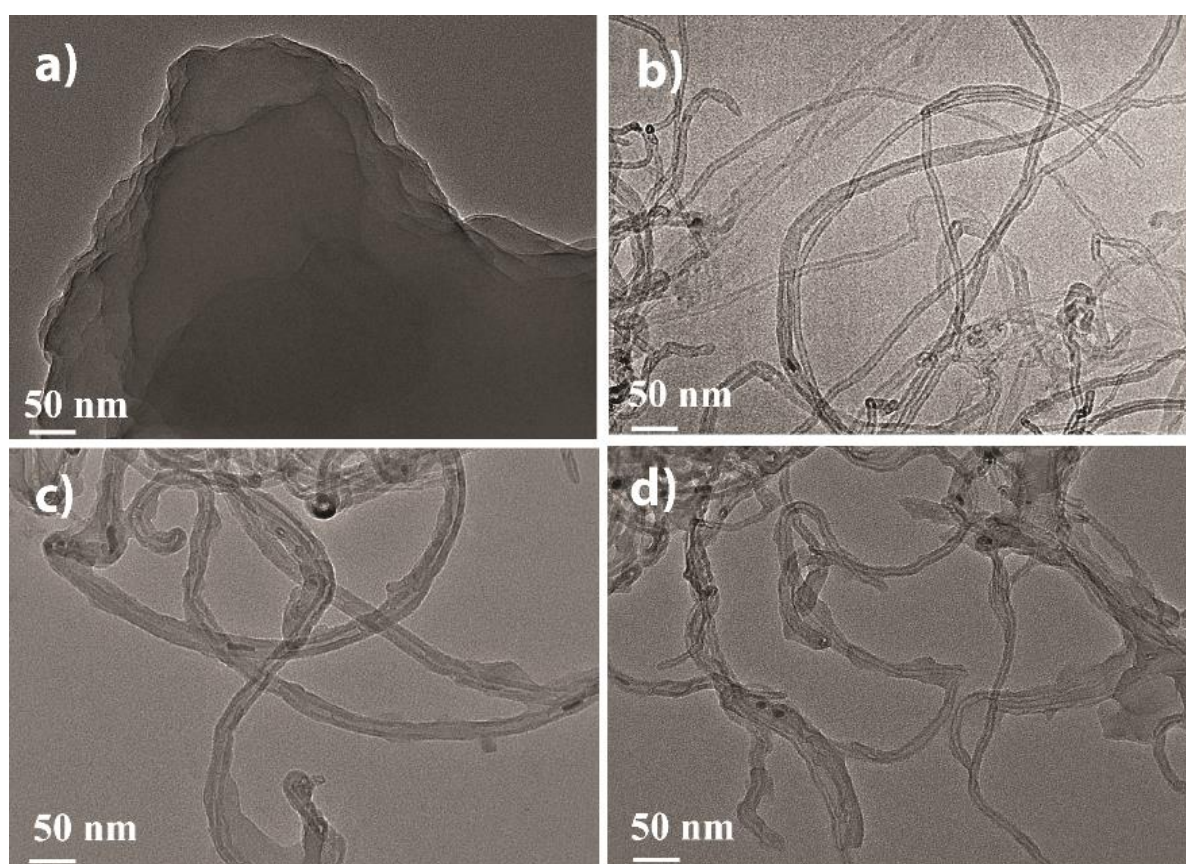


Figure 2.18 HR-TEM images of (a) pristine P-0, (b) neat MWCNT, (c) P-1, and (d) P-2 at 50 nm.

2.4.4 Surface Area and Pore Size.

The nitrogen adsorption desorption isotherms and pore size distribution for MWCNT, P-0, and P-2 composites samples are shown in **Figure 2.19a-b**. P-0 showed predominantly microporous nature of pore size distribution, whereas MWCNT exhibited both micro- and meso-pore

distribution as shown in **Figure 2.19**. As MWCNT increases, the number of pores across the mesoporous area increased in composite polymer P-2 in comparison with P-0 as seen in **Figure 2.19a**. The composite polymer's pore size distribution profile exhibited a similarity to that of MWCNT. The Density Functional Theory (DFT) desorption model indicated the average pore width for polymers were around 3 nm in size, whereas for MWCNTs it was 14 nm. The polymer samples P-0, P-2, and MWCNT exhibited Type III isotherm as depicted in **Figure 2.19b**. The specific surface area values were determined to be MWCNT ($206.0 \text{ m}^2 \text{ g}^{-1}$), P-0 ($11.3 \text{ m}^2 \text{ g}^{-1}$), and P-2 ($84.2 \text{ m}^2 \text{ g}^{-1}$) using the BET model. The BET results show that *in-situ* MWCNT inclusion increases the surface area of the P-2 composites when comparing with the P-0 polymer, where it is consistent to the FE-SEM results. The difference between polymer composite P-2 and P-0 polymer concerning the porous structure is due to their morphological contrast. As demonstrated from FE-SEM and HR-TEM analysis, the polymer layer in the P-2 polymer composites is coated thinly and homogeneously on the surface of MWCNT. The main objective of such hierarchical porous and high surface morphology is to easily transport electrolyte ions when the material is utilized as an electrode, thereby increasing the overall capacity for charge storage.

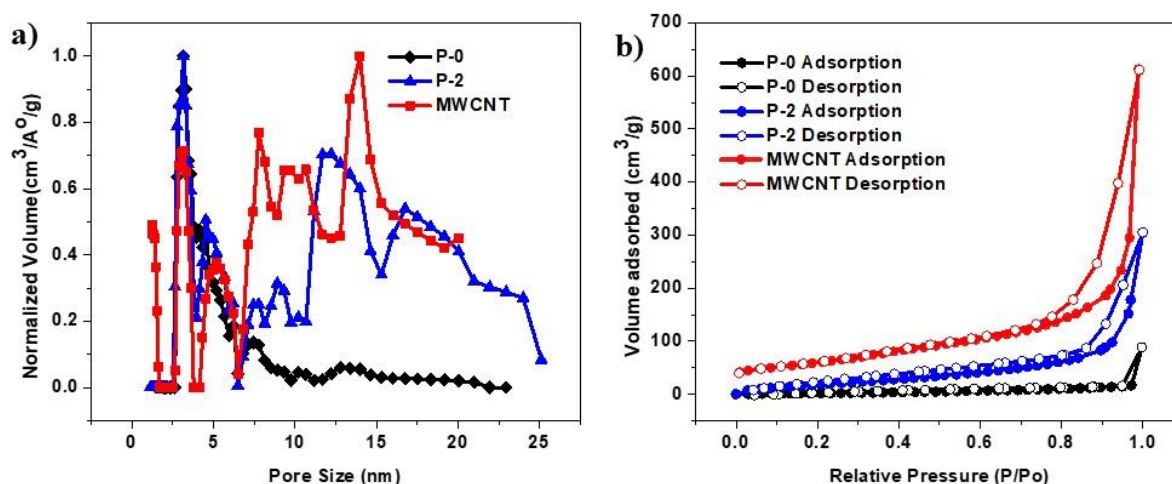


Figure 2.19 a) Pore size distribution profile of P-0, MWCNT and P-2 samples, and b) nitrogen adsorption/desorption isotherms of P-0, b) MWCNT and c) P-2 samples.

2.5 Electrochemical Characterization

The electrochemical efficiency of all electrodes (P-0, P-1, and P-2) was assessed in a three-electrode configuration using a 1 M LiClO₄/PC electrolyte, with Ag/Ag⁺ as the reference electrode, platinum mesh as the counter electrode, and polymer-coated Toray carbon as the

working electrode. As depicted in **Figure 2.20a**, cyclic voltammetry at a scan rate of 10 mV s^{-1} was employed to initially evaluate P-0, P-1, and P-2. The composite polymers P-0, P-1, and P-2 displayed reversible redox peaks, indicative of pseudocapacitive charge storage behavior. The notable increase in current response observed in P-1 and P-2 compared to the pristine polymer P-0 primarily stems from the enhanced exposure and utilization of active sites upon MWCNT addition (**Figure 2.20a**). Additionally, for comparison, the cyclic voltammetry of the MWCNT was conducted with varying scan rates ranging from 5 to 100 mV s^{-1} , as shown in **Figure 2.21a**, revealing a rectangular feature characteristic of EDLC-type charge storage. The lower current response of MWCNT at 10 mV s^{-1} scan rate indicated the absence of participation of MWCNT in redox reactions. Furthermore, the GCD of the MWCNT was well matching with the CV profile and did not show any redox properties during charge-discharge. However, its inclusion in the polymer (P(PrDI2OD-T2)) creates a conducting network for the facile passage of the electrons. P-2 out-performed P-1 as improvement in the current response was observed from CV, which could be due to the higher MWCNT content in the former and also the uniform wrapping of the MWCNT network over the polymer. The CV of P-0, and P-1 is given in the **Figure 2.21a-b**.

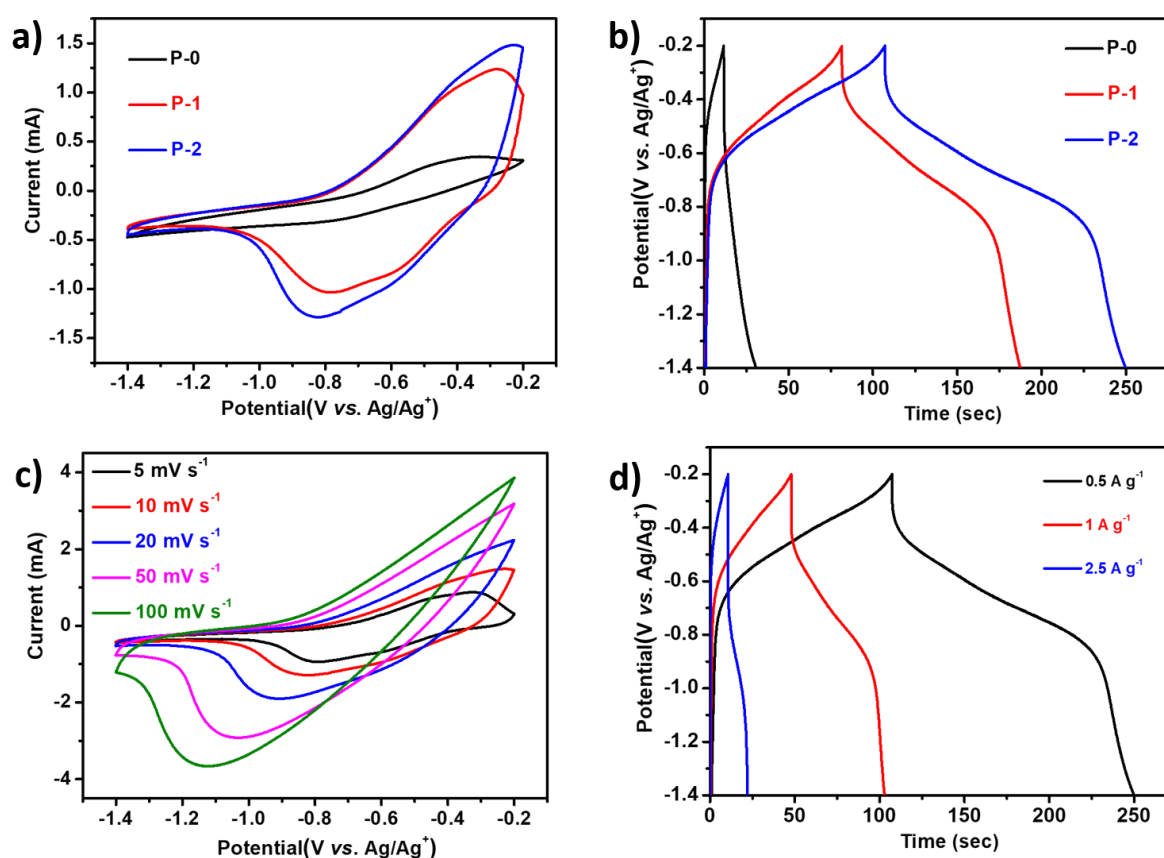


Figure 2.20 a) The CV profile of P-0, P-1, and P-2 measured at a scan rate of 10 mV s^{-1} , b) the GCD of P-0, P-1, and P-2 samples recorded at the current rate of the 0.5 A g^{-1} c) the CV scan at a different scan rate of 5 to 100 mV s^{-1} for P-2 sample, and d) the GCD profile recorded at various current of 0.5, 1.0, and 2.5 A g^{-1} for P-2.

The GCD investigation for P-0, P-1, and P-2 in a three-electrode assembly is given in **Figure 2.20b**. The observed GCD profile closely matches that of the CV curves. Furthermore, the capacitance was calculated for P-0, P-1, and P-2 by using **Equation no. E1. (Section 2.6)**. At a current rate of 0.5 A g^{-1} , the discharge capacitance values for P-0, P-1, and P-2 were measured at 10.0, 61.6, and 92.9 F g^{-1} , respectively. The notably higher capacitance observed in the P-2 composite can be primarily attributed to the enhanced participation of faradic processes facilitated by the higher MWCNT content. It emphasizes the significance of the donor-acceptor polymer modification technique using in-situ MWCNT addition approach. It is worth noting that elevated surface area, and altered porosity for the composites provides ease of electron transport in charge storage by providing a highly accessible surface area and conducting network in composite samples.

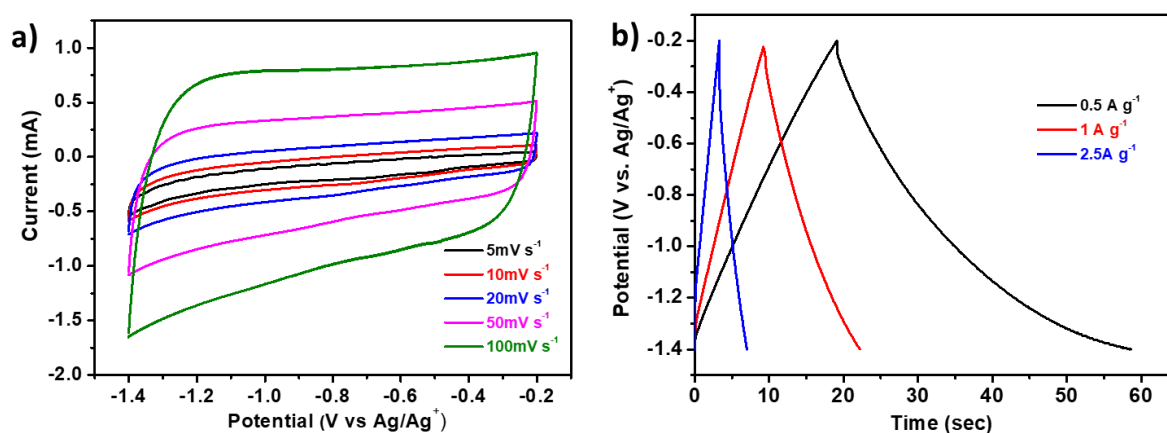


Figure 2.21 (a)- (b) CV and CD profiles were recorded for MWCNT at various scan rates of 5 to 100 mV s^{-1} , and CD profiles at various current densities of 0.5 to 2.5 A g^{-1} .

Figure 2.20c shows the CV profile of the composite P-2 at various scan rates of 5, 10, 20, 50, and 100 mV s^{-1} . The polymer shows reversible peaks at a position at $-0.4 / -0.9 \text{ V vs Ag/Ag}^+$, in 5 mV s^{-1} , and more or less similar feature was observed throughout all the scan rates highlighting the good reversibility of the polymer P-2. **Figure 2.20d** compares the galvanostatic charge-discharge (GCD) profile of P-2 at various current rates 0.5, 1.0 and 2.5 A g^{-1}

g^{-1} . The capacitance obtained was 92.9, 70.7, and 37.4 F g^{-1} respectively. Similarly, the GCD profile was recorded for P-0 and P-1 and given in **Figure 2.22 c-d**. The discharge capacitance obtained for P-0 and P-1 were 10, 2.2, and 0.6 F g^{-1} , and 61.6, 48.3, and 28.5 F g^{-1} at current rate of 0.5, 1.0, and 2.5 A g^{-1} respectively.

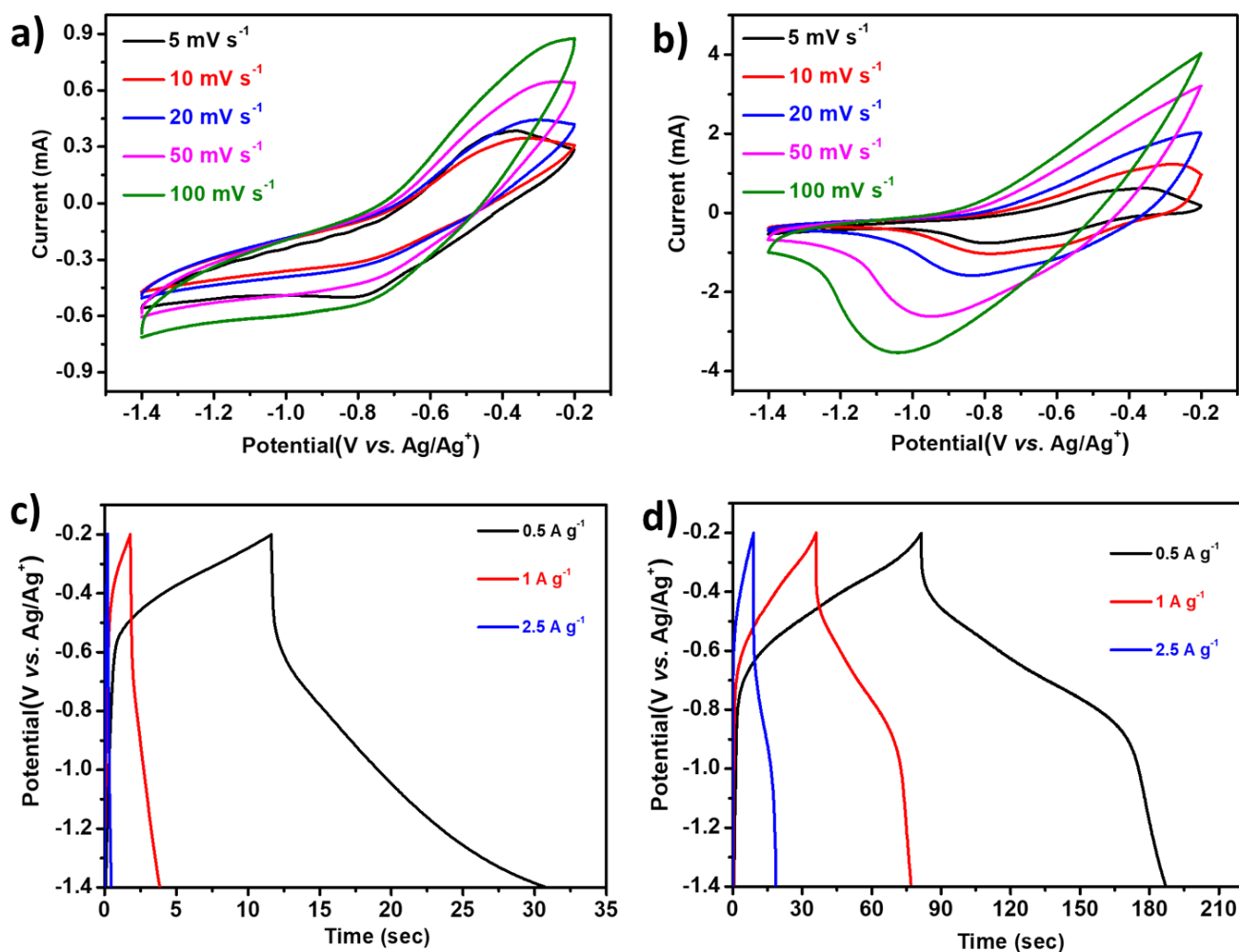


Figure 2.22 CV profiles were recorded at various scan rates for the (a) P-0, (b) P-1, and CD profiles recorded at various current densities for the (c) P-0, and (d) P-1 samples.

An investigation into the material properties of the donor-acceptor polymer P-2 was conducted by fabricating a symmetric device in a liquid electrolyte (1M LiClO_4 in propylene carbonate). The cyclic voltammetry (CV) profiles, spanning from 0.2 V to 3.3 V at various scan rates ranging from 5 to 100 mV s^{-1} , are depicted in **Figure 2.23a**. The high voltage window (3.1V) highlights the importance and the intrinsic property of the polymer, which is higher or comparable to already reported donor-acceptor polymers.^{21,24-26} The reversible redox features originating from the polymer material are maintained throughout all CV scan rate. The GCD of the symmetric device LE-P-2||P-2 (LE-liquid setup) given in **Figure 2.23b** shows a

capacitance of 85.4, 53.0, and 43.9 F g⁻¹ at the current rate of 0.25, 0.5, and 1.0 A g⁻¹ (given current 0.32, 0.64, and 1.28 A to total Z (1.28 mg active mass on both electrodes) respectively calculated using **Equation no. E2 (Section 2.6)**. This value is higher or comparable to that of many reported donor-acceptor polymers and given in **Table 2.2**.

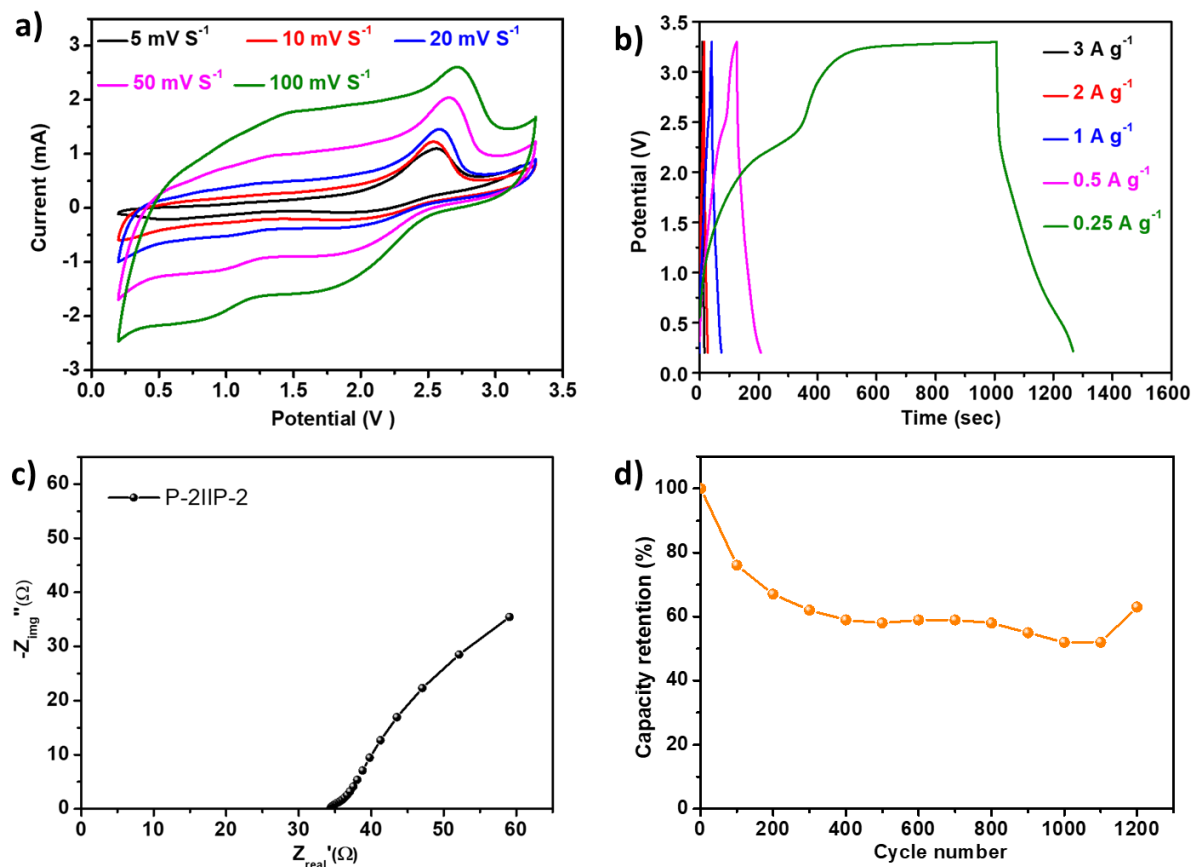


Figure 2.23 Full cell device characterization in the liquid electrolyte (LE-P-2||P-2) a) CV profile of symmetric device with various scan rate, b) the galvanostatic charge-discharge at various current rate, c) EIS measurement of LE-P-2||P2 symmetric device, and d) cycling stability at current rate of 1.0 A g⁻¹.

The internal resistance of electrolytes, charge transfer resistance, and ion diffusion in supercapacitor devices are all studied using electrochemical impedance spectroscopy (EIS). The EIS for symmetric device was determined from the Nyquist plot and is shown in **Figure 2.23c**. The ESR (equivalent series resistance) for the device was obtained at 34.3 Ω, which originates from the solution phase resistance and is lesser when compared with the reported donor-acceptor polymer.^{13,25-26} Furthermore, the small semi-circle (R_{ct}) observed at the x-axis intercept with the value of ~36 Ω followed by Warburg diffusion lines arises due to low charge transfer resistance at electrode-electrolyte interphase and fast diffusion of the Li⁺-ions and vice-

versa and diffusion resistance associated with the electrolyte respectively. The cycling stability and capacitance retention are given in **Figure 2.23d**. It showed 60 % capacity retention over 800 cycles which further increased to 70 % with 1200 of charge-discharge cycles.

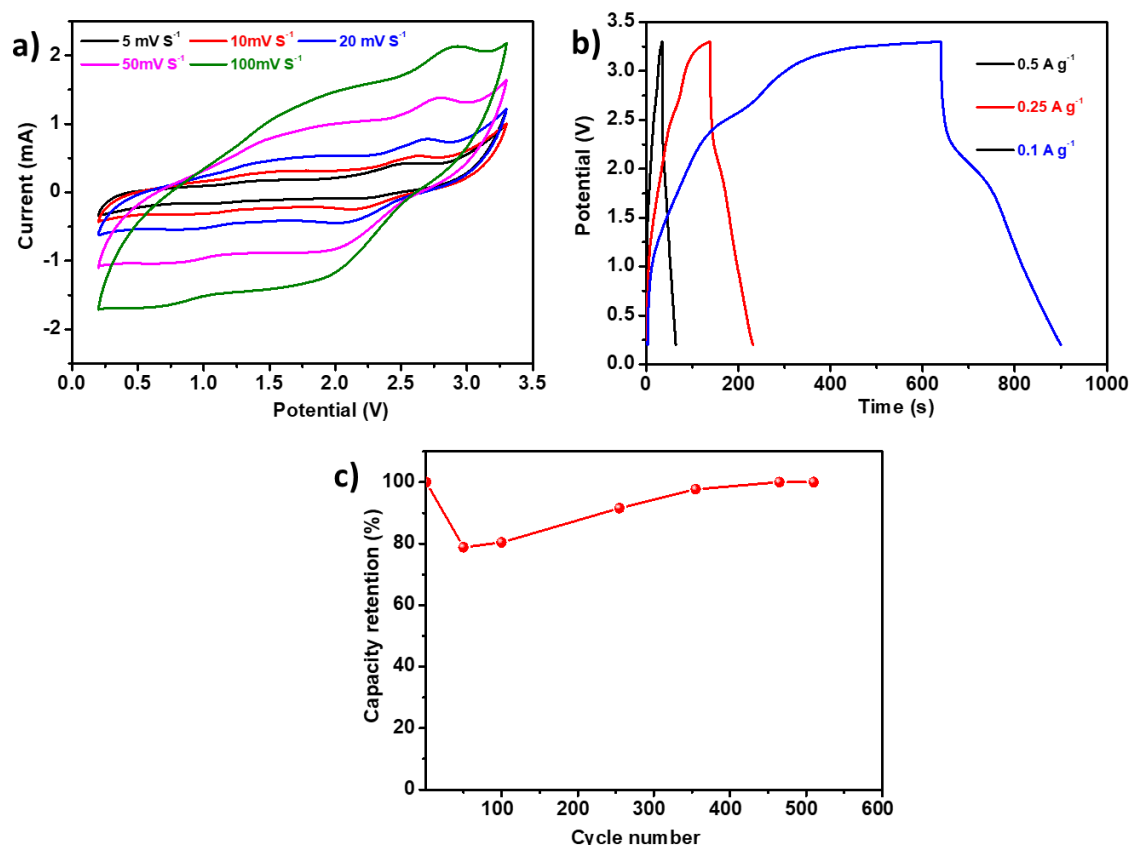


Figure 2.24 Flexible solid-state device and (QE-P-2||P-2) measurements, a) CV profile at various scan rates, b) GCD at the different current rate, and c) durability test at the current rate of 1.0 A g⁻¹.

The fabrication of a flexible solid symmetric device followed the drop-casting method for electrode preparation over a peeled grafoil as detailed given above in 2.2.6 to 2.2.9. A thin layer of quasi-PMMA LiClO₄ electrolyte was applied to the electrodes, and the separator was carefully sealed QE-P2||P-2 device (QE- quasi-solid electrolyte). The CV of the quasi-solid state symmetric device is depicted in **Figure 2.24a**, which exhibits reversible redox features at a scan rate of 5 to 100 mV s⁻¹ scan rate, similar to its liquid counterpart. This indicated the retention of material activity even in quasi-solid state without any compromises in the redox activity. The GCD capacitance (**Figure 2.24b**) obtained at 0.25, 0.5, and 1.0 A g⁻¹ current was 84.2, 60.5, and 38.5 F g⁻¹ respectively. Furthermore, the cycle stability of the quasi-solid-state

device is given in **Figure 2.24c**, which showed 99% of capacitance retention over 500 cycles. Finally, the demonstration of the QE-P-2||P-2 device is shown in **Figure 2.25**. The device was first charged to light the LED bulb. The Ragone plot (Power density vs Energy density) of QE P-2||P-2 is given in **Figure 2.26**.

Table 2.2: The comparison of Power Density and Energy Density at different current rate.

Normalized Current rate (A g ⁻¹)	Power density (W kg ⁻¹)	Energy density (Wh kg ⁻¹)
3.0	18600	20.1
2.0	12400	29.3
1.0	6200	51.4
0.5	3100	80.8
0.25	1550	112.4



Figure 2.25. Quasi solid-state symmetric device demonstration after charging the device.

The device achieved a maximum energy density (ED) of 112.44 Wh kg⁻¹ and a peak power density (PD) output of 18600 W kg⁻¹, as calculated using **Equation E4 (Section 2.6)**. The

comparison of ED and PD is tabulated in **Table 2.2**. The comparable activity of P-2 polymer in liquid and solid-state devices highlights the good intrinsic activity of the material. The superior device performance can be attributed to the enhanced interaction between MWCNT and the polymer, leading to increased accessible surface area, improved electron conductivity, and facilitated transport channels for Li⁺ ions.

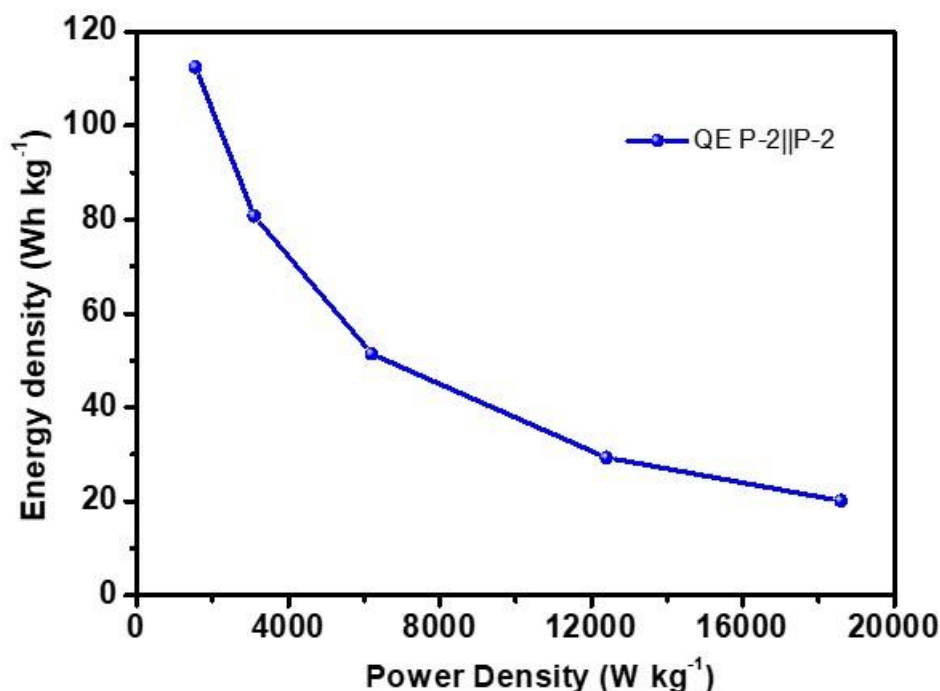


Figure 2.26 Ragone plot of Quasi solid-state symmetric device.

2.6 Electrochemical Calculation

Calculation of the specific capacitance was determined using galvanostatic charge-discharge (GCD) measurements using following equation,

1. **Equation no. E1** for three-electrode assembly,

$$Cs (F g^{-1}) = (I \times \Delta t) / (m \times \Delta V)$$

2. **Equation no. E2** for symmetric device,

$$Cs (F g^{-1}) = 4 (I \times \Delta t) / (Z \times \Delta V)$$

3. **Equation no. E3** for single electrode in the device configuration,

$$Cs_{(F g^{-1} Single)} = 2 \times \frac{(I \times \Delta t)}{(m \times \Delta V)}$$

4. **Equation no. E4** for energy and power density of the device,

$$ED(Wh\ kg^{-1}) = \frac{Cs}{2 \times 3.6} \Delta V^2$$

$$PD(W\ kg^{-1}) = ED/t_h$$

2.7 Conclusion

In Summary, perylenebisimide based donor-acceptor conjugated polymer P(PDI2OD-T2) and their composites were synthesized by modified Stille polymerization procedure in a short reaction time. The in-situ addition of the MWCNT to the polymer matrix enhanced the conductivity of the composite polymer P-2 and improved the surface area and pore size distribution. The active materials' high surface morphology and improved porosity made it easier for electrolyte ion transfer when it was utilized as electrode material in supercapacitor. The material was carefully evaluated and characterized with different characterization techniques. The donor-acceptor polymer P-2 showed a good capacitance of 93 F g⁻¹ at 0.5 A g⁻¹ of the current density. The symmetric device in liquid organic electrolyte (LE--P-2||P-2) and quasi-solid gel electrolyte (QE-P-2||P-2) showed an excellent capacitance of 85.4 F g⁻¹ and 84.2 F g⁻¹ respectively at the current rate of 0.25 A g⁻¹ and a wide potential range of 3.1 V, with good cycle stability. The device showed good energy density of 112.4 Wh kg⁻¹ and an excellent power density of 18600 W kg⁻¹. In addition, the device demonstration was done with the help of an LED light bulb. Overall, this study provides a step forward to use a synthetic approach for utilizing a donor-acceptor conjugated polymer for a wide potential range and high-power density symmetric supercapacitor device.

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CHAPTER 3

**High-Voltage Non-Aqueous Hybrid
Supercapacitor Based on N2200 Polymer
Supported Over Multiwalled Carbon Nanotube**

3.1 INTRODUCTION

Poly{[N,N'-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5'-(2,2'-bithiophene)}, also referred to as Polyera ActivInk N2200, is a nonfullerene acceptor polymer known for its favorable semiconducting properties and remarkable stability in ambient conditions. Primarily used as an acceptor polymer in all-polymer solar cells, N2200 has demonstrated high power conversion efficiencies when paired with suitable donor polymers under controlled fabrication conditions.¹⁻⁷ Initially utilized in rechargeable Li batteries in 2015, leveraging its electron transport pathway and reversible doping characteristics,⁸ our group explored the potential of P(NDI2OD-T2) and its derivatives with naphthalene diimide (NDI) as the acceptor and thiophene-terminated phenylenevinylene as the donor, as electrode materials in supercapacitors, revealing exceptional cycling stability.⁹

The most commonly used conjugated polymers for supercapacitor electrode material are poly(3,4-ethylenedioxythiophene), polypyrrole, polyaniline, etc., which are all p-type (electron-rich) materials with good charge-storage properties.¹⁰⁻¹⁴ In supercapacitor applications, these p-type polymers are usually used as the electrodes for either Type I or Type II devices, where the electrodes are both symmetric or asymmetric, respectively. While reports on Type I and Type II supercapacitor devices using conjugated polymers abound in literature, devices using electron poor or donor-acceptor type π -conjugated polymers are not very common. Like the p-type polymers, donor-acceptor polymers also show pseudocapacitive behavior due to their intrinsic redox properties.^{8,15,16} However, their performance as supercapacitor electrode materials are rarely explored in the literature. There are only one or two other reports on supercapacitors, which use rylenebisimides (perylene or naphthalene) as the electrode material.^{9,15,17} In our earlier work, we demonstrated the electrochemical performance of supercapacitor based on rylenebisimides with excellent stability over long cycles (> 4000 cycles), indicating the potential of the donor-acceptor polymers as efficient electrode materials. Hence, further research towards improving the performance of such polymer materials is indeed essential.

Another intriguing characteristic of the donor-acceptor polymers is their ability to withstand high-voltage windows when used as the electrode material in electrochemical energy storage devices (EESDs). The high-voltage electrodes open up the opportunity to make use of organic electrolytes for realizing high-voltage supercapacitor devices instead of the traditional aqueous electrolyte,¹⁸ which suffers from low voltage stability due to the inevitable water

oxidation at high-voltage. As the energy density (E) of supercapacitor follows the relationship $E = \frac{1}{2} CV^2$, where C is the capacitance and V is the operating voltage, a small increase in the voltage results in significant improvement in the energy density of the device.¹⁹ Therefore, exploring donor-acceptor polymers as the electrode material in combination with organic electrolytes is pertinent towards developing high energy supercapacitors.

Despite their advantages, the organic electrolytes suffer from low ionic conductivity inciting high internal resistance and often leads to inferior electrochemical performance. Therefore, improving the conductivity of the electrode material and the interface between the electrode and electrolyte are the essential requirements to compensate for the electrolyte resistance in organic electrolyte-based supercapacitors. The conductivity of the polymers can be often enhanced by mixing with various carbon materials like carbon nanotube (CNT) or graphene.²⁰⁻²⁶ Multiwalled CNT (MWCNT) is also an excellent conducting additive for electrode fabrication due to its high surface area, low electrical resistivity, and nano-porous structure.²⁷ The conjugated polymers can involve in π - π interactions with the CNT resulting in the unbundling of the CNT aggregates.²⁸⁻²⁹ The composite electrodes usually have a porous structure, which enables good accessibility of the electrolyte to the inner surface of the electrode resulting in improved electrode|electrolyte interface.^{30,31} Compared to the various strategies adopted for mixing CNT with conjugated polymers, the *in-situ* addition of CNT during the polymerization reaction is a better way to achieve uniform mixing of the polymer with the conductive material, which leads to the better electrochemical performance of the material. There are several reports on the application of polyaniline composites with *in-situ* addition of carbon nanotube or graphene as the electrode material in supercapacitors.³²⁻³⁷ These nanocomposites exhibited better charge-storage properties and stability as compared to pristine polyaniline. Similarly, polypyrrole *in-situ* polymerized with carbon nanotube,^{38,39} RGO (reduced graphene oxide),⁴⁰ molybdenum disulfide (MoS_2),⁴¹ and copper sulfide (CuS)⁴² have also shown improved charge-storage performance compared to the pristine polypyrrole. Recently, Smirnov *et al.* reported the *in-situ* synthesis of polypyrrole in the presence of cellulose nanofiber grown over graphene, which showed enhanced specific capacitance (810 F g^{-1}) than the externally mixed sample (371 F g^{-1}).⁴³ The *in-situ* synthesized poly (3-hexylthiophene)/graphene composites also have shown better capacitance value than the *ex-situ* mixed composites.⁴⁴ However, as already mentioned, these composites are tested in aqueous electrolyte, thereby limiting the operating voltage of the devices to 1.2 V.^{45,46}

Therefore, extending the strategy of the *in-situ* incorporation of conducting additives with the pseudocapacitive/battery-type conducting polymers for designing suitable electrode materials for organic electrolyte-based high energy supercapacitors and hybrid supercapacitors is of great importance, yet challenging. In the previous Chapter 2, we reported n-type P(PDI2OD-T2) donor-acceptor polymer and its *in-situ* synthesized composites with MWCNT operated at a high potential window, which exhibited better capacitance as compared to pristine polymer. Further, the symmetric supercapacitor device fabricated with polymer composite P-2 using the liquid organic electrolyte (LE-P-2||P-2), and quasi-solid gel electrolyte (QE- P-2||P-2) exhibited excellent capacitance of 85.4 F g^{-1} as well as 84.2 F g^{-1} respectively at 0.25 A g^{-1} current rate and operated with high-voltage window (3.1 V). Further the device demonstrated good cycling stability over 1200 cycles with $\sim 70 \%$ capacity retention. The flexible device showed an excellent power density of 18600 W kg^{-1} and a good energy density of 112.4 Wh kg^{-1} . This study illustrated the utilization of a synthetic method to fine-tune the morphology to achieve better electrochemical properties of polymeric supercapacitor electrodes.

In this chapter, P(NDI2OD-T2) or N2200 based polymer composites were synthesized by *in-situ* addition of MWCNTs with various weight ratios following a modified Stille polymerization procedure. The P(NDI2OD-T2) polymer is a lower analogue of P(PDI2OD-2) polymer, which could provide the benefit in electrochemical performance due to having low molecular weight of repeating mass, better or high porous morphology. So, the *in-situ* synthetic strategy used in the chapter 2 was extended for developing an efficient electrode material for supercapacitor based on P(NDI2OD-T2). Here, we also synthesized ex-situ mixed polymer composites to investigate the factors contributing to the superior electrochemical performance of *in-situ* polymer composites compared to both pristine polymers and externally mixed polymer composites. The synthesis of P(NDI2OD-T2) and its composites was carried out using the modified Stille polymerization conditions reported in chapter 2, which resulted in high molecular weight polymers with good yields in very short reaction periods. To our knowledge, this is the first report where high molecular weight P(NDI2OD-T2)-based polymers were developed within 2 hours of the polymerization time. The electrochemical performance of the composite materials was tested in an organic electrolyte (1M LiClO₄/propylene carbonate) in a standard three-electrode configuration. The *in-situ* prepared polymer composites delivered $80 \text{ mAh g}^{-1}_{(\text{polymer})}$ specific capacity (considering the loading of polymer in the working electrode), a value substantially higher compared to that of the pristine polymer as well as the physically mixed polymer/MWCNT composite. Moreover, the *in-situ* prepared composite

showed promising performance as the negative electrode coupled with activated carbon positive electrode in a hybrid supercapacitor (HSC) cell. The preparation and electrochemical characterization of the *in-situ* and physically mixed polymer/MWCNT composites are schematically summarized in **Figure 3.1**.

3.2 Experimental Section

3.2.1 Materials

1,4,5,8-Naphthalenetetracarboxylic dianhydride (NTCDA), 2-octyldodecanol, 2-ethylhexyl bromide were purchased from TCI chemicals and used without further purification. 5,5'-bis(trimethylstannyl)-2,2'-bithiophene, bis(triphenylphosphine) palladium (II) dichloride ($\text{Pd}(\text{Ph}_3)_2\text{Cl}_2$), multiwalled carbon nanotube (MWCNT) and propylene carbonate (PC) were purchased from Sigma-Aldrich and used without further purification. 4-tertiary butyl toluene was purchased from Sigma-Aldrich and used after drying.

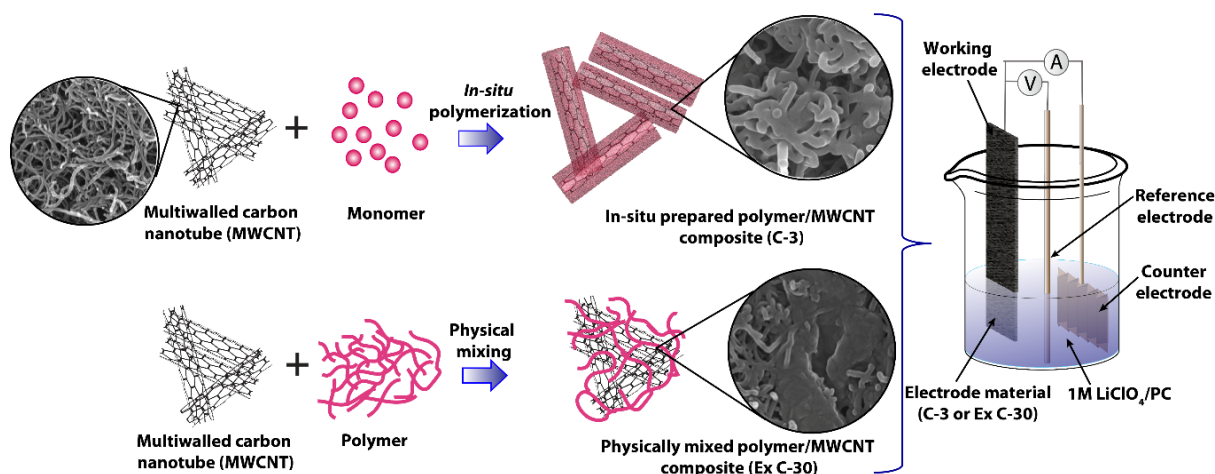


Figure 3.1 Schematic representation summarizing the polymerization of P(NDI2OD-T2) supported over MWCNTs following *in-situ* and physical mixing approaches, and their electrochemical analysis in three electrode cell.

3.2.2 Measurements.

^1H NMR spectra for monomer and polymers were collected on Bruker 200 and 400 MHz NMR spectrophotometer in deuterated chloroform solution with TMS as the reference. The molecular weight of polymers was determined using Gel Permeation Chromatography (GPC) having a Viscotek VE 1122 solvent delivery system at room temperature using tetrahydrofuran (THF) at a flow rate of 1 mL/min as eluent and with the help of Viscotek VE 3580 refractive index (RI) detector. The analyses were carried out using polystyrene as the standard. Absorption

spectra for the polymers were measured using a double beam Perkin Elmer lambda-35 UV/Vis spectrometer with deuterium and tungsten lamps as the source. TGA (Thermogravimetric analysis) was performed with the help of a Perkin Elmer STA (Simultaneous Thermal Analyzer) 6000 thermogravimetric analyzer. Samples were run using a heating rate of 10 °C / min from 40 to 800 °C under the nitrogen atmosphere. TEM images were taken with the help of a JEOL JEM-F200 HR-TEM instrument with an energy dispersive X-ray (EDX) detector for EDX analyses. FE-SEM images were recorded using an FEI NOVASEM 450 FESEM instrument.

3.2.3 Sample Preparation.

The UV–vis absorption studies were recorded in the solution state by dissolving the polymer in chloroform at different concentrations. To calculate the concentration of MWCNT in the C-X polymer composites, the solution was prepared at a concentration of 1 mg / 50 mL in chloroform. For FE-SEM and TEM sample preparation, the polymer was dispersed in methanol as the solvent (1 mg polymer in 2 mL methanol). The dispersion was then drop-casted over mica for SEM and copper grid for TEM analyses.

3.2.4 Electrode Fabrication.

For fabricating the electrodes, a homogeneous slurry was prepared by dispersing 4.75 mg of the desired sample (P-0, C-1, C-2, C-3, or Ex C-30) with 0.25 mg of Polyvinylidene fluoride (PVDF) binder in 500 μL of N-methyl pyrrolidone (NMP). 100 μL of the slurry was coated on 1 cm^2 area of a carbon fiber paper to obtain a total loading of 1.0 mg cm^{-2} . The electrodes were then dried in an oven at 60 °C overnight. For comparison, the electrode coated with MWCNT was also prepared with 0.33 mg cm^{-2} loading.

3.2.5 Electrochemical Measurements.

All the electrochemical tests were carried out using a BioLogic VMP3 instrument. To check the electrochemical performance of the samples, the three-electrode cells were assembled using the carbon fiber paper coated with the desired sample as the working electrode, a platinum mesh as the counter electrode, and Ag/Ag^+ as the reference electrode in 1M LiClO_4/PC electrolyte. The potential window was fixed from -0.2 to -1.4 V vs. Ag/Ag^+ . The discharge capacities of the samples were measured from the galvanostatic charge-discharge (GCD) experiment at different current rates of 0.5, 1.0, 2.5, and 5.0 A g^{-1} . The discharge capacity values of the MWCNT sample were recorded at 1.5, 3.0, and 7.5 A g^{-1} current rates. Here, the

current rates are given, considering the total loading of the electrode material in the working electrode. The discharge capacity of the samples measured in three-electrode cell assembly are reported in the units of $\text{mAh g}^{-1}_{(\text{polymer})}$ and mAh g^{-1} . The $\text{mAh g}^{-1}_{(\text{polymer})}$ indicates that the capacity values are normalized exclusively by considering the loading of P(NDI2OD-T2) polymer in the working electrode (e.g., 0.6 mg for C-3; see **Section 3.7** for the polymer content in other samples). On the other hand, the unit of mAh g^{-1} represents the discharge capacity values normalized by considering the cumulative mass-loading of the working electrode, which includes the polymer, MWCNT, and PVDF binder (mass-loading of 1 mg for P-0, C-1, C-2, and C-3 electrodes). The cyclic voltammetry (CV) analyses were carried out at scan rates of 5, 10, 20, 50, and 100 mV s^{-1} .

The performance of symmetric and hybrid supercapacitor (HSC) devices was first analyzed in 1M LiClO_4/PC liquid electrolyte. Henceforth, HSC devices fabricated using the above-mentioned liquid electrolytes are termed as LS-HSC, where 'LS' stands for the liquid-state electrolyte. For the symmetric device, the electrochemical cell was prepared by dipping two electrodes coated with the C-3 sample (1.0 mg cm^{-2} loading) in 1M LiClO_4/PC electrolyte, and the device was marked as C-3||C-3. The device was characterized by CV analysis at a 50 mV s^{-1} scan rate within 0 to 1.4 V voltage window. The HSC was fabricated using carbon papers coated with C-3 and activated carbon (AC) as the negative and positive electrodes, respectively. The AC electrode was characterized by CV analysis at 50 mV s^{-1} scan rate in 1M LiClO_4/PC liquid electrolyte within the voltage range of -0.2 to 1.0 V vs. Ag/Ag^+ in the three-electrode configuration. To balance the loading to the two electrodes, the charge storage capacity of the AC sample was determined from the GCD analysis at 0.5 A g^{-1} current rate. The ratio of the positive and negative electrode loading was optimized to be 1.5:1 (calculation is given in Section 3.3). The CV data of the LS-HSC device was measured at the scan rates of 10, 20, 50, and 100 mV s^{-1} , and GCD data was recorded at current rates of 2.0, 1.0, 0.4, and 0.2 A g^{-1} within the voltage window of 0 to 2.4 V. Here, the current rates are normalized with respect to the total loading of both the positive and negative electrodes. Hence, the specific capacities are represented in the unit of $\text{mAh g}^{-1}_{(\text{total})}$, where 'total' represents the specific capacity normalized by considering the total mass-loading of the electrode material loaded at the positive and negative electrodes.

For fabricating the quasi-solid-state HSC (QSS-HSC) device, a polymer gel electrolyte made of LiClO_4/PC dissolved in polymethylmethacrylate polymer matrix (PMMA/ LiClO_4/PC)

was used, and the required amount of electrode materials (1 mg of C-3 and 1.5 mg of AC) were coated over 1 cm² area of Grafoil current collector. The CV data for the QSS-HSC device was analyzed at 50, 100, and 200 mV s⁻¹ scan rate and GCD data was recorded at current rates of 3.0, 2.0, 1.0, and 0.4 A g⁻¹. The application of the QSS-HSC device was demonstrated by lighting a red LED bulb.

3.2.6 BET Experimental Setup.

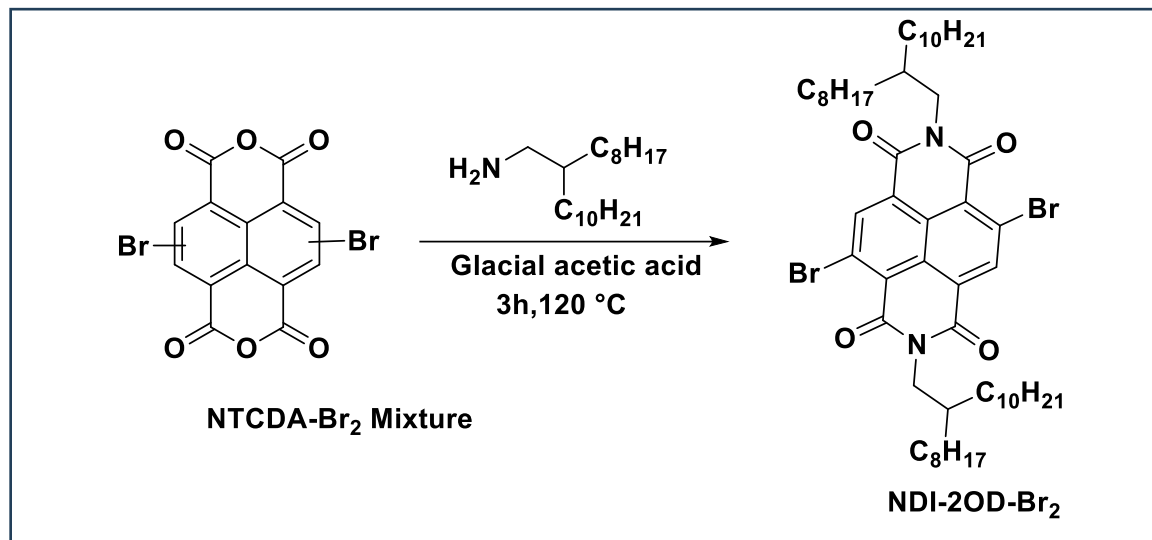
The pore size distribution and nitrogen adsorption/desorption isotherms of MWCNT, P-0, and C-3 composite polymer were measured at 77 K using Quantachrome Quadrasorb SI (automatic surface area and pore size analyzer). The surface area of the samples was determined according to the Brunauer-Emmett-Teller (BET) at 77 K bath temperature, and Nitrogen was used as the adsorption gas. The pore size distribution plots were calculated according to Density Functional Theory (DFT), with N₂ as a model at 77 K on carbon (slit pore, NLDFT equilibrium model).

3.3 Synthesis of Monomers

3.3.1 Synthesis of 2-octyldodecan-1-amine. 2-octyldodecan-1-amine was synthesized using the same procedure as given in last **Chapter 2.3.1**.

3.3.2 Synthesis of N, N'-Bis (2-octyldodecyl)-2,6-dibromo-1,4,5,8-naphthalenediimide (NDI-2OD-Br₂): Synthesis of NDI-2OD-Br₂ was done using the same procedure as reported in earlier literature from our group.⁴⁷ In a two-neck round bottom flask, 2,6-dibromo-1,4,5,8-naphthalenetetracarboxylic acid dianhydride (NTCDA-Br₂) (4.0 g, 9.389 mmol) was combined with 106 mL of glacial acetic acid under a nitrogen atmosphere. The mixture was stirred at 60-70°C for a brief period until a homogeneous dispersion was obtained, followed by the addition of 2-octyldodecylamine (11.17 g, 37.55 mmol). The reaction mixture was refluxed at 120°C until complete dissolution for a duration of 3 hours, following which it was allowed to cool to room temperature. The excess glacial acetic acid was evaporated and reaction mixture was concentrated under reduced pressure by rotary evaporator. Subsequently, the reaction mixture was washed with methanol, resulting in the formation of a reddish-brown powder. This powder was then filtered and dried under vacuum. The crude product underwent purification via column chromatography using a mixture of pet ether and ethyl acetate as eluent. Subsequently, re-crystallization from acetone was carried out to obtain a yellow powder of pure compound. Product was dried in vacuum oven at 60 °C. Yield: 1.97 g (21 %), ¹H NMR spectrum (400 MHz, CDCl₃) δ ppm: 8.93 (s, 2H, aromatic), 4.06-4.10 (d, 4H), 1.92 (m, 2H),

1.16, (m, 64 H), 0.80 (m, 12H). The ^{13}C NMR spectrum, recorded in 100 MHz CDCl_3 , displayed signals at δ ppm: 161.16, 161.01, 139.14, 128.35, 127.73, 125.28, 124.07, 45.44, 36.48, 31.87, 31.55, 30.01, 29.62, 29.61, 29.33, 26.32, 22.65 and 14.10. The MALDI-TOF analysis showed a molecular weight of (985.08) m/z : 985.736.



Scheme 3.1: Synthesis of NDI-2OD-Br₂.

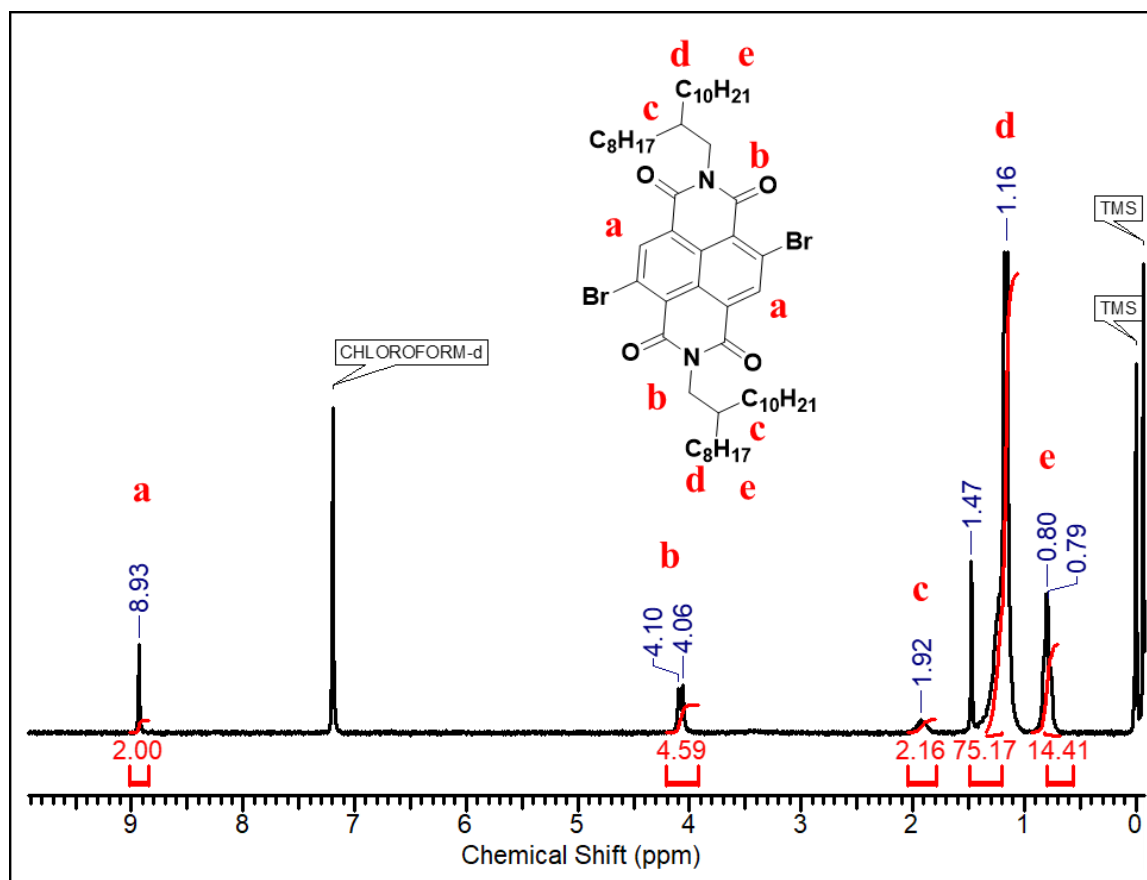


Figure 3.2 ^1H NMR spectra of monomer NDI-2OD-Br₂.

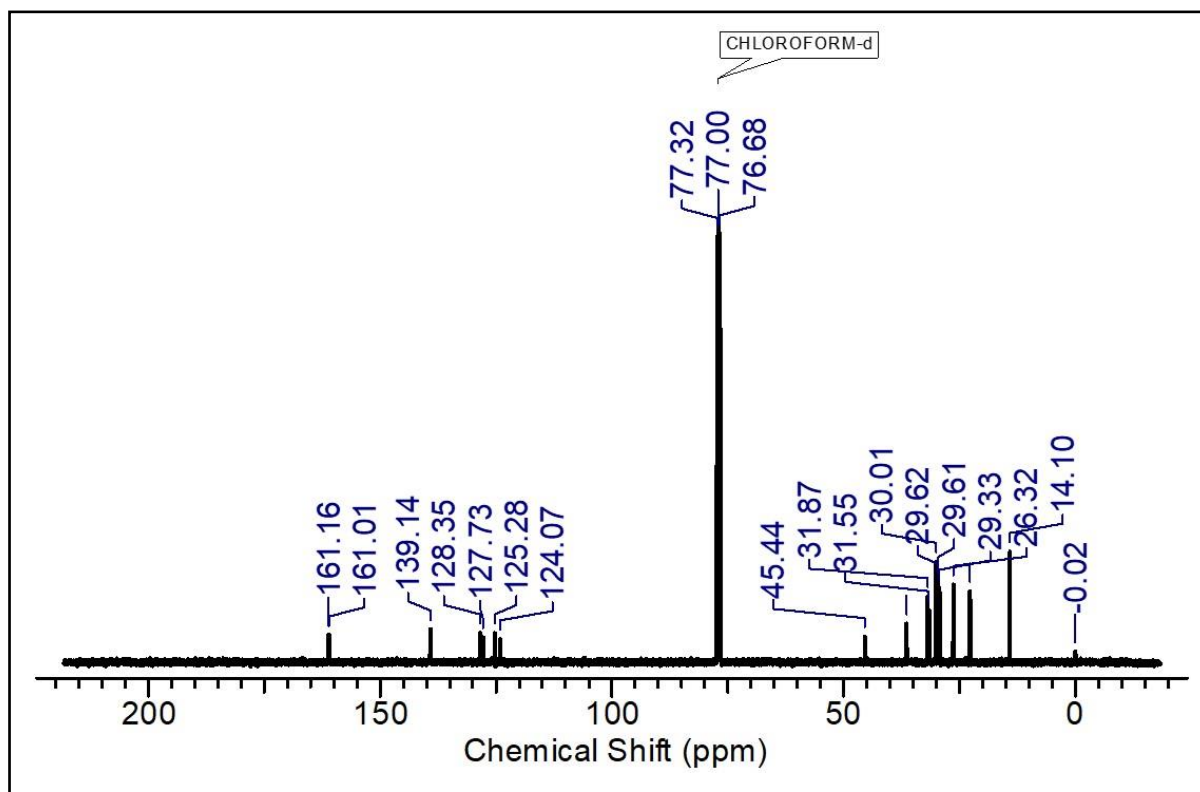


Figure 3.3 ¹³C NMR spectra of monomer NDI-2OD-Br₂.

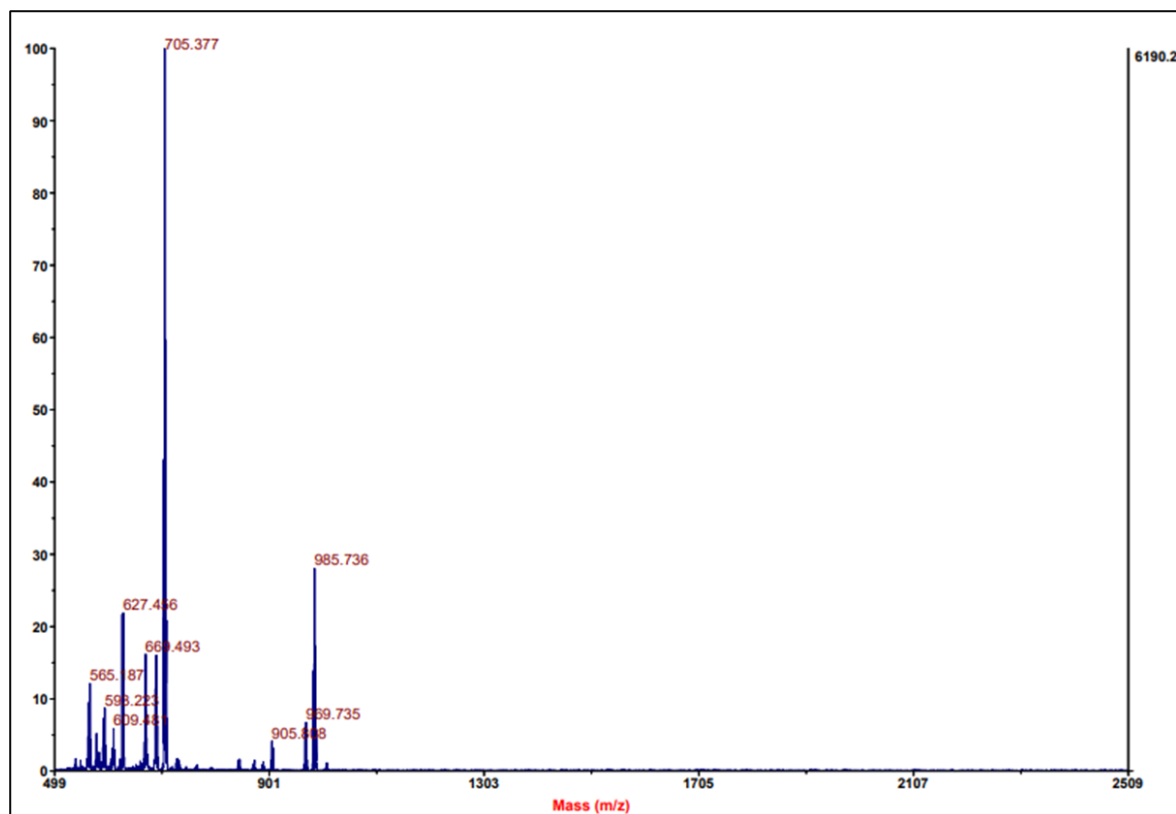


Figure 3.4 MALDI-TOF spectrum for NDI2OD-Br₂ monomer.

3.4 Synthesis of Polymers and their composites

3.4.1 Synthesis of P(NDI2OD-T2) (P-0). The monomer NDI-2OD-Br₂ was synthesized following the previous reports for the same from our group.⁴⁷ NDI-2OD-Br₂ (0.200 g, 0.203 mmol) and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (0.099 g, 0.203 mmol) were precisely weighed and placed into a dry Schlenk tube equipped with a magnetic stirring bar, and 10 ml of dry 4-ter-butyl toluene was added to it. This was followed by nitrogen purging for half an hour with constant stirring at room temperature. Bis(triphenylphosphine)palladium(II) dichloride (Pd(Ph₃)₂Cl₂) (5.84 mg, 0.005075 mmol) was added to the above solution under a nitrogen atmosphere and again kept for nitrogen purging for half an hour; Afterward, the Schlenk tube was transferred into a preheated oil bath at 160°C, and stirring was maintained for a duration of 2 hours. Following this, the mixture was cooled to ambient temperature and dissolved in chloroform and precipitated in methanol. The resulting precipitate was then filtered using a Büchner funnel. The polymer underwent purification through Soxhlet extraction in methanol for a period of 24 hours, followed by extraction in acetone. Subsequently, it was dried in a vacuum oven at 60°C. Yield (191 mg, 95 %). ¹H NMR spectrum (400 MHz, CDCl₃) δ ppm: 8.83–8.52 (br, 2H aromatic), 7.34 (br, 4H), 4.12 (br, 4H), 1.99 (br, 2H), 1.26 (br, 64H), 0.86 (br, 12 H). M_n: 188000, M_w: 59700, Đ_M: 3.18.

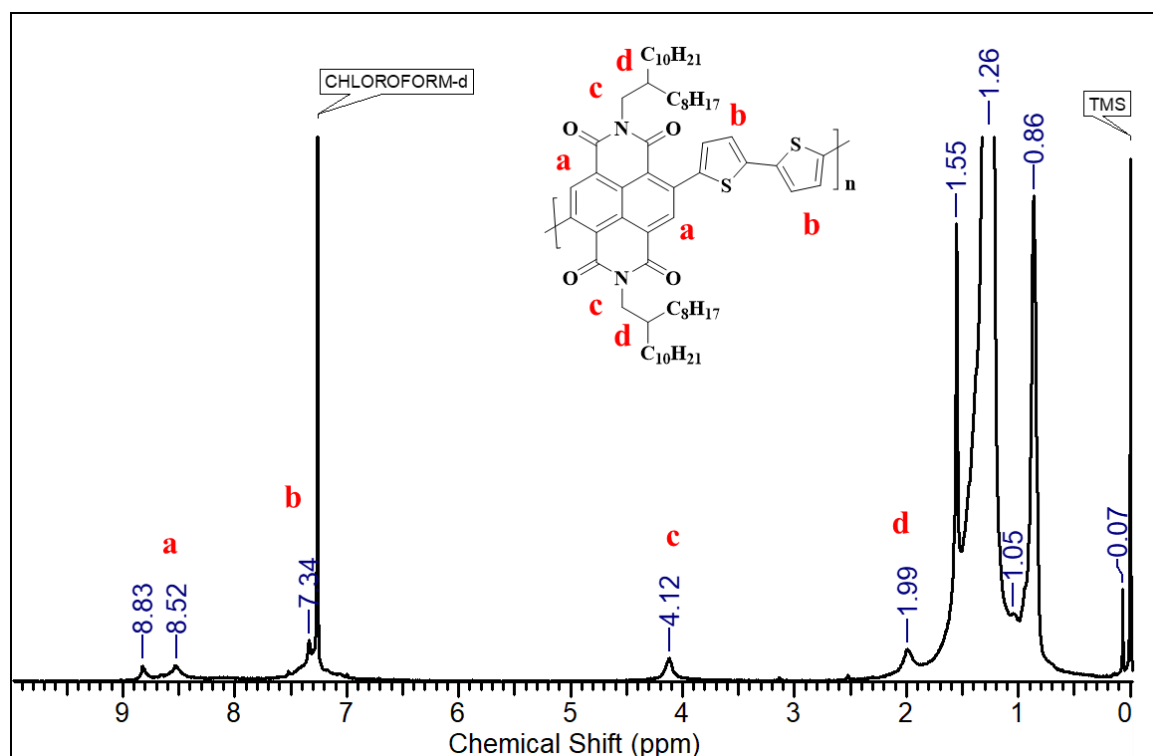


Figure 3.5 ¹H NMR spectrum of P(NDI2OD-T2) P-0/P-1/P-2 Polymer.

3.4.2 Synthesis of Polymer Composite C-X. The MWCNT and P(NDI2OD-T2) polymer composites (named as C-X) were synthesized using the same procedure as that for P(NDI2OD-T2), except for the addition of the required amount of MWCNT.

a) Synthesis of Polymer Composite C-1.

The same quantities of monomers, catalyst, and solvents were employed as detailed in **Section 3.4.1**. Additionally, 30 mg of MWCNTs were introduced into the Schlenk tube containing a stirring magnet. Subsequently, the procedures followed were identical to those described for the synthesis of P(PDI2OD-T2) (P-0) polymer in **Section 3.4.1**. After completion of reaction, cool it to room temperature and the polymer was directly precipitated in methanol (dissolution of the polymer in THF before precipitation into methanol was avoided to retain the MWCNT incorporated polymer network obtained during the *in-situ* polymerization) and filtered on a Büchner funnel. Yield (224 mg – 30 mg MWCNT = 194 mg, 96 %). ¹H NMR spectrum (400 MHz, CDCl₃) δ ppm: 8.84–8.55 (br, 2H aromatic), 7.36 (br, 4H), 4.15 (br, 4H), 2.0 (br, 2H), 1.29 (br, 64H), 0.89 (br, 12 H). M_n: 144000, M_w: 351000, Đ_M: 2.44.

b) Synthesis of Polymer Composite C-2. For the synthesis C-2 followed identical steps as mention in **Section 3.4.1(P-0)**, but used 60 mg MWCNT. Yield (253 mg – 60 mg MWCNTs = 193 mg, 96 %). ¹H NMR spectrum (400 MHz, CDCl₃) δ ppm: 8.84–8.55 (br, 2H aromatic), 7.36 (br, 4H), 4.15 (br, 4H), 2.0 (br, 2H), 1.29 (br, 64H), 0.89 (br, 12 H). M_n: 189000, M_w: 465000, Đ_M:2.46.

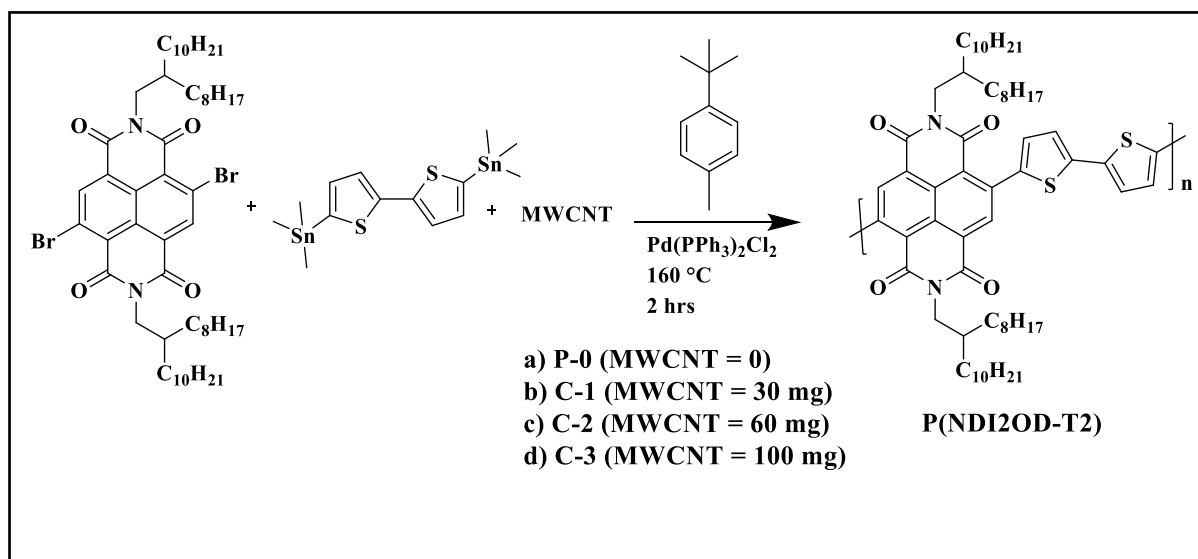
c) Synthesis of Polymer Composite C-3. Followed similar procedure as mentioned for P(PDI2OD-T2) (P-0) polymer (**Section 3.4.1**), but using 100 mg MWCNT. Yield (289 mg – 100 mg MWCNTs = 189 mg, 94.0 %). ¹H NMR spectrum (400 MHz, CDCl₃) δ ppm: 8.84–8.55 (br, 2H aromatic), 7.36 (br, 4H), 4.15 (br, 4H), 2.0 (br, 2H), 1.29 (br, 64H), 0.89 (br, 12 H). M_n: 123000, M_w: 320000, Đ_M: 2.60.

d) Ex-C-30 Polymer Composite. For the purpose of comparison, an externally mixed MWCNT polymer composite was also prepared by mixing 30 mg of MWCNT with P(NDI2OD-T2) polymer, and the composite was marked as Ex C-30, where the 'Ex' indicates externally mixed.

3.5 Results and Discussion

3.5.1 Synthesis and characterization

NDI-2OD-Br₂ was synthesized using a previously reported procedure in the literature.⁴⁷⁻⁴⁹ The synthetic scheme and characterization of NDI-2OD-Br₂ are given in 3.2.7, **Scheme 3.1** and **Figure 3.2-3.4**. **Scheme 3.2** illustrates the synthesis of P(NDI2OD-T2) and its composites with MWCNT following the *in-situ* strategy.



Scheme 3.2: Synthetic scheme for P(NDI2OD-T2) (P-0) polymer and its composites with MWCNT (C-X).

The reported procedure for synthesizing P(NDI2OD-T2) polymer typically requires long reaction time (around 3 days).^{3,47-49} Here, we have followed the similar polymerization conditions as reported in chapter 2 and successfully synthesized P(NDI2OD-T2) polymer within a 2 hours of reaction time. In this chapter, the pristine polymer P(NDI2OD-T2) synthesized by this modified procedure is referred to as P-0. The composites of P(NDI2OD-T2) with MWCNT were synthesized *via in-situ* polymerization by taking varying amounts of MWCNT along with the reactants at the start of the polymerization. These composites were named as C-X, where x = 1, 2, and 3 represented the three composites with increasing MWCNT content in the feed. The polymers were directly precipitated into methanol (instead of the traditional method of dissolving in THF and precipitating into methanol and repeating this a couple of times) to avoid loss of the incorporated MWCNT. The probable weight percentage incorporation of MWCNT in the three composites was calculated by dividing the feed weight of the MWCNT with the final total yield obtained after drying the precipitate from methanol. Thus, the weight percent incorporation of MWCNT was calculated to be 13.4 %, 23.7 %, and 34.6 % for C-1, C-2, and C-3, respectively.

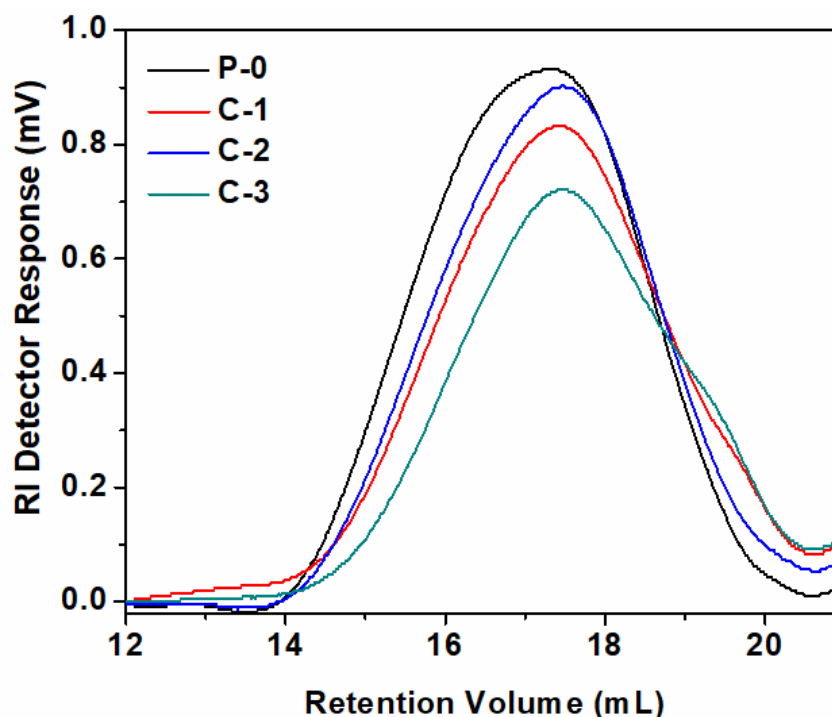


Figure 3.6 Gel permeation chromatogram (GPC) of P(NDI2OD-T2) and their composites.

Table 3.1 Molecular weight and thermal characterization of the P(NDI2OD-T2) polymer (P-0) and C-X composites.

Sr. No	Polymer	M_n^a (Kg mol ⁻¹)	M_w^a (Kg mol ⁻¹)	$\bar{D}_M^b$	% Yield	% weight of MWCNT in feed ^c	% weight of MWCNT from TGA	% weight of MWCNT from absorption spectroscopy ^d
1.	P-0	188	597	3.18	95	0	0	0
2.	C-1	144	351	2.44	96	13.4	13.91	16.0
3.	C-2	189	465	2.46	95	23.7	24.06	27.3
4.	C-3	123	320	2.60	92	34.6	35.08	38.8

(^a M_n and M_w are number average and weight average molecular weights, respectively determined by GPC using THF as the eluent and PS as standards; ^b $\bar{D}_M$ is the dispersity of the polymers; ^c determined with respect to the obtained total yield; ^d determined by dissolving 1.0 mg of the composite polymer in 50 ml chloroform.)

The structural characterization of the polymers was conducted using proton NMR spectroscopy, as depicted in **Figure 3.5**. The determination of molecular weight was carried out utilizing GPC (gel permeation chromatography) in THF. Prior to analysis, the samples were filtered using filter paper and subsequently passed through polytetrafluoroethylene (PTFE) filters to eliminate the MWCNT. The composite polymers exhibited good solubility in tetrahydrofuran (THF) and chloroform; they were sparingly soluble in dichloromethane (DCM) and chlorobenzene and insoluble in Dimethylformamide (DMF). In all the solvents, the MWCNT remained insoluble. The molecular weight data is given in **Table 3.1**. The polymers exhibited high molecular weights with M_n ranging from 123000 to 189000 g/mol and M_w in the range of 320000 to 597000 g/mol and GPC graphs are shown in **Figure 3.6**.

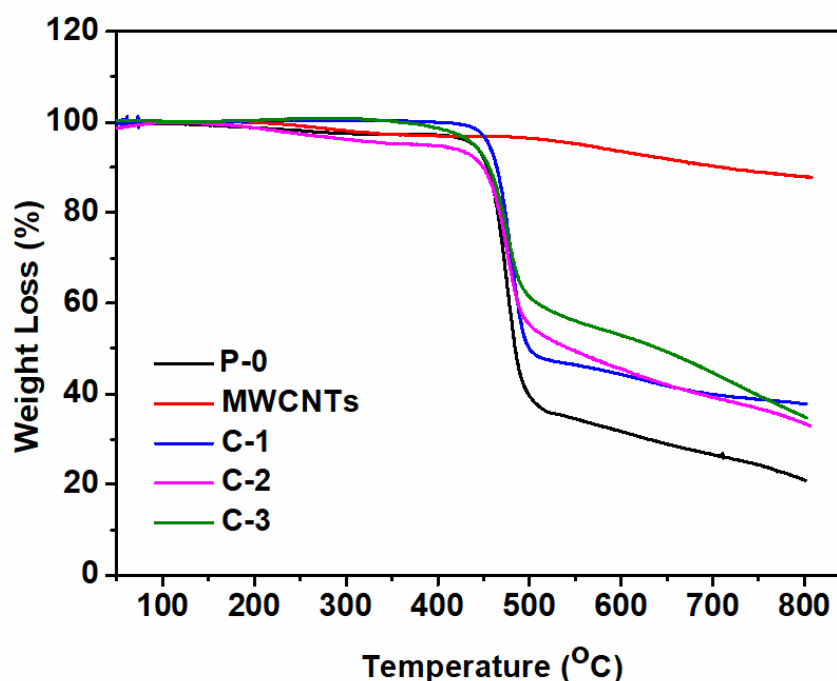


Figure 3.7 Thermogravimetric analysis data of P-0, MWCNT, and the C-X samples taken in the temperature range of 40 to 800 °C at a heating rate of 10 °C/min under nitrogen.

Thermal characterization of both the polymer and composites was conducted through thermogravimetric analysis (TGA) under a nitrogen atmosphere. The TGA plots for the P-0 and C-X samples along with that of pristine MWCNT shown in **Figure 3.7**. The polymers displayed commendable thermal stability, with an onset decomposition temperature (T_d) exceeding 450°C. The TGA curves were also used to determine the incorporation of MWCNT in each of the polymer composites using the formula given below.⁵⁰

% of MWCNT incorporated

$$= \% \text{ remaining pristine MWCNT} - \left(\frac{\% \text{ loss of composite}}{\% \text{ loss of Pure polymer}} \times 100 \right)$$

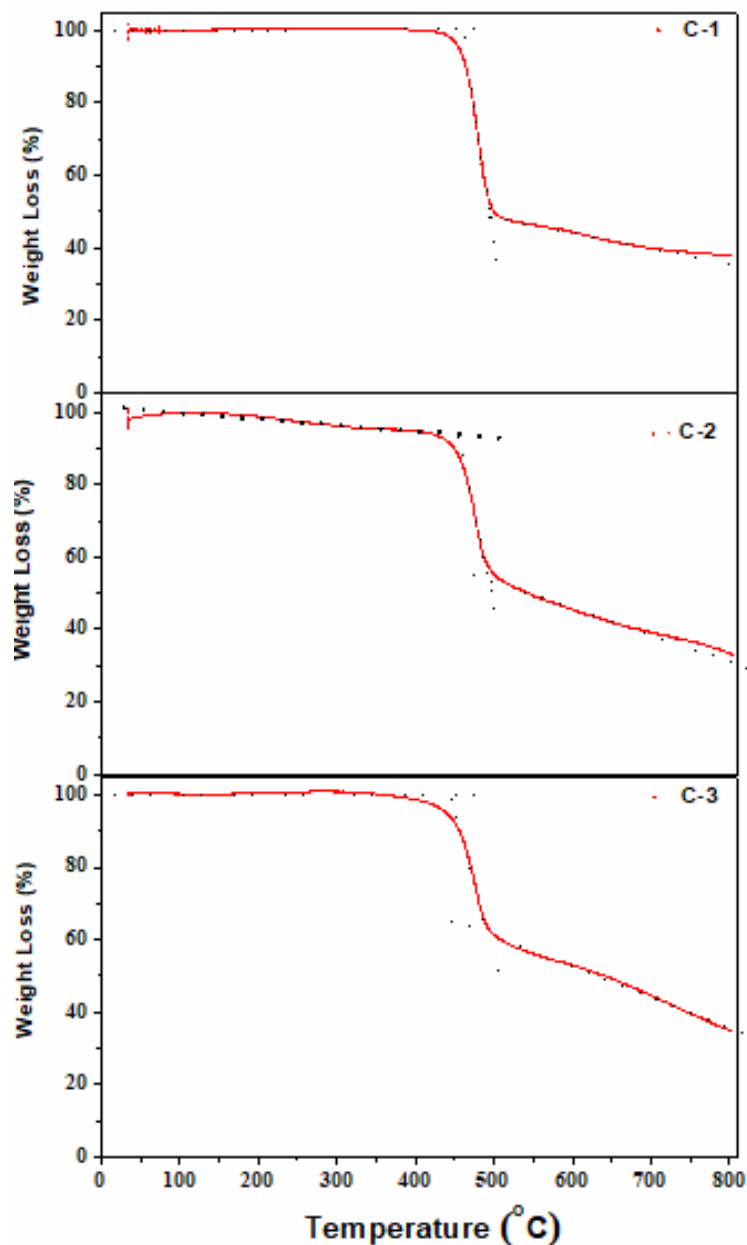


Figure 3.8 TGA curves of the polymer composites.

The mass loss was determined as the vertical distance between the two tangential lines drawn on the mass loss curve, as illustrated in **Figure 3.8**.⁵¹ The % remaining for pristine MWCNT was 96.44, and the % loss of pure polymer (P-0) was 62.43. The percentage of MWCNT incorporation in the three composites C-1, C-2, and C-3 was determined to be 13.91, 24.06, and 34.81 %, respectively. Quantification of the polymer (and thereby MWCNT) was also

estimated using absorption spectroscopy. The absorption spectra of the pristine polymer P-0 and the composite polymers C-X recorded in chloroform and shown in **Figure 3.10**. P-0 shows two absorption bands in the spectra corresponding to the π - π^* transition (300 nm to 450 nm) and the intramolecular charge transfer (ICT) band between 500 and 800 nm.⁴⁹ The molar extinction coefficient (ϵ) of P-0 was estimated to be $35954 \text{ L M}^{-1}\text{cm}^{-1}$ using the Beer-Lambert Law (**Figure 3.9**). Applying this value of ϵ , the concentration of polymer in the composites C-X was calculated as detailed in 3.5.2. The % MWCNT estimated from the absorption spectra is tabulated in **Table 3.1**. Compared to the % incorporation of MWCNT obtained from TGA analysis, these values obtained from the absorption spectra are on the higher side for all the C-X samples. One reason for this variation could be the scattering of incident light due to the presence of the MWCNT observed in the composites compared to the P-0 sample.

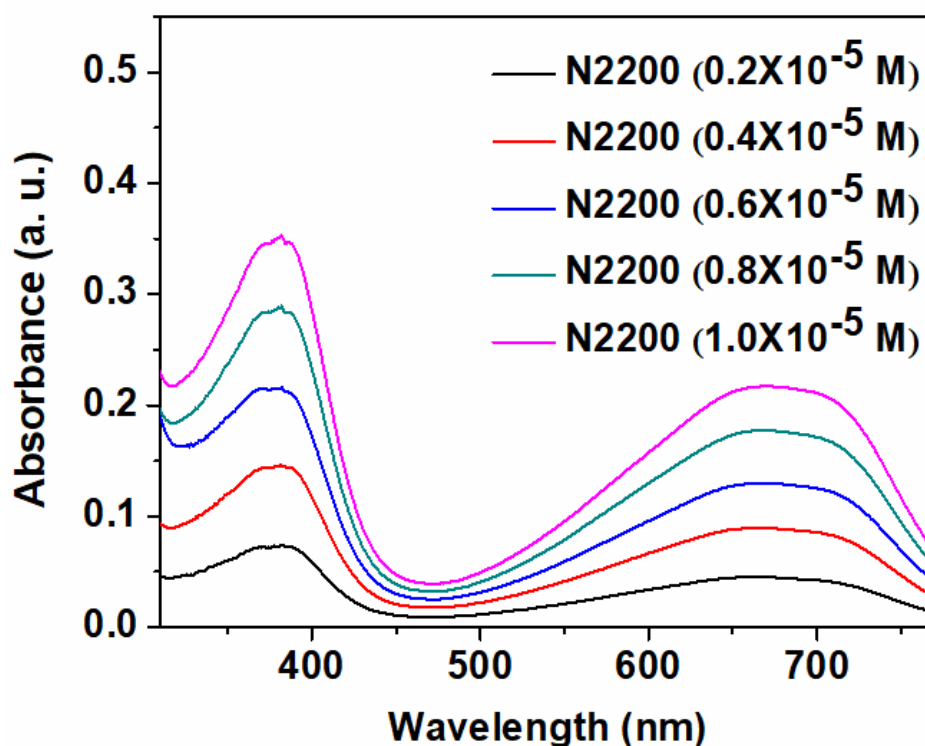


Figure 3.9 UV-vis absorption spectra for P(NDI2OD-T2).

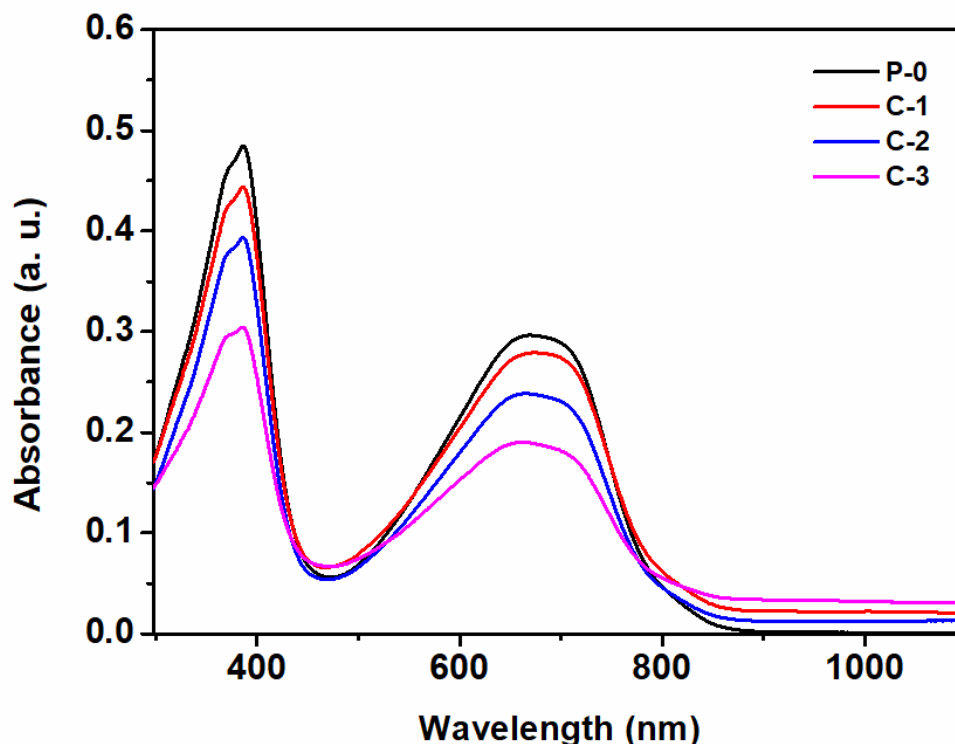


Figure 3.10 UV-Vis Absorption spectra of P-0, C-1, C-2, and C-3 polymers recorded in chloroform at a concentration of 1 mg 50 ml⁻¹.

3.5.2 Calculation for quantification of the MWCNT and polymer using absorption spectroscopy.

Calculation of molar absorptivity coefficient for P(NDI2OD-T2) polymer and concentration of polymer in the composites C-X using molar absorptivity coefficient.

Molar absorptivity coefficient was calculated at 383 nm by using Lambert-Beers law, $A = \epsilon cl$

Where, A= Absorbance, C= concentration g/mole, l= path length, $\epsilon = 35954 \text{ L M}^{-1}\text{cm}^{-1}$.

The calculation for obtaining the concentration of polymer in the composites is shown below.

P-0 $C = A/\epsilon$ $A = 0.7826$; $C = 0.7826/35954 = 2.1767 \times 10^{-5} \text{ M}$

1 M = 988 gm of Polymer (repeating unit mass) = $2.1767 \times 10^{-5} \times 988 = 0.02151 \text{ gm}$, for 1000 ml solution.

As 1 mg polymer was dissolved in 50 ml of chloroform: $(0.02151 \times 50) / 1000 = 1.075 \times 10^{-3} \text{ g} = 1 \text{ mg}$

C-1 $A = 0.6086$;

$$C = 0.6086/35954 = 1.6927 \times 10^{-5} \text{ M} = 1.6927 \times 10^{-5} \times 988 = 0.01672 \text{ gm.}$$

$$\text{In 50 ml: } (0.01679 \times 50) / 1000 = 8.362 \times 10^{-4} \text{ g} = 0.836 \text{ mg}$$

$$\text{Amount of CNT} = 1\text{mg} - 0.839 \text{ mg polymer} = 0.16 \text{ mg CNT}$$

C-2 $A = 0.5292$;

$$C = 0.5292/35954 = 1.4719 \times 10^{-5} \text{ M} = 1.4719 \times 10^{-5} \times 988 = 0.01454 \text{ gm.}$$

$$\text{In 50 ml: } (0.01454 \times 50) / 1000 = 0.727 \text{ mg}$$

$$\text{Amount of CNT} = 1\text{mg} - 0.727 \text{ mg polymer} = 0.273 \text{ mg CNT}$$

C-3 $A = 0.4453$;

$$C = 0.4453/35954 = 1.2385 \times 10^{-5} \text{ M} = 1.2385 \times 10^{-5} \times 988 = 0.012236 \text{ gm.}$$

$$\text{In 50 ml: } (0.012236 \times 50) / 1000 = 0.6118 \text{ mg}$$

$$\text{Amount of CNT} = 1\text{mg} - 0.6118 \text{ mg polymer} = 0.388 \text{ mg CNT.}$$

3.5.3 Morphology.

The morphology of all the samples under study was characterized by FE-SEM and TEM analysis. As shown in **Figure 3.11**, the FE-SEM image of P-0 (**Figure 3.11a**) exhibits ribbon-like structures of polymer, whereas the MWCNT (**Figure 3.11b**) possesses an entangled tubular network structure. **Figure 3.11c-e** compares the morphology of the composite polymers with increasing loading of MWCNT. The uniform growth of the polymer layer over the *in-situ* incorporated MWCNT can be evidenced from the FESEM images. The entangled porous network of the pristine MWCNT is also retained in all the polymer composites, and no bulk or agglomerated growth of polymer is observed, indicating the maximum contact of the polymer layer with the carbon support. However, compared to C-1 (**Figure 3.11c**), the morphology of the C-2 (**Figure 3.11d**) and C-3 (**Figure 3.11e**) samples appear to be more porous, which suggests that a higher percentage of MWCNT results in better dispersion of the polymer during the course of the polymerization reaction.

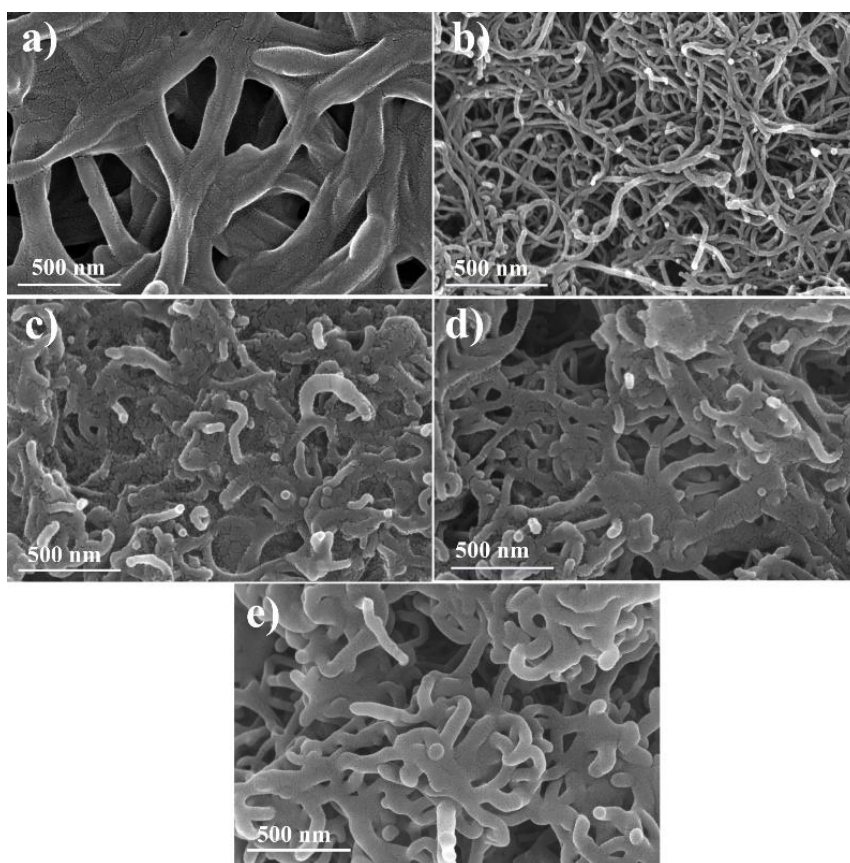


Figure 3.11 FE-SEM images of (a) pristine P-0, (b) neat MWCNTs, (c) C-1, (d) C-2 and (e) C-3.

The samples were further characterized by TEM. **Figure 3.12** shows the ribbon-like morphology of the polymer, as observed in the FE-SEM image (**Figure 3.11**). The tubular structure of MWCNT with an average diameter of 8-15 nm is shown in **Figure 3.12b**. The TEM images of the composite polymers (**Figure 3.12c-e**) further confirm the uniform dispersion of the polymer over the carbon nanotubes. An overall increase in the average diameter of the tubular structure to 30 - 50 nm is clearly observed (in contrast to the 8- 15 nm for the pristine MWCNT), which further confirms the uniform growth of the polymer along the MWCNT in the C-X samples. In order to bring out the contrast between the *in-situ* MWCNT incorporation versus the physical mixing of MWCNT to the polymer, carbon nanotube was externally mixed with the polymer. A 30 wt% of MWCNT in P-0 (Ex C-30) was prepared by dispersing them together in methanol and drop-casting on a silicon wafer or TEM grid for FE-SEM and TEM imaging, respectively.

The agglomerated deposition of the polymer on the MWCNT is clearly visible in the FE-SEM image (**Figure 3.13**) of the Ex C-30 composite. The TEM image in **Figure 3.13** shows that the

polymer is spread over the MWCNT network as a layer. Such inhomogeneous distribution and undesired agglomeration were absent in the polymer composite samples prepared by the *in-situ* process. The microscopy images prove the effectiveness of the *in-situ* mixing of MWCNT with the monomers prior to polymerization. The uniform distribution of the polymer chains on the MWCNT network is expected to enhance the electrochemical performance of the C-X composites compared to the pristine polymer and physically mixed polymer/MWCNT composite.

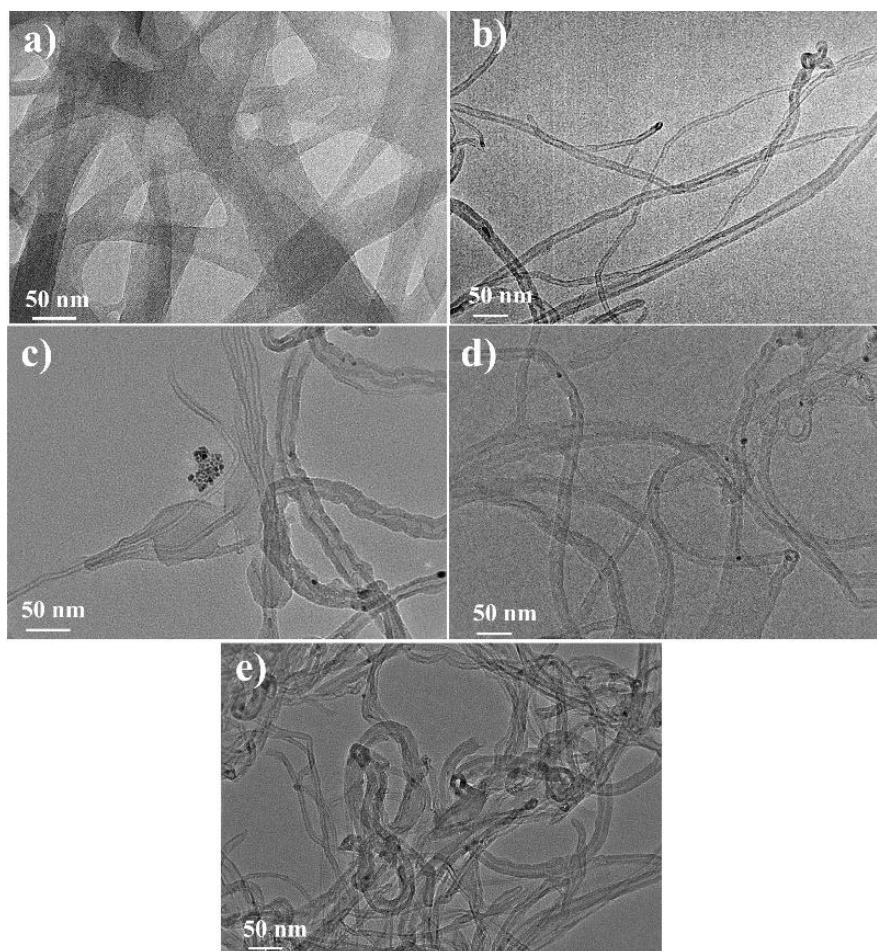


Figure 3.12 TEM images of (a) pristine P-0, (b) neat MWCNT, (c) C-1, (d) C-2 and (e) C-3.

3.5.4 Surface Area and Pore Size.

Nitrogen adsorption/desorption measurements at 77 K were conducted to assess the surface area and porosity characteristics of the MWCNT, P-0, and C-3 composite. **Figure 3.14** illustrates the nitrogen adsorption/desorption isotherms (**Figure 3.14a-c**) and pore size distribution (**Figure 3.14d-f**) of P-0, MWCNT, and C-3 composite polymer. Both MWCNT and C-3 composite exhibit a characteristic Type III isotherm (**Figure 3.14a-c**). The specific

surface area values, calculated using the Brunauer-Emmett-Teller (BET) model, were determined as follows: MWCNT ($200.7 \text{ m}^2 \text{ g}^{-1}$), P-0 ($81.1 \text{ m}^2 \text{ g}^{-1}$), and C-3 ($224.8 \text{ m}^2 \text{ g}^{-1}$). These BET data indicate that the in-situ incorporation of MWCNT enhances the surface area of the C-3 composite compared to the pristine polymer, corroborating with the FESEM data of the respective samples.

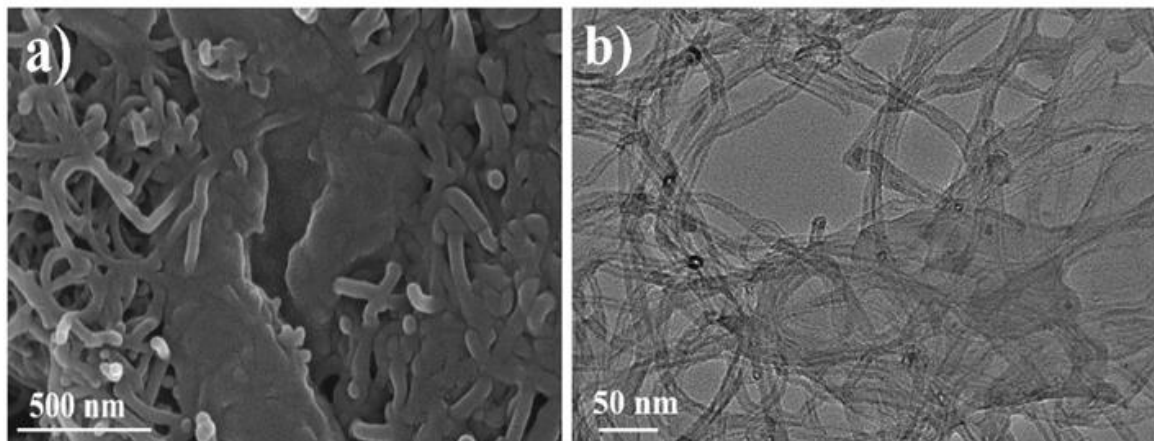


Figure 3.13 FE-SEM (a) and TEM (b) images of Ex C-30 sample.

The pore size distribution profiles for the P-0 (**Figure 3.14d**), MWCNT (**Figure 3.14e**) and C-3 (**Figure 3.14f**) show that MWCNT exhibits both microporous as well as mesoporous nature with more percentage of the latter. The pore size distribution of the pristine polymer is mostly in the microporous domain. On the other hand, in the composite (C-3), the pores are distributed in both microporous and mesoporous regimes. The average pore diameter of MWCNT was $\sim 12 \text{ nm}$, while that for the polymers was in the range of $\sim 3 \text{ nm}$, as calculated using Density Functional Theory (DFT) desorption model. **Figure 3.14f** shows that with the inclusion of MWCNT, the number of pores in the mesoporous region increases compared to the P-0 sample (**Figure 3.14d**). The difference between C-3 composite and P-0 polymer originates from the morphological contrast between them. As evidenced in the FE-SEM and TEM analysis, in C-3, the polymer layer is grown in a thin and homogeneous manner over the MWCNTs without blocking the void space created by the entangled MWCNTs. As a consequence, the porous architecture of MWCNT containing both micropores and mesopores is retained in the C-3 composite. It is anticipated that such a mesoporous framework could facilitate the electrolyte's infiltration when the sample is employed as the electrode material in EESDs.

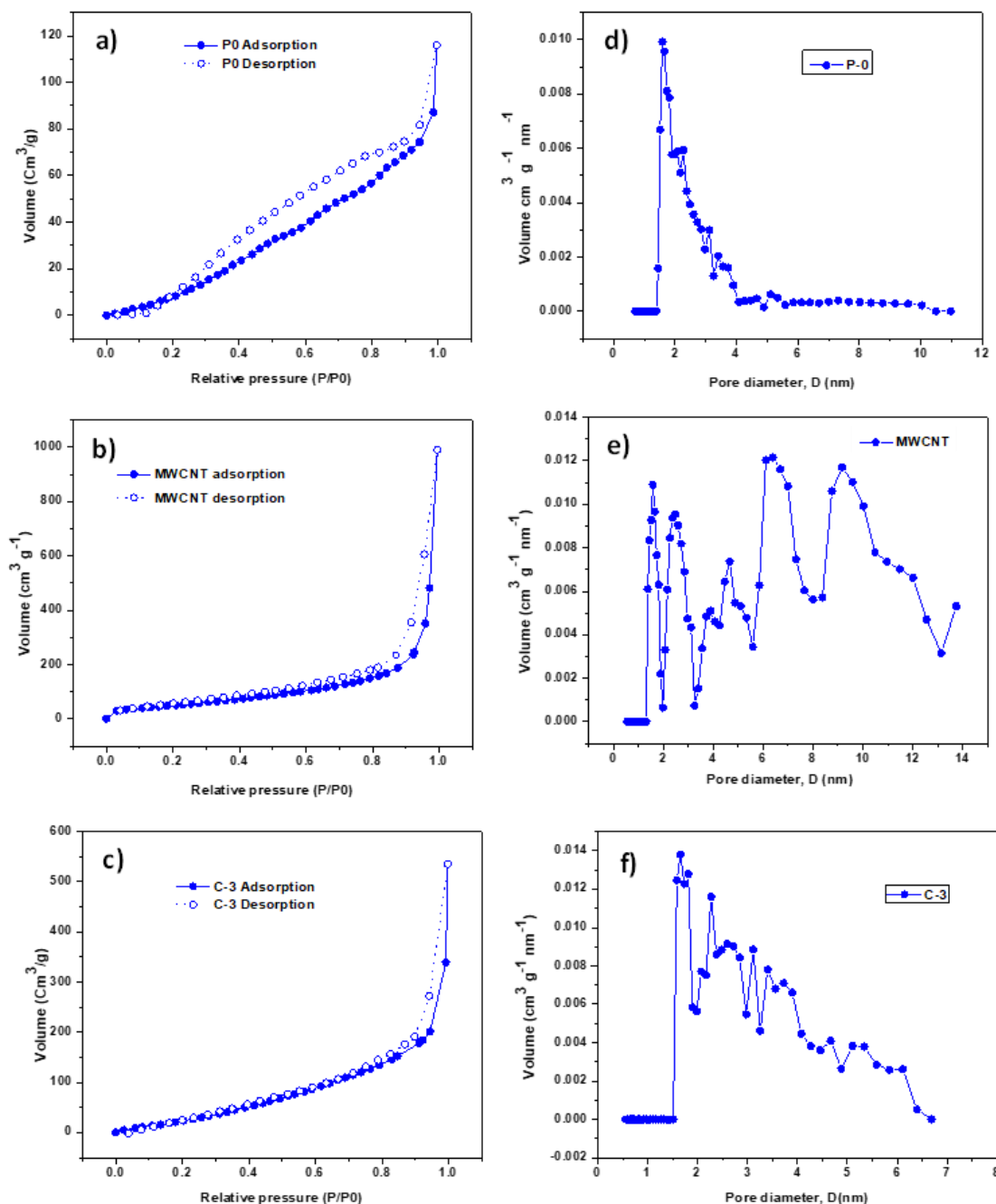


Figure 3.14 Nitrogen adsorption/desorption isotherm of a) P-0, b) MWCNT c) C-3, and Pore size distribution profile for d) P-0, e) MWCNT f) C-3 samples.

3.6 Electrochemical Characterization.

The electrochemical performance of all the samples was investigated by cyclic voltammetry (CV) analyses carried out in a three-electrode cell in 1M LiClO_4/PC electrolyte.¹⁷ **Figure 3.16a** compares the CV profiles for the P-0, C-X, and Ex C-30 samples recorded at a scan rate of 10 mV s^{-1} . The CV profiles show the prominent redox peaks during the cathodic and anodic scan

in all the cases. Compared to P-0, all the samples exhibit high current signifying the augmented charge storage capacity of the polymer composites with MWCNT. However, the enhancement in the current response (and redox behavior) is much more prominent in the C-X samples than in the Ex C-30 sample. The CV plots of MWCNT in **Figure 3.15** display nearly rectangular feature which is associated with the electric double-layer capacitor (EDLC). Furthermore, the current response observed in the CV plots of MWCNT is significantly low compared to that of the C-X samples. The EDLC behavior of MWCNT confirms that the MWCNT does not take part in the redox reactions; instead, the presence of MWCNT in the polymer composites eases the transport of the electrons by providing a conducting network. Therefore, it is reasonable to say that the observed enhancement in the faradaic current of the composite samples originates exclusively from the intrinsic redox activity of the P(NDI2OD-T2) polymer.

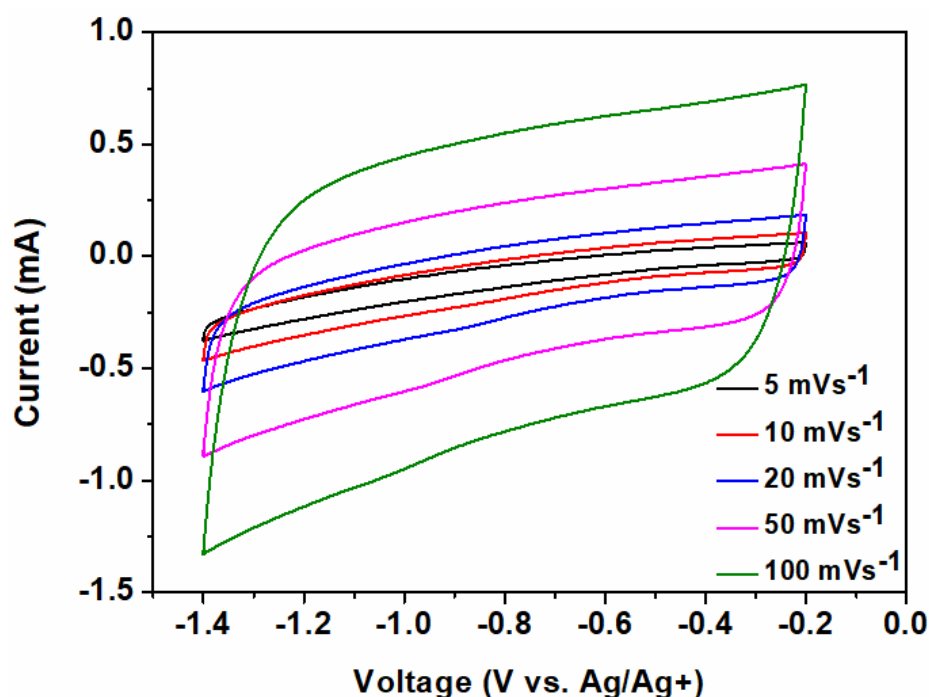


Figure 3.15 CV profiles of MWCNT recorded at various scan rates.

The position of the redox peaks ($-0.9/-1.2$ V and $-0.65/-1.04$ V vs. Ag/Ag^+) was found to be more or less similar in all the composites (**Figure 3.16a**), implying that the mode of MWCNT incorporation does not affect the redox property of the samples. However, compared to the physical mixing, the inclusion of MWCNT following the *in-situ* strategy allows more number of redox-active centers being exposed for participating in the faradaic reactions and enhances the redox activity of the polymer in C-X composites. To validate this, electrochemical impedance spectroscopy (EIS) analyses of the samples were carried out. **Figure 3.16b**

compares the Nyquist plots corresponding to the C-3 and Ex C-30 samples (Nyquist plots for the other samples are given in **Figure 3.17**). The equivalent series resistance (ESR) of the C-3 sample was found to be $47\ \Omega$, which is comparable to all the other samples under study. Interestingly, despite the similar ESR value, the Nyquist plot for the Ex C-30 sample exhibits a small semicircle at a higher frequency region, signifying the charge transfer resistance (R_{ct}) at the electrode|electrolyte interface, which is not noticed in the case of the other samples. This observation suggests that MWCNT present in C-X composites could facilitate the electron transfer more effectively than in Ex C-30, revealing the advantage of the *in-situ* strategy for the inclusion of MWCNT into the P(NDI2OD-T2) polymer.

Figure 3.16c compares the discharge capacity of all the samples evaluated from the galvanostatic charge-discharge (GCD) experiment at the current rate of $0.50\ \text{A g}^{-1}$. It can be noticed that the discharge curves of the polymer composites appear with apparent voltage plateau, consistent with the distinct reduction peak observed in the respective voltammogram profiles. Hence, the nature of the CV and galvanostatic discharge profiles of the polymer composites points out the battery-type behavior of the materials; therefore, in this work, the performance of the composite materials is quantified in terms of capacity rather than capacitance.^{52,53} On the other hand, MWCNT exhibits a linear voltage response during the GCD process (**Figure 3.19a**), which is the characteristic of capacitor-like charge storage behavior, and the corresponding electrochemical performance is quantified as capacitance.

As evident in **Figure 3.16c**, the average discharge capacities obtained for the C-X samples are considerably higher than the P-0 and Ex C-30 samples, which is in line with their CV data (**Figure 3.16a**). The specific capacities obtained for P-0 and Ex C-30 samples are 2 and 20 $\text{mAh g}^{-1}_{(\text{polymer})}$, respectively, at the current rate of $0.50\ \text{A g}^{-1}$. The reason behind the incredibly low capacity of the P-0 sample is that the sample does not contain any conducting additives. Therefore, the active centers could not participate in the Faradaic processes due to the lack of facile transport of electrons throughout the electrode. This indicates the necessity of conducting additives in the electrode to achieve the desired electrochemical performance. The C-3 sample delivers a discharge capacity of $80\ \text{mAh g}^{-1}_{(\text{polymer})}$, which is the highest among all the C-X samples (54 and $74\ \text{mAh g}^{-1}_{(\text{polymer})}$ for C-1 and C-2, respectively). It must be noted that the capacity values given in **Figure 3.16c** are normalized with respect to the loading of active material (*i.e.*, P(NDI2OD-T2)) in the working electrode owing to the negligible contribution from the MWCNT additive (**Figure 3.19a**) to the total capacity of the composite electrode.

Moreover, the capacity values considering the total loading of the electrodes (**Figure 3.19b**) also highlight the superior performance of the polymer composites prepared using the *in-situ* method. Additionally, the discharge performance of the C-X composites is found to improve at higher content of MWCNT.

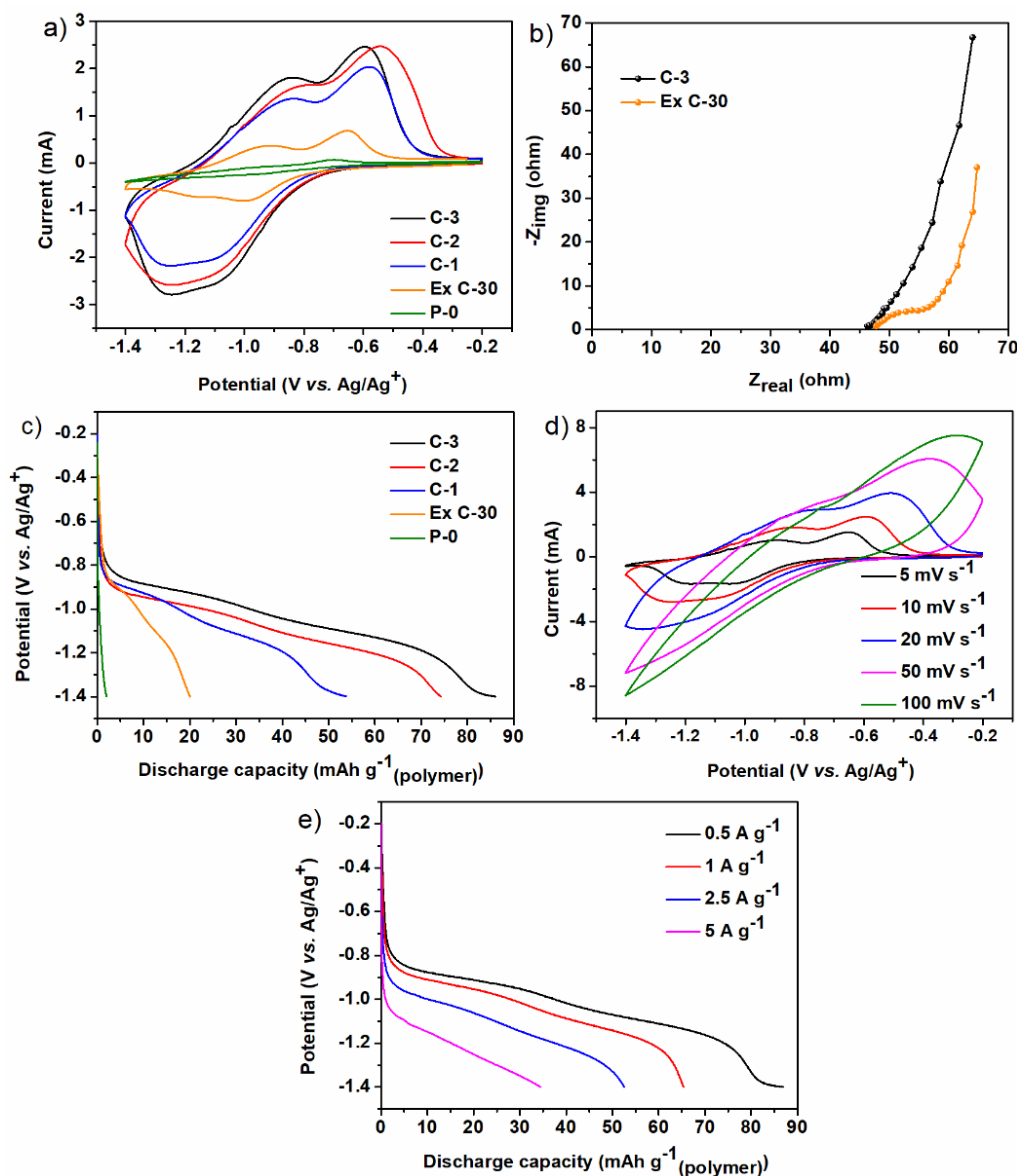


Figure 3.16 (a) CV profiles for the P-0, C-1, C-2, C-3, and Ex C-30 samples recorded at 10 mV s⁻¹ scan rate; (b) Nyquist plots recorded for the C-3 and Ex C-30 samples; (c) discharge profiles for the P-0, C-1, C-2, C-3, and Ex C-30 samples plotted at a current rate of 0.5 A g⁻¹; (d) CV data of the C-3 sample recorded at different scan rates, and (e) discharge profiles plotted at different current rates for the C-3 sample, respectively.

The C-X samples' improved capacity values could be attributed to their porous morphology with a uniform coating of the polymer layer over the MWCNT network, as observed in the FE-SEM and TEM images (**Figure 3.11c-e** and **Figure 3.12c-e**). As a result, the exposed redox-active moieties could readily access the electrons traveling through the MWCNT network. Moreover, the porous architecture and improved surface area favor the electrolyte infiltration into the bulk of electrode material and facilitates the diffusion of the electrolyte ions. Therefore, the short diffusion path for the electrons and electrolyte ions offers maximum participation of the redox-active centers during the charge/discharge process. On the other hand, in the case of the Ex C-30 sample, the inhomogeneous distribution of the agglomerated polymer layer over the MWCNT network (**Figure 3.13a** and **b**) blocks the transport of the charge carriers. Therefore, only a fraction of the redox-active centers could participate in the electrochemical reactions as reflected in the low discharge capacity (**Figure 3.16c**) and high R_{ct} value (**Figure 3.16b**) of the Ex C-30 sample.

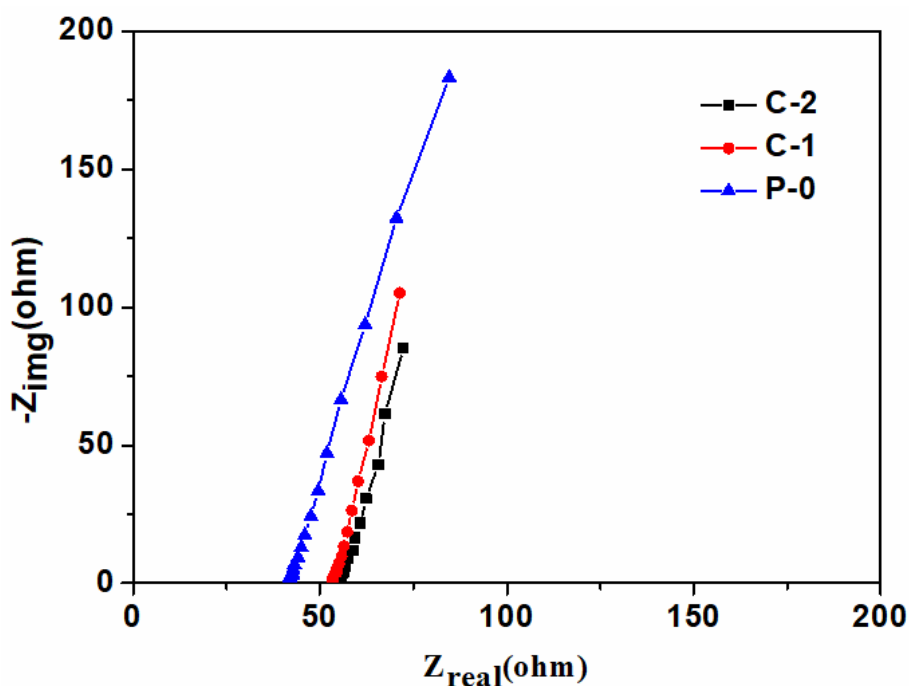


Figure 3.17 Nyquist plots recorded for the P-0, C-1, and C-2 samples.

The CV data recorded at various scan rates for the C-3 sample is given in **Figure 3.16d** (the similar plots for the other samples are summarized in **Figure 3.18a-d**). **Figure 3.16d** shows that peak current during the anodic and cathodic scan gradually increases with an increase in the scan rate from 5 mV s^{-1} to 50 mV s^{-1} . However, at a higher scan rate ($> 50 \text{ mV s}^{-1}$), the shape of the CV curve shows significant deviation, and the prominent redox peaks are

found to disappear. This could be due to the low ionic conductivity of the organic electrolyte, which impedes the access of electrolyte ions to the redox centers of the electrode material at a higher scan rate. The discharge profiles for the polymer composites at different current rates are also recorded. As shown in **Figure 3.16e**, the C-3 sample exhibits 40 % retention of capacity when the current rate increases from 0.50 A g^{-1} to 5 A g^{-1} . The discharge profiles at different current rates for the other samples are given in **Figure 3.19c-f**.

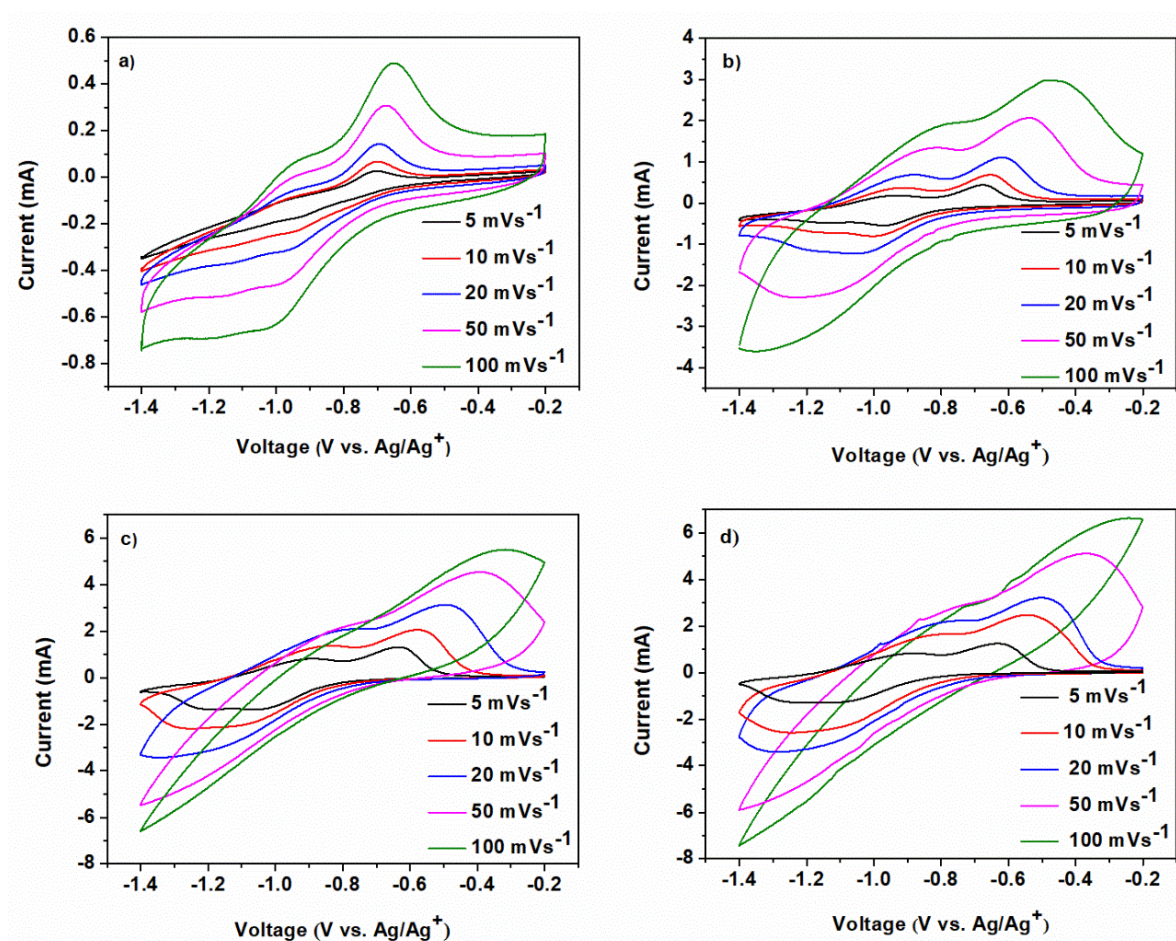


Figure 3.18 CV profiles recorded at various scan rates for the (a) P-0, (b) Ex C-30, (c) C-1, and (d) C-2 samples.

Followed by electrochemical characterization in the three-electrode configuration, polymer composite C-3 was taken forward to demonstrate its performance in the real device. At first, a device in symmetric configuration (C-3||C-3) was fabricated in 1M LiClO₄/PC electrolyte using two electrodes coated with C-3 composite materials. Surprisingly, no significant redox behavior was observed during the CV analysis at a scan rate of 50 mV s^{-1} (**Figure 3.20a**). Nevertheless, the current response was found to be very less even at a working voltage window

of 1.4 V, which is slightly higher than the potential used during the electrochemical analysis in the three-electrode cell (*i.e.*, 1.2 V vs. Ag/Ag⁺).

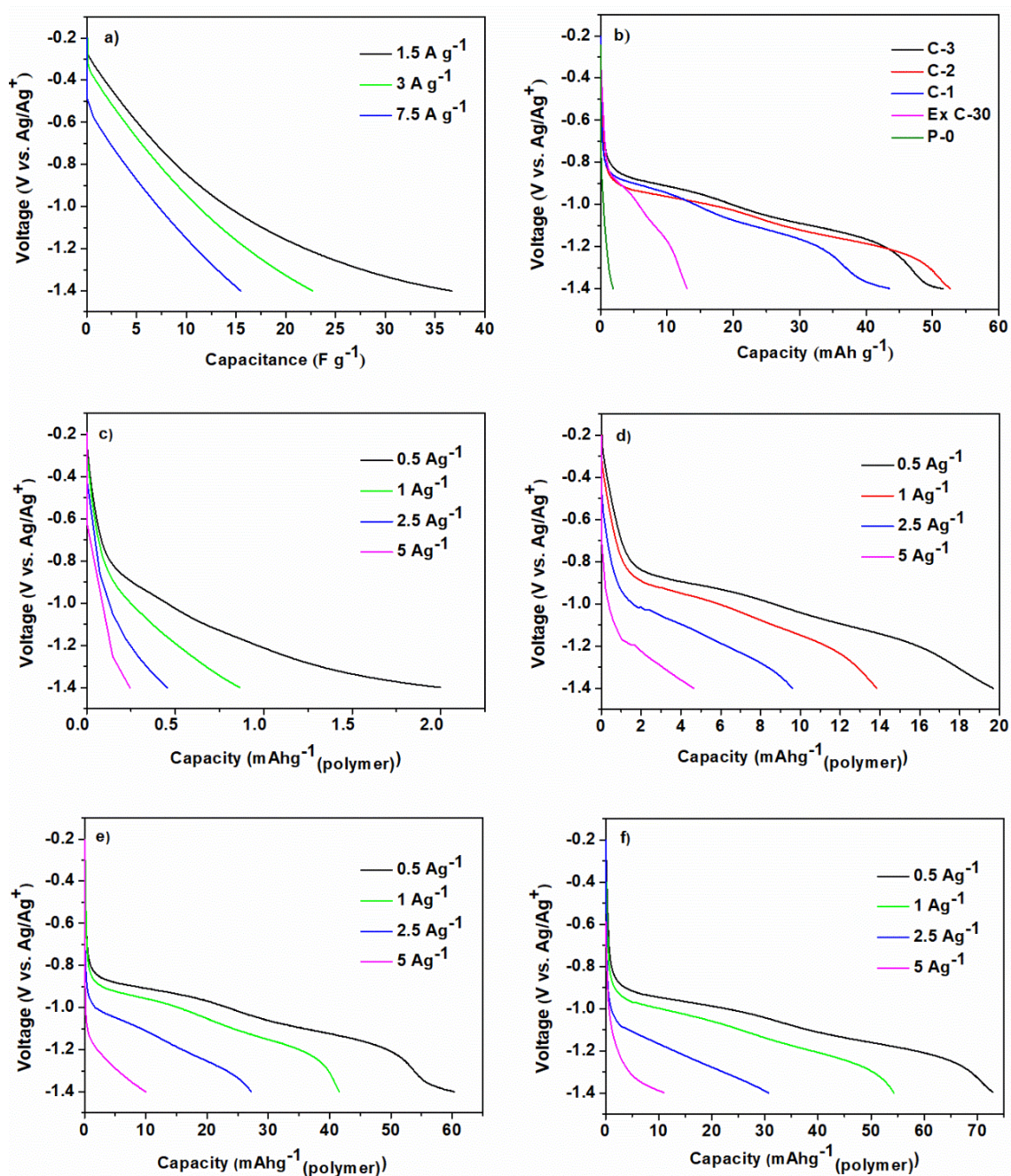


Figure 3.19 (a) Discharge profiles recorded at various current rates for MWCNT and (b) discharge profiles of P-0, C-1, C-2, C-3, and Ex C-30 samples recorded at 0.5 A g⁻¹ considering the total loading of electrode material (1 mg cm⁻²); discharge profiles recorded at various current rates for the (c) P-0, (d) Ex C-30, (e) C-1, and (f) C-2 samples.

The device-level performance of the C-3 polymer composite was explored by fabricating an asymmetric device (AC||C-3)⁵⁴ using the C-3 sample as the negative electrode and activated

carbon (AC) as the positive electrode material in 1M LiClO₄/PC electrolyte. The asymmetric configuration enables expanding the voltage window of the device without hampering the electrode and electrolyte stability. **Figure 3.20b** and **c** compare the electrochemical performance of the positive electrode (-0.2 to 1.0 V vs. Ag/Ag⁺), and the negative electrode (-1.4 to -0.2 V vs. Ag/Ag⁺) obtained from the CV and GCD experiments within the corresponding voltage range. The ratio of the active material loading in the positive and negative electrode is 1.5:1 (AC: C-3), which was calculated by considering the capacity of the individual electrodes measured from the three-electrode study. The details of the calculation are given in the 3.7.

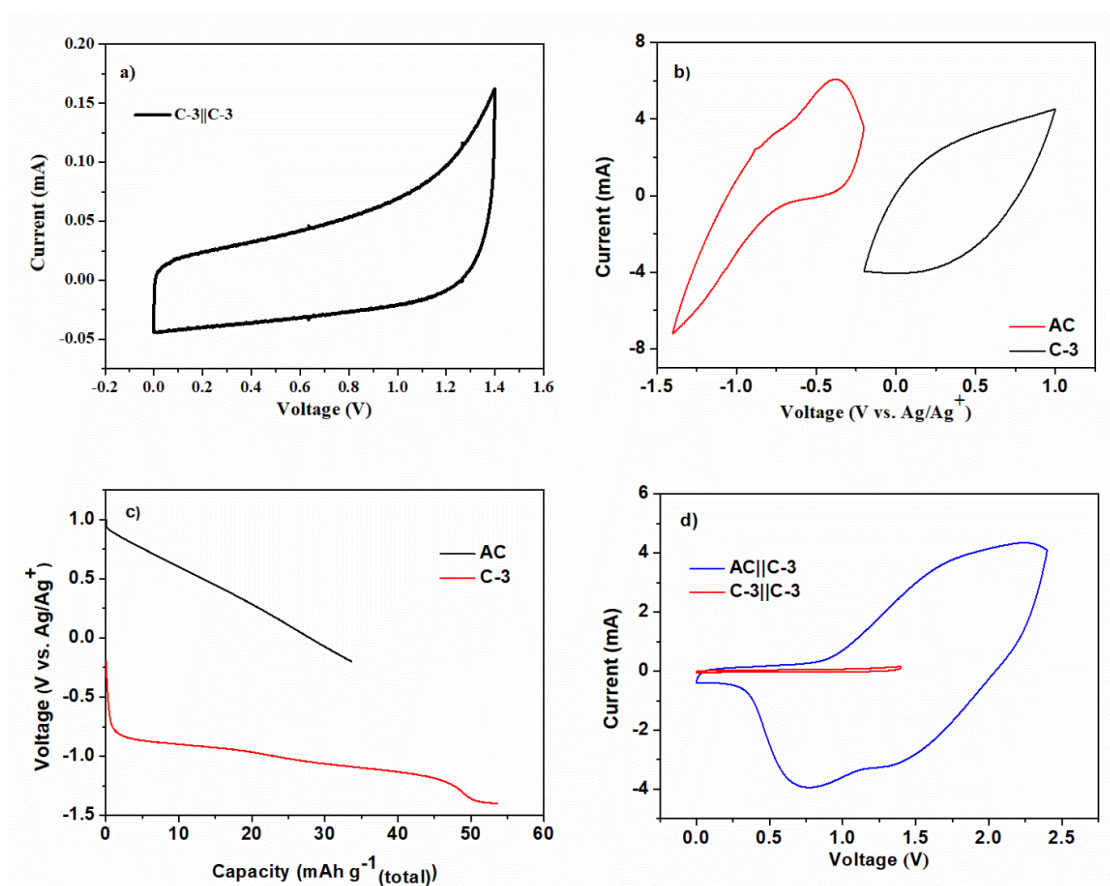


Figure 3.20 (a) CV data taken for the C-3||C-3 symmetric device at 50 mV s⁻¹ scan rate; (b) CV data recorded at 50 mV s⁻¹ scan rate and (c) discharge profiles recorded at 0.50 A g⁻¹ (considering total loading of electrode material) for the activated carbon (AC) and C-3 samples in three-electrode configuration; (d) CV profiles recorded for the C-3||C-3 symmetric device and AC||C-3 HSC device in 1M LiClO₄/PC liquid electrolyte at 50 mV s⁻¹ scan rate.

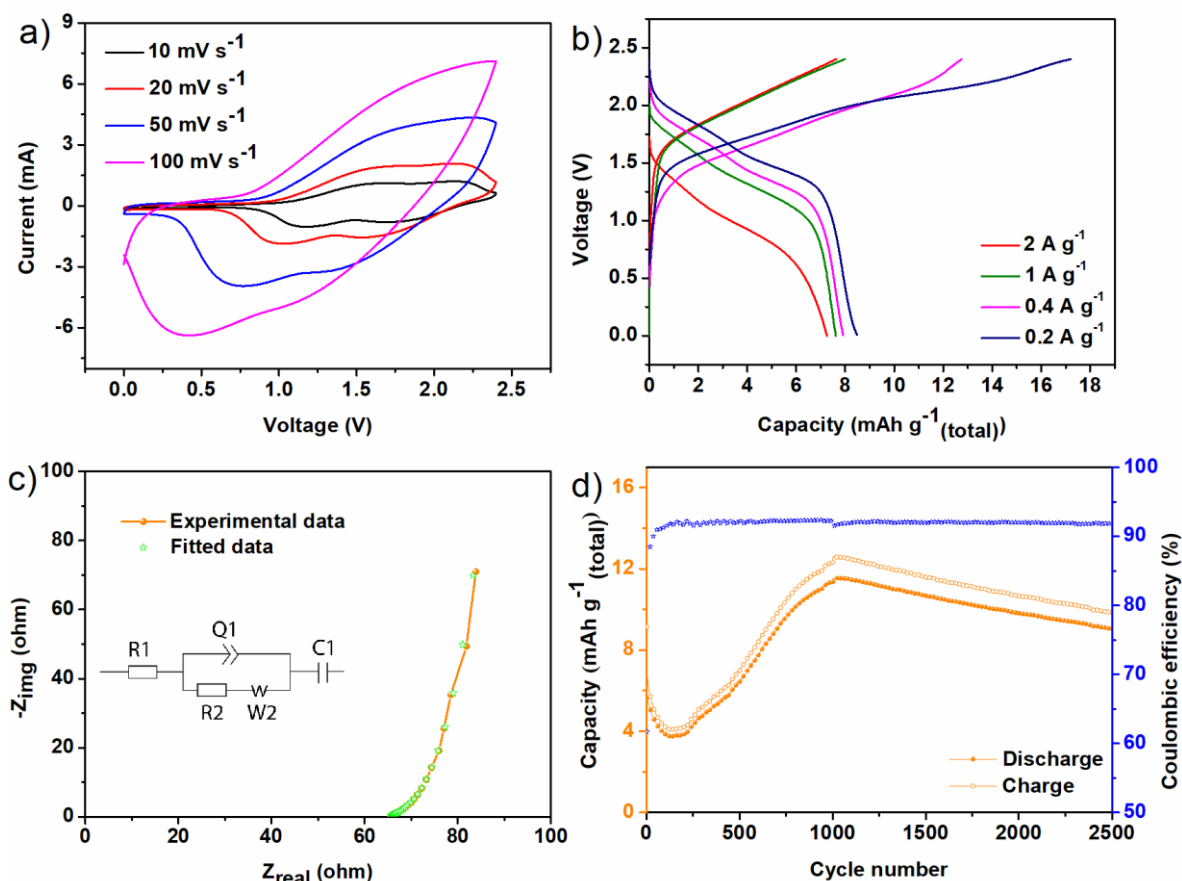


Figure 3.21 (a) CV profiles recorded at different scan rates, (b) GCD profiles recorded at different current rates, (c) impedance plot, and (d) cycling stability data for the AC||C-3 HSC device in 1M LiClO₄/PC (LS-HSC device) recorded at a current rate of 1.0 A g⁻¹.

As the asymmetric configuration demonstrated in this study contains two electrodes with different charge storage mechanisms, i.e., one EDLC type (AC) and the other battery-type (C-3 composite), the devices are called hybrid capacitors/supercapacitors.^{55,56} The electrochemical performance of AC||C-3 hybrid supercapacitor device containing 1M LiClO₄/PC liquid electrolyte (LS-HSC) was analyzed within the extended voltage range of 0 to 2.4 V (**Figure 3.20d**). In contrast to the C-3||C-3 device, the feature of the CV plot in the LS-HSC device (**Figure 3.20d**) indicates the involvement of Faradaic reactions during the anodic and cathodic scan. Besides, a remarkable improvement in the current response was achieved with the LS-HSC compared to that in the symmetric (C-3||C-3) device (**Figure 3.20d**). These observations suggest that the high working voltage (2.4 V) of the LS-HSC device helps to accomplish the redox activity of the C-3 composite in the two-electrode cell assembly. The CV and GCD profiles of the LS-HSC device are given in **Figure 3.21a** and **b**. As observed from **Figure 3.21b**, the LS-HSC device delivers 8.5 mAh g⁻¹ (total) and 7.0 mAh g⁻¹ (total) of the specific capacity

at the current rate of 0.2 A g^{-1} and 2.0 A g^{-1} respectively (current rate and capacity values are normalized for the total mass-loading at the positive and negative electrodes). In the Nyquist plot (**Figure 3.21c**), equivalent series resistance (ESR) for LS-HSC device exhibits $65 \text{ } \Omega$. During the cycling stability experiment of LS-HSC (**Figure 3.21d**), the device's capacity increases gradually during initial cycles and reaches the maximum value of $11 \text{ mAh g}^{-1}_{(\text{total})}$ after 1000 cycles. Owing to the initial increase in capacity during the prolonged cycling of the device, the capacity recorded at 1.0 A g^{-1} current rate after 1000 cycles is close to the value obtained at 0.2 A g^{-1} . The improvement in capacity during the cycling stability test is possibly due to the enhanced electrochemical activity of the material during cycling. However, in the subsequent cycles, the device's capacity drops gradually, showing 80% retention of the maximum capacity after 2500 cycles with 92% Coulombic efficiency.

Later, a QSS-HSC device (quasi-solid-state AC||C-3) was fabricated using PMMA/PC/LiClO₄ polymer gel electrolyte. The CV profiles recorded at various scan rates for the QSS-HSC device are given in **Figure 3.22a**. The device exhibits $11 \text{ mAh g}^{-1}_{(\text{total})}$ discharge capacity at a current rate of 0.4 A g^{-1} (**Figure 3.22b**). Also, it retains $6.9 \text{ mAh g}^{-1}_{(\text{total})}$ of the specific capacity even at 3.0 A g^{-1} , indicating good rate capability of the system. It is observed that the charging capacity values of the device at 0.4 and 1.0 A g^{-1} are higher compared to the corresponding discharge capacities resulting in low Coulombic efficiency of the device at lower current rates. However, the device could perform better at higher current rates with more than 95% Coulombic efficiency. The resistance of the QSS-HSC device is measured from the EIS analysis, and the corresponding Nyquist plot is given in **Figure 3.22c**. The device exhibits an ESR of $8.8 \text{ } \Omega$ without a prominent semicircle feature at the high-frequency region of the Nyquist plot. It is worth mentioning that the overall resistance observed for QSS-HSC is much lower than many of the organic electrolyte-based supercapacitors reported earlier.⁵⁷⁻⁵⁹ The low resistance of QSS-HSC is attributed to a seamless pathway for the transport of charge carrier species throughout the electrode, which is achieved by creating a uniform and intimate contact of the polymer layer with the MWCNT backbone in the C-3 polymer composite, as already explained in the previous sections.

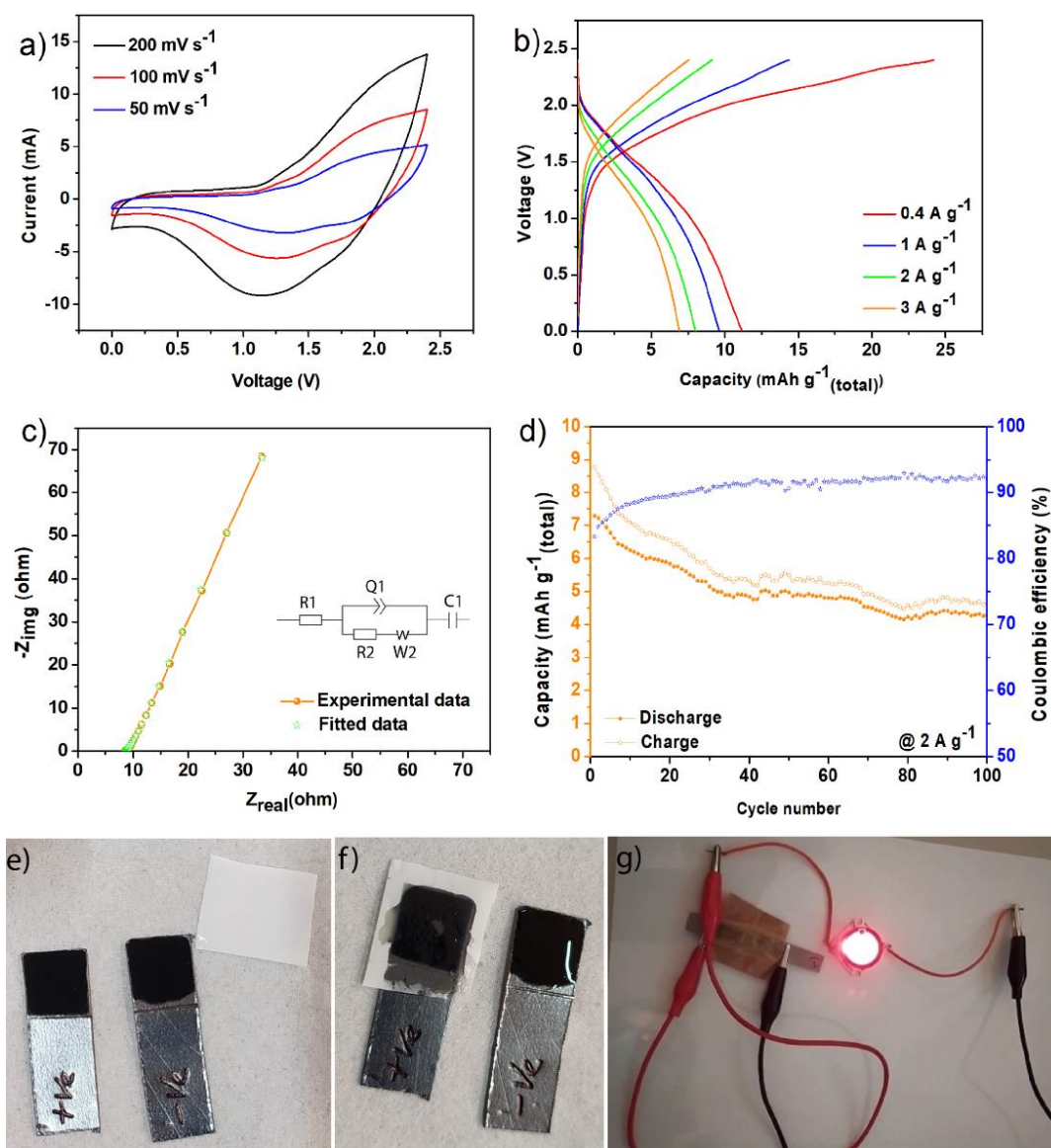


Figure 3.22 (a) CV profiles recorded at different scan rates, (b) GCD profiles recorded at different current rates, (c) Nyquist plot, and (d) cycling stability data recorded at a current rate of 2.0 A g^{-1} for the QSS-HSC device; photographs of the QSS-HSC device fabrication: (e) photograph of the positive and negative electrodes and separator, (f) electrodes coated with PMMA/PC/LiClO₄ polymer gel electrolyte, and (g) demonstration of the QSS-HSC device used for lighting an LED.

The cycling stability of the QSS-HSC device was carried out at a current rate of 2.0 A g^{-1} . As seen in **Figure 3.22d**, the device could retain 60 % of the initial capacity after 100 cycles. The overall electrochemical performance of the C-3 composite-based LS-ASHC and QSS-HSC devices indeed highlights that the Faradaic charge storage properties of the P(NDI2OD-T2) polymer is improved by means of *in-situ* inclusion of MWCNTs into the

polymer matrix. The electrochemical performance of C-3 composite in the three-electrode cell and QSS-HSC device is obtained higher or comparative with some of the previously reported redox-active polymers used as active electrode material in supercapacitors.^{9,15,17,60-66} Furthermore, for demonstrating the device-level application, a 2.4 V QSS-HSC device is used for lightening a red LED bulb. Photographs of the various steps involved in the device fabrication are presented in **Figure 3.22e** and **f**. Photograph of the glowing LED bulb powered with the QSS-HSC device is given in **Figure 3.22g**, and a demonstration image is given in **Figure 3.23**.

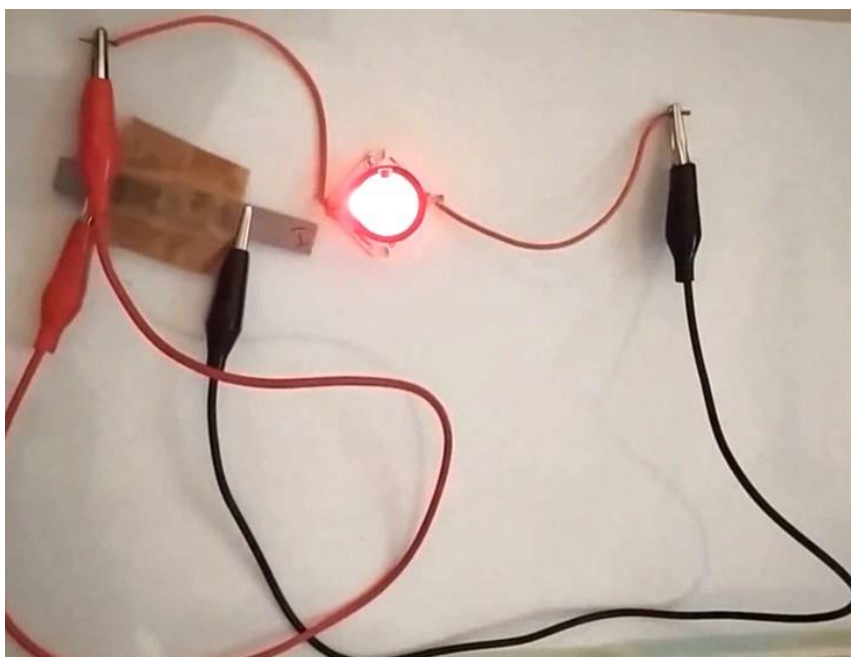


Figure. 3.23 Demonstration of LED bulb powered with the QSS-HSC device.

3.7 Electrochemical Calculation

1) Calculation of the specific discharge capacity in the three-electrode cell:

$$\text{Charge (Q)} = \int i \times t$$

where i (in A) and t (in sec) are current and time, respectively.

$$\text{Capacity (mAh)} = \frac{Q \times 1000}{3600}$$

Therefore, the equation for specific discharge capacity (mAh g⁻¹) can be presented as

$$\text{Specific discharge capacity (mAh g}^{-1}\text{)} = \frac{\text{Applied current (A)} \times \text{discharge time (sec)}}{\text{electrode loading (mg)} \times 3600} \times 1000$$

(Equation S1)

As already mentioned, the total loading of the P-0, C-1, C-2, C-3, and Ex C-30 electrodes were 1.0 mg. In the case of the MWCNT electrode, the total loading was 0.33 mg.

2) Calculation of specific discharge capacity considering the loading of only the redox-active polymer (mAh g⁻¹_(polymer))

$$= \frac{\text{Applied current (A)} \times \text{discharge time (sec)}}{\text{loading of the polymer (mg)} \times 3600} \times 1000 \quad (\text{Equation S2})$$

The loading of the polymer in the respective electrodes is given below:

Sample	MWCNT content (%)	PVDF content (%)	Polymer content (mg)
P-0	0	5	0.95
C-1	14	5	0.8
C-2	24	5	0.7
C-3	35	5	0.6
Ex C-30	30	5	0.65

3) Calculation for balancing the loading in the positive (AC) and negative electrode (C-3) in the hybrid supercapacitor device:

The mass ratio of the electrodes was calculated by following equation,

$$\frac{M_{AC}}{M_{C-3}} = \frac{Q_{C-3}}{Q_{AC}} \quad (\text{Equation S3})$$

In this context, M_{AC} represents the total loading of positive electrodes, while M_{C-3} denotes the total loading of negative electrodes.¹¹

Q_{AC} and Q_{C-3} represent the discharge capacity values (considering the total mass-loading in the respective electrode) of the positive and negative electrodes obtained from the three-electrode study.

$$\frac{M_{AC}}{M_{C-3}} = \frac{53 \text{ mAh g}^{-1}}{34 \text{ mAh g}^{-1}}$$

$$\frac{M_{AC}}{M_{C-3}} = \frac{1.5}{1.0}$$

Therefore, the total loadings in the positive and negative electrodes were taken as 1.5 mg and 1 mg, respectively.

4) Equation for the capacity of the hybrid supercapacitor device:

$$\text{Capacity (mAh g}_{total}^{-1}) = \frac{\text{Discharge time (hour)} \times \text{applied current (mA)}}{\text{total mass-loading of the electrode materials in both the positive and negative electrodes (mg)}} \times 1000$$

(Equation S4)

3.8 Conclusions

In summary, we have developed a facile synthesis protocol for P(NDI2OD-T2) (P-0) polymer with high molecular weight within a short period of time (2h) for the first time by means of the modified Stille polymerization method. The inclusion of MWCNT during the polymerization reaction was found to improve the physicochemical property of the composite material compared to that of the pristine polymer. As a result, the composite sample prepared with 35% MWCNT content (C-3) following the *in-situ* approach exhibited an 80 mAh g⁻¹_(polymer) discharge capacity, which is substantially higher than that of the pristine polymer and the composite prepared by physically mixing MWCNT with the same quantity (Ex C-30). The C-3 polymer composite was further used for fabricating a high-voltage (2.4 V) hybrid supercapacitor taking the C-3 composite as a negative electrode (battery-type) and activated carbon (AC, capacitive electrode) as the positive electrode material. The electrochemical performance of the AC||C-3 device was analyzed in 1M LiClO₄/PC liquid electrolyte (LS-HSC) and PMMA/PC/LiClO₄ polymer gel electrolyte (QSS-HSC). Both devices show comparable performance, which is attributed to the porous morphological architecture of the C-3 composite possessing intimate contact of the polymer with the MWCNT conducting framework. This work opens up new opportunities toward the designing of conducting polymer-based robust electrode materials for non-aqueous hybrid supercapacitors.

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CHAPTER 4

Continuous Flow Synthesis of High-Performance n-type Polymers based on Naphthalene and Perylene diimide

4.1 INTRODUCTION

Donor-acceptor conjugated polymers offer significant potential for various energy-related applications, including in organic field-effect transistors (OFETs), organic photovoltaics (solar cells), and energy storage devices.¹⁻⁴ The D-A polymers have garnered significant attention across various fields owing to their multitude of advantages. These include their structural and functional adaptability through molecular design, solution processability, lightweight and flexible nature, availability in diverse colors, ease of synthesis, and low processing costs.⁵⁻⁹ Moreover, their distinct electronic and optical characteristics render them highly adaptable for various applications. However, ensuring the uniformity of synthesis in D-A conjugated polymers presents a significant challenge. Maintaining consistency in their molecular weight is especially critical, as it profoundly affects both material attributes and their efficacy in organic devices.¹⁰

Thus, there is an important requirement for control over the polymerization process to produce conjugated polymers with accurately regulated and consistent molecular weights. Most of the donor-acceptor conjugated polymers are often synthesized using Stille and Suzuki polymerization methods. These methods most commonly followed the conventional batch polymerization. Despite their advantages, batch polymerization reactions suffer from drawbacks such as extended reaction times and limited scalability due to variability in molecular weight and polydispersity from batch to batch. Hence, the advancement of novel synthetic methodologies to tackle this issue of reproducibility signifies a substantial stride towards the commercialization and enhanced adoption of these materials in high-performance organic electronic devices.¹¹

The variability in molecular weight and dispersity from batch to batch can greatly affect the performance of polymer materials in energy applications. This inconsistency can have significant implications for the performance and reliability of the polymers in various applications, few examples are outlined here. Bumjoon J. Kim et al.¹² synthesized a donor polymer, PPDT2FBT with different molecular weight, used for all-polymer solar cell (PSC) in combination with P(NDI2OD-T2) as the electron acceptor polymer. PSC devices displayed different power conversion efficiencies (PCEs) of 3.78%, 4.18%, and 5.03% for the electron donor PPDT2FBT polymers with molecular weights (M_n) of 12, 24, and 40 kg/mol, respectively. This study highlights the substantial impact of varying polymer molecular weights on solar cell performance. In another study, Alex K. Y. Jen et al.¹³ demonstrated Organic Field-Effect Transistors (OFETs) using a donor-acceptor PIDSe-DFBT polymer with

three different number average molecular weights: 30.1, 46.3, and 61.8 kg/mol. They observed that the polymer with the highest molecular weight exhibited superior performance in terms of both electron mobility and hole mobility. Sunghun Cho and colleagues¹⁴ demonstrated two-electrode symmetric supercapacitors utilizing PPy:PSS electrodes with varying molecular weights (Mw) of Poly(4-styrenesulfonate) (PSS). The molecular weights of PSS used in the supercapacitors were 1000 kg/mol, 200 kg/mol, and 70 kg/mol. Capacitance values of the PPy:PSS supercapacitor were measured as 25.3, 13.0, and 109.5 F g⁻¹ at 0.05 A g⁻¹, respectively. This study emphasizes the considerable influence of polymer molecular weight on the energy storage performance of supercapacitors.

In **chapters 2 and 3** of the thesis, our primary focus was on the batch synthesis of rylenebisimide-based D-A conjugated polymers and their composites for application as electrode material in supercapacitors. As we already discussed, the batch polymerization poses limitations when it comes to scaling up for commercial applications. Thus, the focus of this chapter is predominantly on synthesizing donor-acceptor conjugated polymers based on rylenebisimide, employing batch, microwave, and continuous flow methodologies.

The Microwave polymerization is the prominent approach to overcome the many limitations of batch polymerization and offers several advantages including shorter reaction times, higher reaction yields, and improved control over the polymerization process.¹⁵ M. Heeney et al.¹⁶ and Farrell et al.¹⁷ synthesized defect-free polymers by microwave polymerization and achieved comparable molecular weights within short time. In another study, M. E. Nicho et al,¹⁸ synthesized P3HT polymer by oxidation of 3-hexylthiophene and decreased reaction time from 24 h to 1 h. The studies indicated that, the properties of polymers remained consistent with those obtained in conventional heating experiments.

Continuous flow technology is another interesting technique which offers several advantages over conventional batch reactors. It is an attractive technique for scaling and commercializing the conjugated polymer with reproducible molecular weight and polydispersity and it also offers benefits in terms of reduction in reaction time, proper heat transfer and reduced side products.^{11,19-22} It also enables highly efficient rapid mixing due to short diffusion pathways, thereby enhancing mass transport and ensuring uniform reaction conditions.²³⁻²⁵ A flow reactor possesses an extensive specific surface area (surface area to volume ratio), leading to superior heat exchange properties.²⁶⁻²⁸ Seyler and co-authors, synthesized benzodithiophene and thieno[3,4-b]thiophene polymers by continuous flow method.²² Pirotte and colleagues, synthesized PCE-11 polymer by continuous flow and studied the impact of reaction conditions

on molecular weight.²⁹ In another study, PBDTTPD and PBDTTZ-4 were synthesized using a continuous flow synthesis.³⁰⁻³¹ The conjugated polymers discussed above, along with numerous others synthesized via continuous flow methods, have been employed in various energy applications, demonstrating comparable or even superior performance compared to batch-synthesized polymers. Implementing continuous flow polymerization methods can provide better control over reaction conditions and enhance consistency in polymer properties compared to traditional batch processes. Continuous flow systems enable precise regulation of reactant flow rates, reaction temperatures, and residence times, resulting in more uniform polymerization and reduced variability between batches.

The N2200 or P(NDI2OD-T2) polymer has been employed as an acceptor in all-polymer solar cells, yielding high power conversion efficiencies when paired with appropriate donor polymers under carefully controlled device fabrication conditions. In **chapter 3**, we have also studied this polymer as electrode material in supercapacitor energy storage device and obtained excellent capacity and stability. The polymer shows excellent performance due to its redox active behaviour. While offering advantages in various energy applications, these materials demonstrated a notable propensity to aggregate in different organic solvents, leading to pronounced phase separation on a significant scale. The previous report from our group by Sandip Sharma and coworkers³² illustrated a range of novel n-type naphthalene (NDI) or perylene (PDI) bithiophene based random copolymers incorporating varying amount of PDI along with NDI. These copolymers were utilized as acceptors in combination with commercially available donor polymers such as PTB7 or PTB7-Th in all-polymer solar cells. Among all the synthesized random copolymers, NDI-Th-PDI-30 (incorporating approximately 30% PDI) showed a notable power conversion efficiency (PCE) of 5.0%, outperforming P(PDI2OD-T2), which achieved a PCE of 2.97%. The donor-acceptor conjugated polymers P(NDI2OD-T2) and NDI-Th-PDI-30 serve effectively as acceptor polymers in all-polymer solar cells. Apart from these polymers, a variety of highly efficient conjugated polymers have been synthesized using batch processes. However, the utilization of these polymers for large-scale device fabrication is hindered by the inconsistency in molecular weight and polydispersity between batches.

In this chapter, we are mainly concentrating on synthesizing these rylenebisimide-based donor-acceptor conjugated polymers via stille polymerization using batch method, microwave polymerization, and continuous flow polymerization. The typical procedure for synthesizing

P(NDI2OD-T2) and NDI-Th-PDI-30 via Stille polymerization usually requires a prolonged reaction time of approximately 3 days to complete.³²⁻³⁵ The donor-acceptor polymer P(NDI2OD-T2) was synthesized using Microwave approach, completing the synthesis within just 30 minutes. This method yielded comparable molecular weights while offering the advantage of a significantly shorter reaction time and energy-efficient technique. Subsequently, both the P(NDI2OD-T2) and NDI-Th-PDI-30 polymers were synthesized in batch mode using 4-tertiary butyl toluene. Finally, the continuous flow method was utilized to synthesize the P(NDI2OD-T2) polymer, resulting in a high molar mass polymers achieved within a brief reaction time of 104 minutes. The continuous flow approach was also utilized to synthesize the NDI-Th-PDI-30 random copolymer, achieving high molecular weights. The general diagrammatic representation of continuous flow polymerization is provided in **Figure 4.1**.

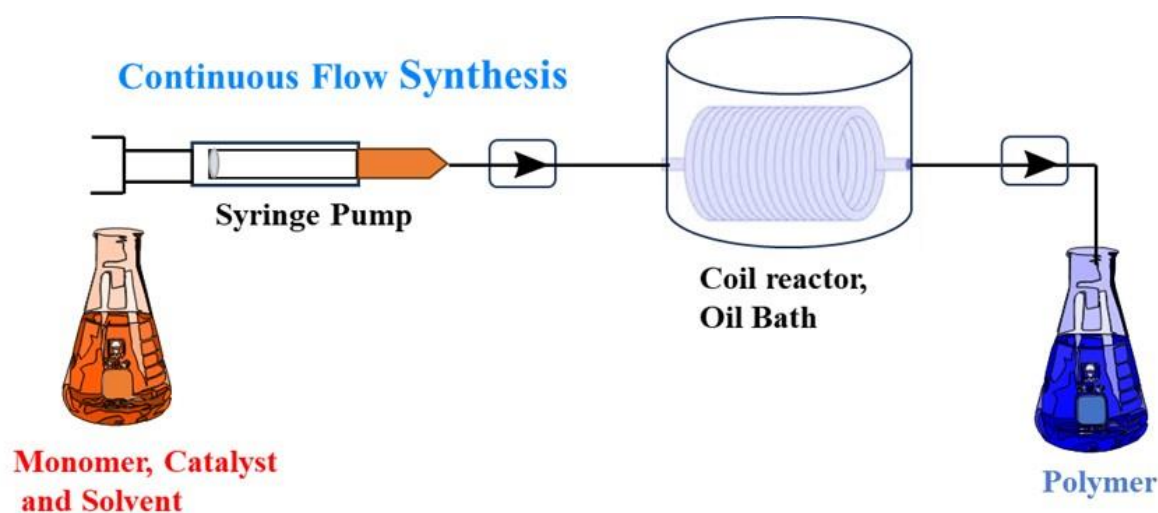


Figure 4.1 Diagrammatic representation of continuous flow polymerization.

4.2 Experimental Section

4.2.1 Materials

2-Ethylhexyl amine was procured from TCI Chemicals and utilized without additional purification. All other materials were used as given in **Chapter 2.2.1**.

4.2.2 Measurements.

The molecular weight of polymers synthesized via batch and microwave methods was assessed using gel permeation chromatography (GPC) at room temperature. Chloroform was used as eluent and flow rate of 1 mL/min was maintained, and detection was facilitated by refractive index (RI) detector. Polystyrene was utilized as the standard for the analyses. The molecular

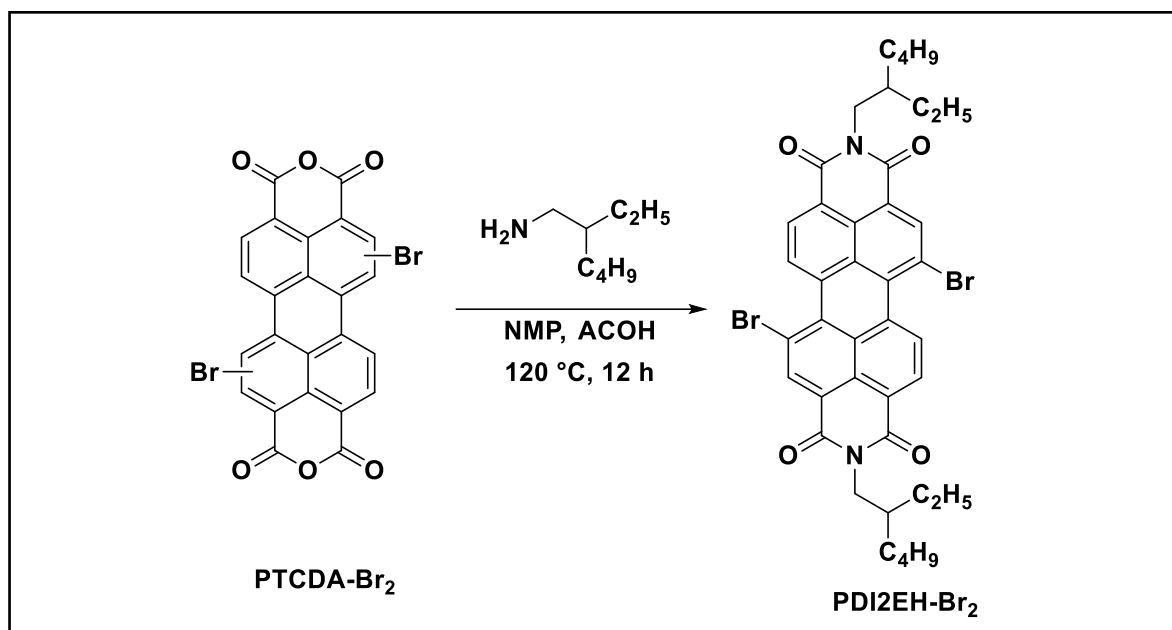
weight for continuous flow (final optimized) polymers were analyzed using gel permeation chromatography with an Agilent system, featuring a high-temperature setup and a RI detector. The eluent used was 1,2,4-trichlorobenzene (TCB), flowing at a rate of 1 mL/min and maintained at a temperature of 140 °C. Differential Scanning Calorimetry (DSC) analyses were conducted using a TA Discover 250 instrument. All other measurement details for polymers are the same given in **Chapter 2.2.2**.

4.3 Synthesis of Monomers

4.3.1 The synthesis of 2-octyldodecan-1-amine, PTCDA-Br₂ (1,7-Dibromo-3,4,9,10-perylenetetracarboxylic acid dianhydride) and NDI-2OD-Br₂ monomer followed the procedures outlined in **Chapter 2.3.1** and **Chapter 3.3.2** respectively.

4.3.2 Synthesis of PDI2EH-Br₂ (N, N'-Bis (2-ethylhexyl)-1,7-dibromo -3,4,9,10-perylene tetracarboxylic dianhydride) Monomer

PTCDA-Br₂ (3.0 g, 5.453 mmol) was combined with glacial acetic acid (20 mL) and N-methyl pyrrolidine (60 mL), along with 2-Ethylhexyl amine (2.11 g, 16.36 mmol) in a reaction vessel. The synthesis of PDI2EH-Br₂ followed a procedure similar to that described for PDI-2OD-Br₂ in **Chapter 2.2**. (Yield=29%). ¹H NMR spectrum (400 MHz, CDCl₃) δ ppm: 9.39-9.41 (d, 2H), 8.85 (s, 2H), 8.61-8.63 (d, 2H), 4.08-4.19 (m, 4H), 1.93-1.97 (m, 2H), 1.27-1.45 (m, 16 H), 0.88-0.98 (m, 12H). ¹³C NMR spectrum (100 MHz, CDCl₃) δ ppm: 163.12, 162.62, 137.97, 132.61, 129.94, 128.34, 126.83, 123.05, 122.62, 120.75, 44.43, 37.92, 30.70, 28.66, 24.01, 23.04, 19.13, 14.09, 10.59. The MALDI-TOF analysis showed a molecular weight of (772.56) m/z: 773.98, 795.96 (M⁺ Na⁺).



Scheme 4.2 Synthesis of PDI2EH-Br₂.

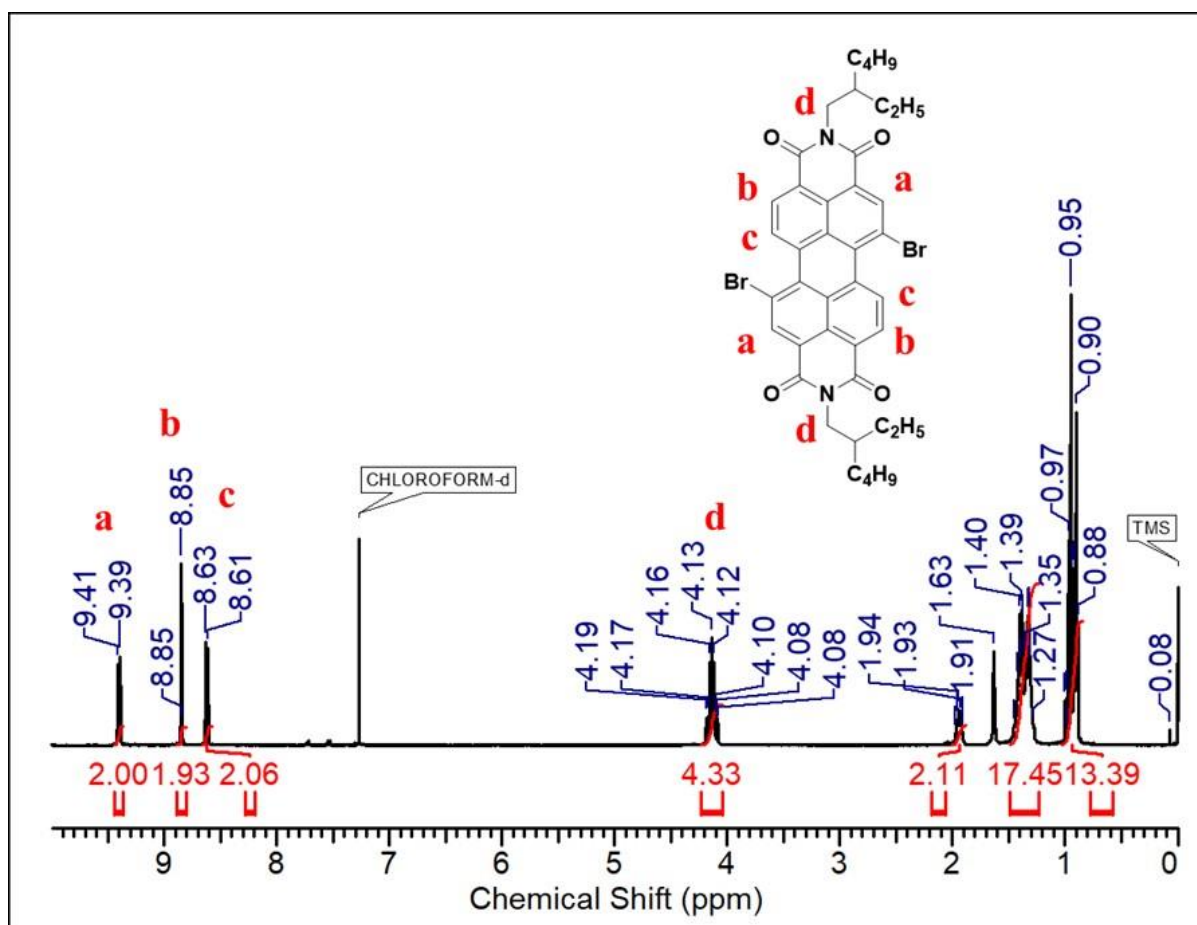


Figure 4.1 ¹H NMR spectrum of PDI2EH-Br₂ monomer.

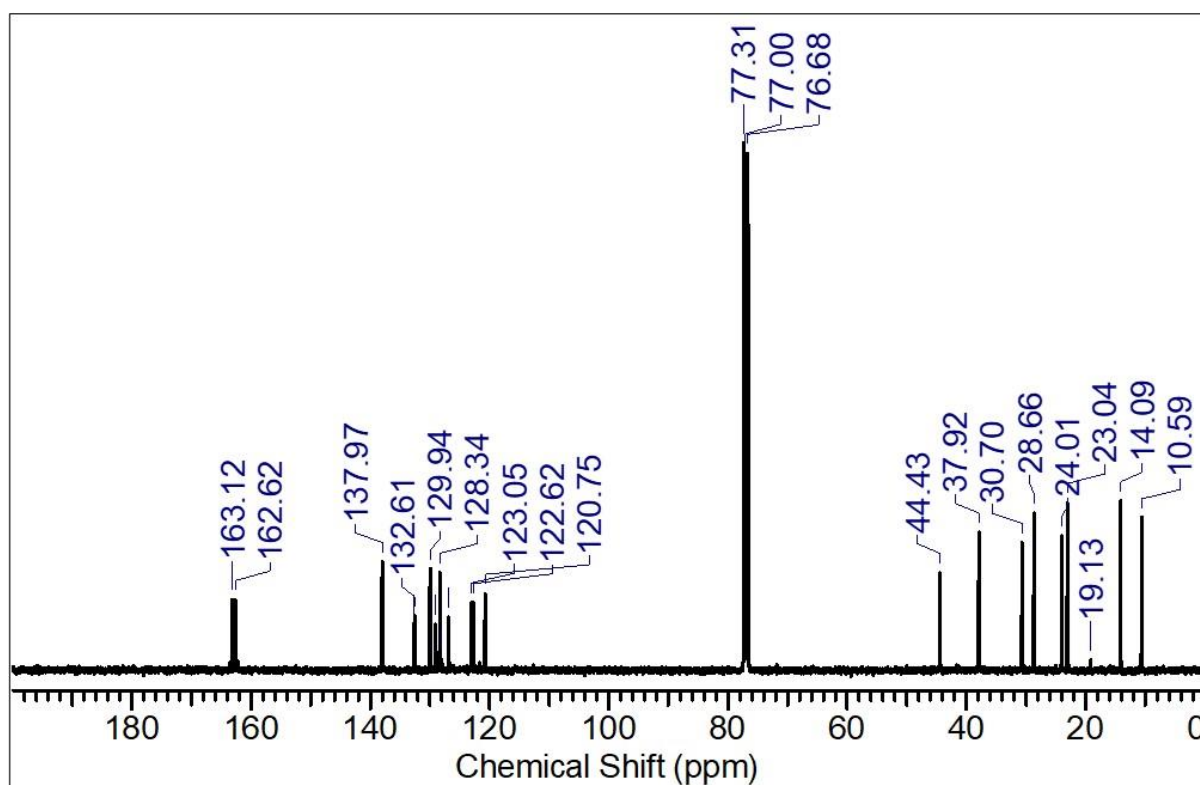


Figure 4.3 ¹³C NMR spectrum of monomer PDI-EH-Br₂.

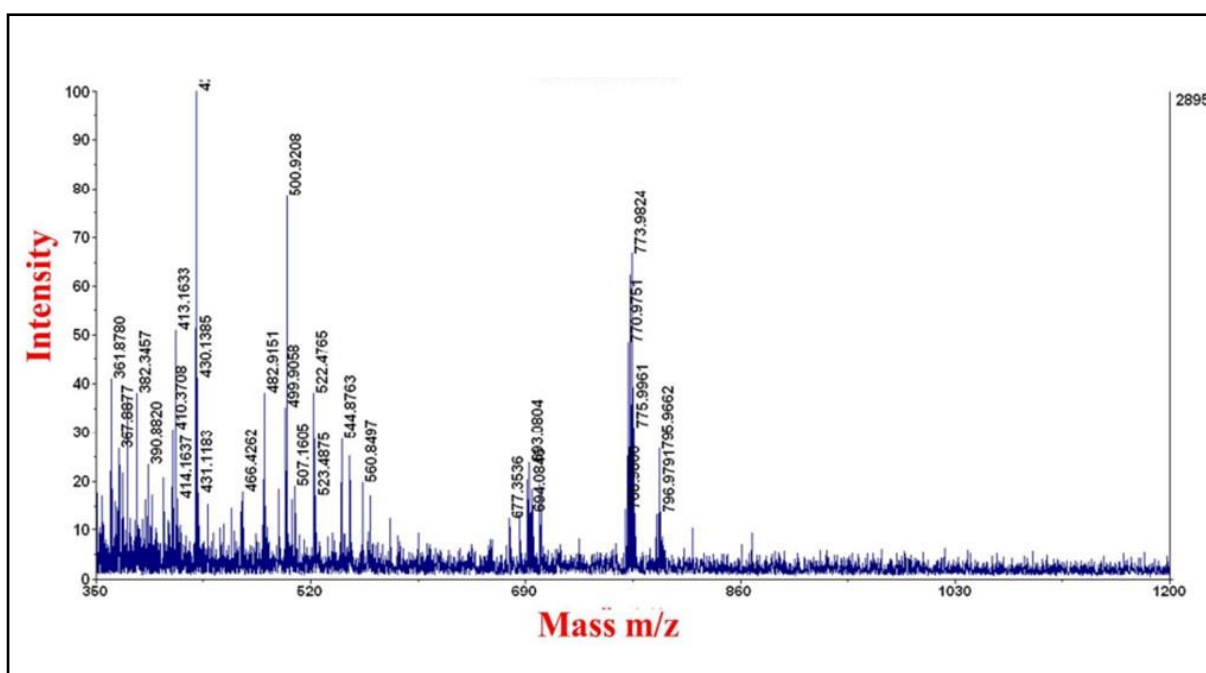


Figure 4.4 MALDI-TOF spectrum for PDI-2EH-Br₂ monomer.

4.4 Batch Synthesis of P(NDI2OD-T2) polymer for time optimization

Three sets of P(NDI2OD-T2) polymerization reactions were performed to optimize the reaction time, with the following details provided: NDI-2OD-Br₂ (0.200 g, 0.203 mmol) and 5,5'-

bis(trimethylstannyl)-2,2'-bithiophene (0.099 g, 0.203 mmol) were combined inside a moisture-free Schlenk tube with a magnetic stirring bar, followed by the addition of toluene (18 mL). The mixture underwent nitrogen purging for thirty minutes with continuous stirring at room temperature. Subsequently, under a nitrogen atmosphere, bis(triphenylphosphine)palladium(II) dichloride ($\text{Pd}(\text{Ph}_3)_2\text{Cl}_2$) (0.01015 mmol) was introduced to the solution, followed by an additional thirty-minute nitrogen purge. The Schlenk tube was then submerged into an oil bath that had been set to 90 °C. Three sets of similar reactions were conducted with varying time durations of 6 hours, 12 hours, and 24 hours. Afterwards, the reaction mixtures were cooled down to ambient temperature, the product dissolved in chloroform, precipitated in methanol, and filtered through a Büchner funnel. The polymer underwent purification through Soxhlet extraction in methanol for 24 hours, followed by additional purification using acetone. The molecular weight checked using Chloroform GPC. For the 6-hour reaction, an $M_n = 13600$ was obtained with a PDI of 3.2. Similarly, for the 12-hour reaction, $M_n = 14500$ with a PDI of 3.4, and for the 24-hour reaction, number average molecular weight (M_n) = 13200 with a PDI of 3.6. In summary, comparable molecular weights were obtained for reactions conducted over varying durations.

4.5 Microwave polymerization

Following the optimization of reaction time in conventional batch method, we proceeded with the with microwave assisted polymerization reaction. Four different reaction setups were employed with varying power rates to increase the reaction temperature and with different reaction time, the details are discussed below and summarized in **Table 4.1**. The molecular weight of microwave assisted polymers was checked using Chloroform GPC.

1st Experiment:

Identical quantities of monomers, catalyst, and solvents were utilized as described in the **Section 4.4** and combined in flask. Toluene (18 mL) was then added. Subsequently, $\text{Pd}(\text{Ph}_3)_2\text{Cl}_2$ catalyst (0.01015 mmol) was introduced to the solution, and the RB flask was then placed in the microwave and connected to a condenser. In these reaction, 350 watts (50% power) were applied, achieving a temperature of 90 °C, maintained for 1 hour. The remaining procedure was carried out following the protocol outlined in **Section 4.4**. $M_n = 6500$ to 11000 g/mol was obtained for given reaction times of 30 minutes to 1 hour.

2nd Experiment:

The identical quantities of monomers, catalyst, and solvents were utilized as described in the **Section 4.4**. In the second set of reactions, 450 watts (65% power) were applied, resulting in a temperature of 110 °C, maintained for 1 hour. Mn = 3300 to 15000 g/mol for given reaction time 15 minutes to 1 hour. This experiment followed exactly similar procedure used for the 1st experiment.

Table 4.1 Optimization conditions for the microwave polymerization.

Microwave Experiment No	Time	Power and set Temp	Actual Temp	Molecular weight (Mn)* (g/mol)	DM (Mw/Mn)
1	15 min	350 watt (50 % power), 90 °C	90 °C	-	-
	30 min	350 watt (50 % power), 90 °C	90 °C	6,500	1.8
	45 min	350 watt (50 % power), 90 °C	90 °C	9,200	2.2
	1 h	350 watt (50 % power), 90 °C	90 °C	11,000	2.5
2	15 min	450 watt (65 % power), 110 °C	110 °C	3,300	1.8
	30 min	450 watt (65 % power), 110 °C	110 °C	7,200	2.3
	45 min	450 watt (65 % power), 110 °C	110 °C	10,400	3.2
	1 h	450 watt (65 % power), 110 °C	110 °C	15,000	2.7
3	15 min	450 watt (65 % power), 130 °C	125 °C	2,900	1.7
	30 min	450 watt (65 % power), 130 °C	125 °C	6,400	2.3
	45 min	450 watt (65 % power), 130 °C	125 °C	11,700	3.4
	1 h	450 watt (65 % power), 130 °C	125 °C	13,300	3.4
4	15 min	750 watt (100 % power), 160 °C	160 °C	9,000	2.1
	30 min	750 watt (100 % power), 160 °C	160 °C	14,100	3.0

* Molecular weight determined using Chloroform GPC.

DM = Polydispersity index (Mw/Mn)

3rd Experiment:

The same amounts of monomers, catalyst, and solvents were used as described in the **Section 4.4**. In this experiment, 450 watts (65% power) were used, reaching a temperature of 130 °C,

and continued for 1 hour. Mn= 3000 to 13000 g/mol for reaction times of 15 minutes to 1 hour. This experiment followed exactly same procedure as given for 1st experiment.

4th Experiment:

The quantities of monomers, catalyst, and solvents remained consistent with those outlined in the **Section 4.4**. In this experiment, 750 watts (100%) power was applied, achieving a temperature of 160 °C, and continued for half an hour. Mn= 9000 to 14000 g/mol for 15 minutes and 30 minutes of reaction time. This experiment utilized exactly similar procedure as given for 1st experiment.

4.6 Optimization of continuous flow polymerization

The details of experiments are described below and given in **Table 4.2**. The molecular weight of polymers synthesized in this section was checked using Chloroform GPC.

1st Flow Set up:

Here, identical quantities of monomers, catalyst, and solvents as described in the **Section 4.4** were taken in a Schlenk tube. Further, toluene (30 mL) was poured in the reaction mixture and purged it with the help of nitrogen gas. Then the reaction mixture was taken out in a 30 mL syringe and placed over a flow-syringe pump and connected it with a flow coil reactor. The flow coil reactor was then immersed in an already heated oil bath. In the first experiment, toluene was utilized as solvent with a flow rate of 0.25 ml/min with oil bath temperature set at 130 °C temperature for 30 minutes. The product was continuously collected in collector. The workup followed the similar procedure as given in **Section 4.4**. The molecular weight of the polymers checked using Chloroform GPC. Mn= 3,300 g/mol.

2nd Flow Set up:

The quantities of monomers, catalyst, and solvents remained consistent with those outlined in the **Section 4.4** and experiment details are summarized in Table 4.2. Mn= 7200 g/mol.

3rd Batch Setup (optimization of o-xylene solvent):

The same amounts of monomers, catalyst, and solvents were used as described in the **Section 4.4**. The batch polymerization reaction was carried out using o-xylene solvent for 6 hours at 120 °C and followed similar procedure as given in **Section 4.4**. Mn= 1800 g/mol.

4th Flow Setup:

The identical quantities of monomers, catalyst, and solvents were utilized as described in the **Section 4.4**. This flow polymerization setup used high boiling o-xylene solvent instead of toluene solvent used in 1st and 2nd flow setup. The conditions for experiments are provided in **Table 4.2** and all-other procedure followed as given for 1st flow setup. Mn= 3000 g/mol.

Sr. No	Solvent	Time	Flow Rate (ml/min)	Temp. (°C)	Molecular Weight (Mn)* (g/mol)	ĐM (Mw/Mn)
1st Flow Setup	Toluene	30 min.	0.25	130 °C	3,300	1.8
2nd Flow Setup	Toluene	1 h	0.091	120 °C	7,200	2.3
3rd Batch Setup	O-xylene	6 h	-	120 °C	1800	3.9
4th Flow Setup	O-xylene	1 h	0.0861	120 °C	3000	4.3

* Molecular weight determined using Chloroform GPC.

ĐM = Polydispersity index (Mw/Mn)

Table 4.2 The optimization details for both batch and continuous flow setups.

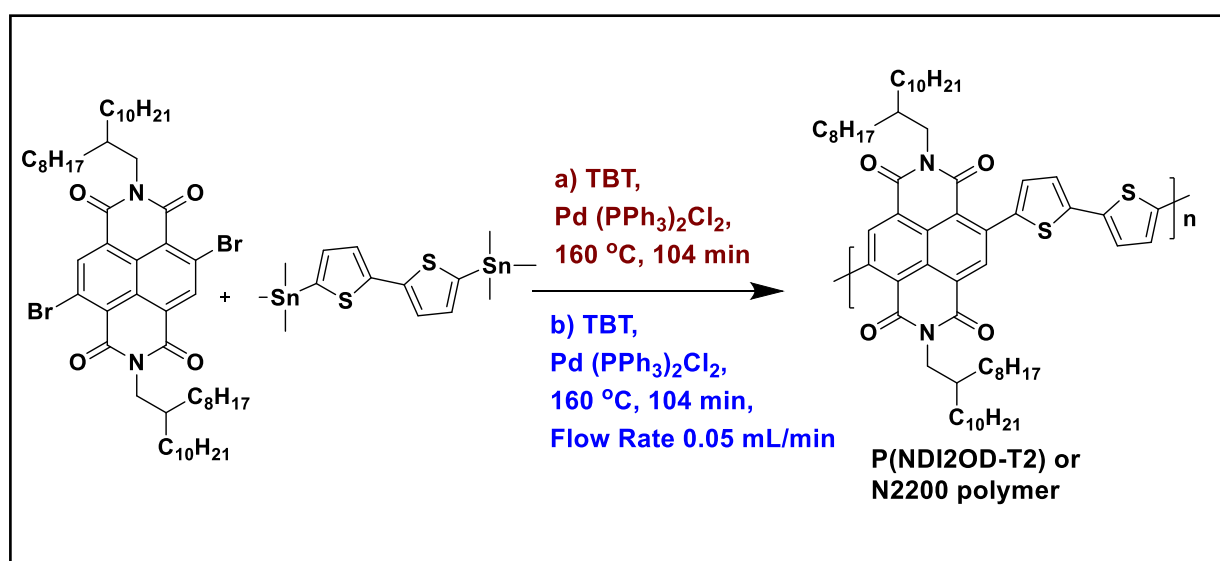
4.7 Batch and Continuous flow synthesis of P(NDI2OD-T2) polymer with Optimized conditions

4.7.1 P(NDI2OD-T2) polymer synthesis by Batch Method

The quantities of monomers, and catalyst remained consistent with those outlined in **Section 4.4**. For this reaction, a new high-boiling solvent, 4-tertiary butyl toluene (10 mL) was employed and the reaction was allowed to proceed for 104 minutes under continuous stirring. The polymerization process followed a procedure similar to that described in **Section 4.4**. The yield obtained was 99%. The ¹H NMR (400 MHz, tetrachloroethane-d₂) spectra showed signals at δ ppm: 8.97-8.13 (br, 2H NDI aromatic), 7.51 (br, 4H bithiophene), 4.32-4.25 (br, 4H), 2.52-2.16 (br, 2H), 1.40 (br, 64 H), and 1.03-1.0 (br, 12 H). The molecular weight was determined using GPC with 1,2,4-Trichlorobenzene at 140 °C. Mn= 78900, Mw: 253000, and ĐM: 1.6

4.7.2 Synthesis of the P(NDI2OD-T2) polymer by Continuous flow synthesis

NDI-2OD-Br₂ (0.500 g, 0.5075 mmol) and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (0.2496 g, 0.5075 mmol) were combined inside a moisture-free Schlenk tube with a magnetic stirring bar. Then, 30 mL of 4-tertiary butyl toluene (TBT) was poured, and purged with nitrogen with constant stirring. Catalyst Pd(Ph₃)₂Cl₂ (0.02537 mmol) was introduced to the reaction mixture under nitrogen atmosphere, followed by another round of nitrogen purging with constant stirring. The reaction mixture was transferred into a syringe and connected to a syringe pump for subsequent processing. The reaction mixture was subsequently fed into a coil reactor positioned in a preheated oil bath set at 160 °C, with a flow rate of 0.05 mL/min, resulting in a 104-minute residence time for polymerization. The product was continuously collected in collector. The remaining procedure is similar to that outlined in **Section 4.4**. The yield obtained was 98%. The ¹H NMR (400 MHz, tetrachloroethane-d₂) spectra exhibited signals at δ ppm: 8.97-8.13 (br, 2H NDI), 7.51 (br, 4H bithiophene), 4.32-4.25 (br, 4H), 2.52-2.16 (br, 2H), 1.40 (br, 64 H), and 1.03-1.0 (br, 12 H). The molecular weight was determined using GPC with 1,2,4-Trichlorobenzene at 140 °C. Mn= 61000, Mw: 102000, and ĐM: 1.6.



a)= reaction condition for batch polymerization and

b)= reaction condition for continuous flow polymerization.

Scheme 4.2 illustrates batch and continuous flow synthesis of P(PDI2OD-T2) polymer

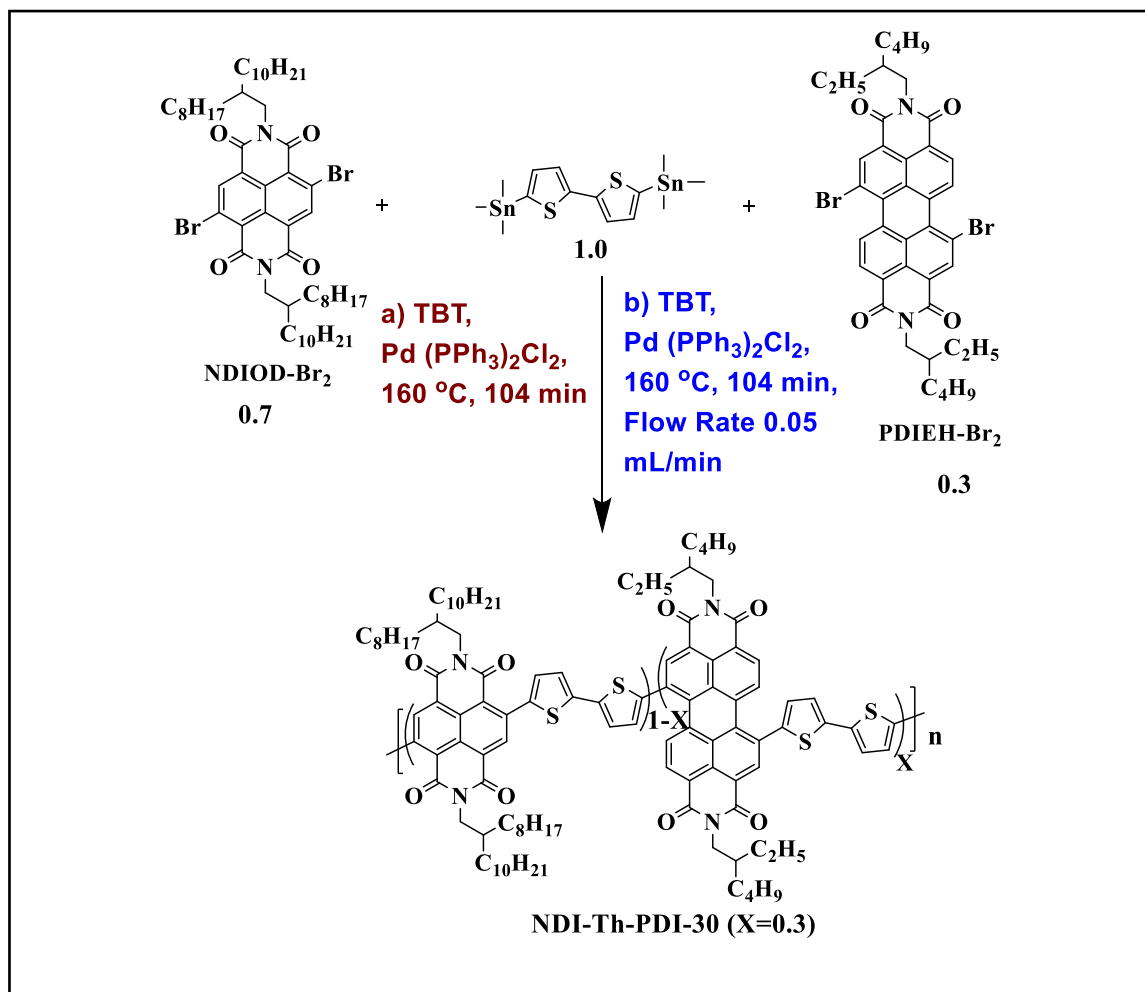
4.8 Experimental conditions for Batch and Continuous flow synthesis of NDI-Th-PDI-30 polymer with Optimized conditions

4.8.1 Synthesis of the NDI-Th-PDI-30 polymer by Batch synthesis

In a dry Schlenk tube (containing magnetic stirring bar), NDI2OD-Br₂ (0.175 g, 0.17789 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (0.125 g, 0.2541 mmol), and PDI2EH-Br₂ (0.059 g, 0.07623 mmol) were combined. After adding 10 mL of 4-tert-butyltoluene, the mixture was nitrogen-purged for 30 minutes with continuous stirring. The catalyst Pd(Ph₃)₂Cl₂ (0.01270 mmol) was added to the reaction mixture. The remaining steps were completed in accordance with the procedure described in **Section 4.7.1**. Yield: (80%). ¹H NMR spectrum (400 MHz, tetrachloroethane-d₂) δ ppm: 8.81-8.74 (br, 2H NDI aromatic and 2H PDI aromatic), 8.40 (br, 4H PDI aromatic), 7.36-7.30 (br, 4H bithiophene), 4.12 (br, 8H), 2.0 (br, 4H), 1.34-1.23 (br, 80H), 0.91-0.83 (br, 24 H). The molecular weight was determined using GPC with 1,2,4-Trichlorobenzene at 140 °C. Mn: 11500, Mw: 31500, ĐM: 2.7.

4.8.2 Synthesis of the NDI-Th-PDI-30 polymer by continuous flow

NDI2OD-Br₂ (0.350 g, 0.3558 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene, 0.250 g (0.5082 mmol) and PDI2EH-Br₂ 0.118 g (0.1525 mmol) were taken in dry Schlenk tube and 30 mL of 4-tertiary butyl toluene and Pd(Ph₃)₂Cl₂ (0.02541 mmol) catalyst was added. The subsequent steps were carried out following the procedure outlined in **Section 4.7.2**. Yield: (96.5%). ¹H NMR spectrum (400 MHz, tetrachloroethane-d₂) δ ppm: 8.83-8.74 (br, 2H NDI and 2H PDI), 8.40-8.39 (br, 4H PDI), 7.37-7.30 (br, 4H bithiophene), 4.12 (br, 8H), 2.0 (br, 4H), 1.33-1.23 (br, 80H), 0.92-0.82 (br, 24 H). The molecular weight was determined using GPC with 1,2,4-Trichlorobenzene at 140 °C. Mn: 28900, Mw: 59200, ĐM: 2.0.



a)= reaction condition for batch polymerization and

b)= reaction condition for continuous flow polymerization.

Scheme 4.3 Batch and continuous flow synthesis of NDI-Th-PDI-30 polymer.

4.9 RESULT AND DISCUSSION

4.9.1 Synthesis and characterization

The method for synthesizing the NDI-2OD-Br₂ monomer is detailed in **Chapter 3.2.7**, while the PDI2EH-Br₂ monomer was prepared by brominating the 3,4,9,10-Perylenetetracarboxylic dianhydride, as outlined in **Chapter 2.2.10**, followed by imidization with 2-Ethylhexyl amine. **Scheme 1** depicts the synthetic process for producing PDI2EH-Br₂. The structural analysis of the monomer PDI2EH-Br₂ via ¹H, ¹³C NMR spectroscopy and MALDI spectra is illustrated in **Figures 4.2, 4.3** and **4.4**. The conjugated polymer was conventionally synthesized through batch polymerization, which posed several drawbacks including extended reaction times, scalability issues, hindrances in commercialization, and variability in molecular weight and

polydispersity from batch to batch. To address these challenges, we utilized alternative synthetic techniques such as microwave and continuous flow methods. Initially, we conducted three sets of P(NDI2OD-T2) batch polymerization reactions via Stille polymerization, varying the reaction times to optimize the process. These durations ranged from 6 hours to 24 hours. Subsequently, we achieved comparable molecular weights for polymers synthesized under different reaction durations. The analysis of the polymers' molecular weights (M_n & M_w) and polydispersity index ($\mathcal{D}$) was conducted via gel permeation chromatography (GPC), utilizing chloroform as the eluent. The M_n ranged from 13000 to 14500 g mol⁻¹, with dispersity values varying from 3.2 to 3.6, as summarized in **Table 4.1**.

Subsequently, the polymerization of P(NDI2OD-T2) was then carried out with the assistance of microwave. The monomers, catalyst, and solvents were combined in flask along with toluene as the solvent. Subsequently, the round-bottom flask was placed in the microwave oven. The four different sets of polymerization reactions were performed with varying conditions such as power (350 watt to 750 watts to achieve 90-160 °C) and reaction time (15 min to 1 hour) and details are summarized in **Table 4.1**. GPC was used to calculate the molecular weights of the polymers, with chloroform serving as the solvent. The number average molecular weight and dispersity of polymers ranged from 6500 to 15000 g/mol and 1.7 to 3.4 respectively and the details are provided in **Table 4.1**. The highest molecular weight of 15000 g/mol was obtained for the 2nd experiment with 1 hour reaction time. Consequently, the comparable molecular weight of 14000 g/mol was obtained for the 4th experiment within 30 minutes of reaction time. Overall, we were able to achieve a comparable molecular weight and polydispersity within a very less reaction time of 30 minutes. These molecular weights are comparable with batch synthesized polymer in this work (**Section 4.4**) and with many reports where P(NDI2OD-T2) polymerization require around 3 days of reaction time.³²⁻³⁵

Afterwards, we have carried out continuous flow polymerization in order to make use of the standardized conditions in microwave polymerization. The monomers, catalyst, and solvents were combined in a Schlenk tube, followed by the addition of solvent to the reaction mixture, which was subsequently purged with nitrogen gas. Subsequently, the reaction mixture was transferred into a 30 mL syringe and connected to a flow reactor via a syringe pump. The flow reactor, already immersed in a preheated oil bath, facilitated the initial setup. The experimental conditions are provided in **Table 4.2**. The first experiment was carried out utilizing toluene and only oligomers of 3,300 g/mol number average molecular weight could be obtained. This could

be attributed to the vaporizing of toluene and escaped from the reactor due to its low boiling point, while oligomer molecules became trapped inside the reactor. Hence, for the second experiment, the temperature was lowered to 120°C, and the residence time of the reaction was extended to 1 hour. Despite these adjustments, the number average molecular weight only increased to 7200 g/mol, which remained low compared to literature reports and polymers synthesized via microwave techniques. Further, we conducted batch and continuous flow polymerization using high boiling o-xylene as the solvent by replacing toluene. Initially, a batch polymerization reaction was set up using o-xylene solvent following a similar procedure to that used with toluene. The reaction was carried out for 6 hours at 120 °C, but only oligomers with Mn of 1800 g/mol were obtained. Subsequently, continuous flow polymerization was conducted using o-xylene solvent, employing a procedure similar to that used with toluene. In this experimental setup, the reaction was carried out at a temperature of 120°C with a residence time of 1 hour. However, in this continuous flow experiment, only oligomers with Mn of 3000 g/mol were obtained. The details of these preliminary experiments are summarized in **Table 4.2**.

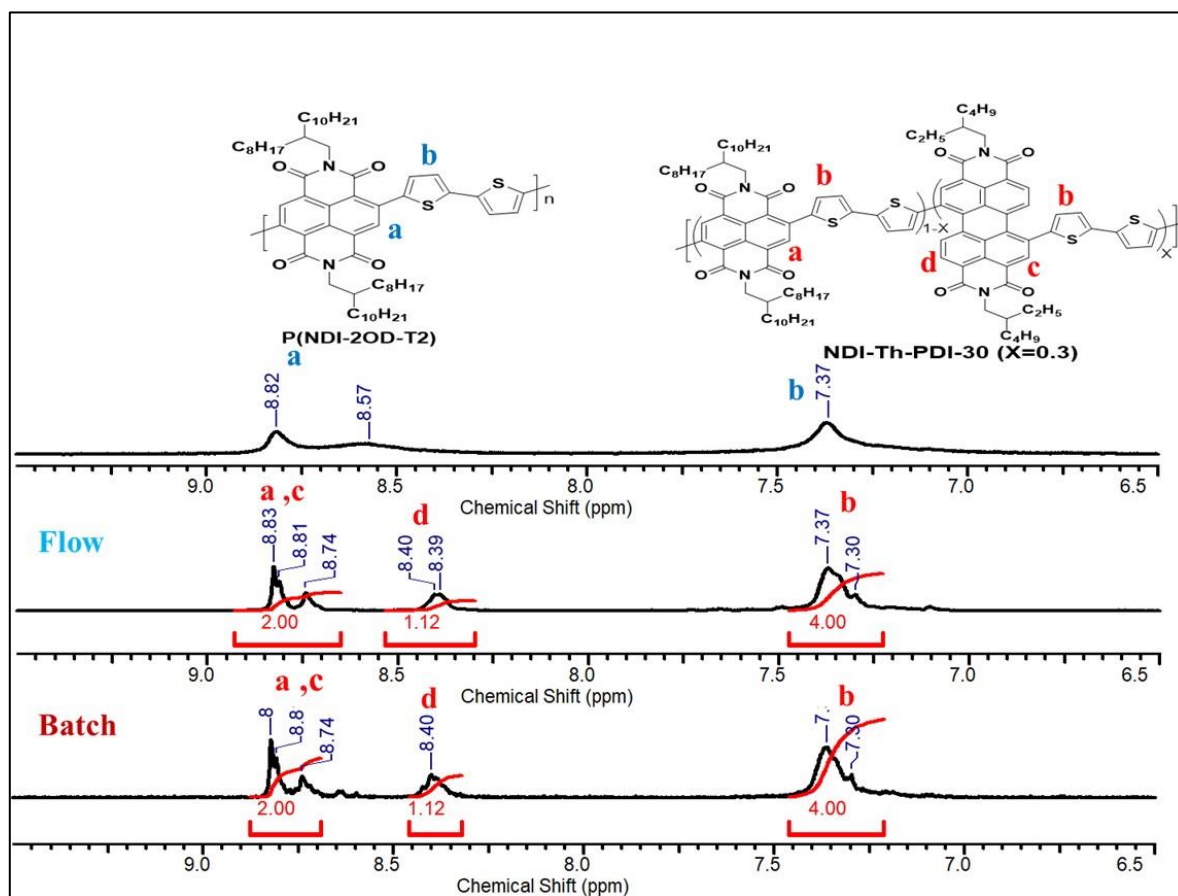


Figure 4.5 ¹H NMR spectra of polymers recoded in tetra chloro ethane-d₂.

In last **chapter 2**, we reported a modified Stille technique that was used to synthesize P(NDI2OD-T2) polymer. The batch polymerization reaction completed with t-butyl toluene (TBT) as the solvent at 160 °C, resulted in a M_n of 188 kDa and a dispersity of 3.1, all accomplished within a 2-hour timeframe. The molar mass was determined using GPC, where polystyrene standards and tetrahydrofuran (THF) were employed as the eluent. In this chapter also, after numerous trials, we opted for t-butyl toluene solvent as a superior option for the polymerization of P(NDI2OD-T2) and NDI-Th-PDI-30. These Both copolymers synthesized using t-butyl toluene solvent were optimized. **Scheme 4.2** and **4.3** shows the synthesis of P(NDI2OD-T2) and NDI-Th-PDI-30 polymer by batch and continuous flow technique. Initially, the synthesis of P(NDI2OD-T2) polymer was conducted, with t-butyl toluene solvent. The monomers, catalyst and solvent were combined and agitated for 104 minutes at 160°C in batch polymerization. In the continuous flow setup, the reaction mixture was extracted using a syringe connected to a syringe pump, which was then connected to a coiled flow reactor. A flow rate of 0.05 ml/min was maintained to achieve a residence time of 104 minutes for the reaction. Subsequently, the product was continuously collected in collector. The random copolymer NDI-Th-PDI-30 was also synthesized using similar procedure. To synthesize the NDI-Th-PDI-30 polymer, 0.7 mol% of NDI-2OD-Br₂ and 0.3 mol% of PDI-EH-Br₂ monomer were reacted with 1.0 mol% of 5,5'-bis(trimethylstannyl)-2,2'-bithiophene, utilizing the Pd(Ph₃)₂Cl₂ catalyst. The similar procedure was followed for the synthesis as provided for the P(NDI2OD-T2) polymerization. The polymers were soluble in chloroform and tetrachloroethane. The structure of polymers was determined using ¹H NMR spectroscopy using Tetra-chloroethane-d₂ solvent. Furthermore, we assessed the incorporated PDI percentage in the random copolymer using ¹H NMR spectroscopy. **Figure 4.5** depicts the ¹H NMR spectra of the polymers P(NDI2OD-T2) and NDI-Th-PDI-30. The ¹H NMR spectrum of the P(NDI2OD-T2) polymer displayed an additional broad peak around ~8.57 ppm, attributed to significant interchain aggregation.³⁶⁻³⁸ Interestingly, in the NDI-Th-PDI-30 random copolymers, the aggregation peak at 8.57 disappeared after the inclusion of Perylene (PDI) core. Moreover, two additional peaks emerged, corresponding to the aromatic protons of the PDI units, with one peak merging with the NDI aromatic proton. Consequently, the PDI incorporation was estimated to be 28% for both the batch and flow-synthesized NDI-Th-PDI-30 random copolymer. The “d” protons at 8.40-39 ppm corresponding to the 4 H aromatic proton of PDI with an integration of 1.12 which means 1 proton is equivalent to 0.28 i.e. 28% incorporation.

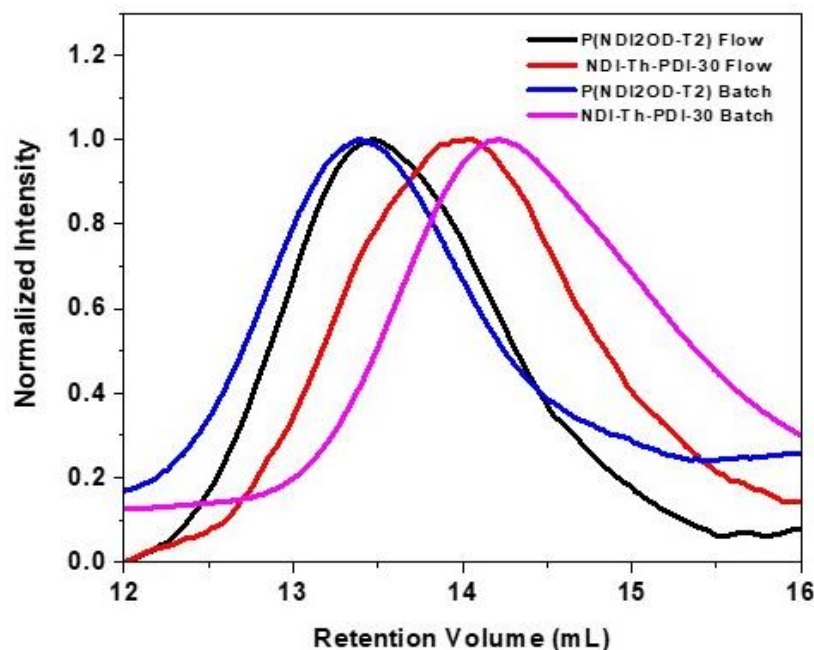


Figure 4.6 Gel permeation chromatogram (GPC) of P(NDI2OD-T2) and NDI-Th-PDI-30 polymer synthesized by batch and continuous flow recorded in 1,2,4 Trichlorobenzene at 140 °C.

Table 4.3 The molecular weight and thermal characterization of polymers.

Sr. No.	Polymers	Mn* (g mol ⁻¹)	Mw (g mol ⁻¹)	ĐM	% Yield	Td (°C) TGA (10%)	Tm (°C)	ΔHm d (J/g)
1.	P(NDI2OD-T2) Batch	78900	125300	1.6	99	450	311.4	9.93
2.	P(NDI2OD-T2) Flow	61000	102000	1.6	98	456	318.4	13.39
3.	NDI-Th-PDI-30 Batch	11500	31500	2.74	80	456	265.8	2.88
4.	NDI-Th-PDI-30 Flow	28940	59180	2.0	96.4	454	282.4	4.59

* Molecular weight determined using GPC with 1,2,4-Trichlorobenzene at 140 °C.

ĐM = Polydispersity index (Mw/Mn)

The molecular weights of P(NDI2OD-T2) and NDI-Th-PDI-30 polymers synthesized via batch and continuous flow methods were assessed using 1,2,4-Trichlorobenzene as the eluent at 140 °C, as depicted in **Figure 4.6**. P(NDI2OD-T2) polymer synthesized by batch and flow

demonstrated highest molecular weight (M_n) of 78,900 g/mol and 61,000 g/mol, respectively, along with a low polydispersity of 1.6. The batch and continuous flow synthesized NDI-Th-PDI-30 exhibited M_n of 11500 and 28900 with polydispersity of 2.7 and 2.0 respectively. The NDI-Th-PDI-30 copolymer showed comparatively low molecular weight, which could be due to the lower solubility of PDI core unit. These number average molecular weights are comparable or higher than that of literature reports.

4.9.2 Photophysical Properties

The UV-vis absorption spectra of P(NDI2OD-T2) and NDI-Th-PDI-30 polymers synthesized via batch and continuous flow methods were recorded in chloroform and are illustrated in **Figure 4.7**. The copolymers synthesized using the batch method exhibited absorption spectra akin to those observed in the polymers synthesized using continuous flow method. The P(NDI2OD-T2) polymer displays π - π stacking interactions among the aromatic protons of naphthalene, evident from the absorption spectra. These spectral analyses provide information about the ordering within the P(NDI2OD-T2) polymer. Both the polymer exhibited two absorption bands in the spectra: one attributed to the π - π^* transition (ranging from 300 nm to 450 nm) and the other corresponding to the intramolecular charge transfer (ICT) band, observed between 500 and 800 nm.^{34,36} The P(NDI2OD-T2) polymer displayed an absorption peak at around 400 nm (π - π^*) and another peak at around 686 nm (inter/intramolecular charge transfer). In the NDI-Th-PDI-30 random copolymers, a hypsochromic shift (blue-shift) was observed in the ICT absorption peak, which occurred at 610 nm. This shift is attributed to the decreased planarity in NDI-Th-PDI-30 than P(NDI2OD-T2). The P(NDI2OD-T2) polymer is known for its propensity to self-aggregate in chloroform solvent, resulting in a red-shifted band.³⁶ This aggregation reduced after inclusion of PDI core in the backbone of polymer.³⁹ As a result, the inter/intramolecular charge transfer peak shifted to lower wavelengths. Additionally, NDI-Th-PDI-30 random copolymer showed a new peak around 500 nm. The notable blue shift of the ICT band of NDI-Th-PDI-30 random copolymer suggests reduced interchain stacking and aggregation compared with P(NDI2OD-T2). This provides benefits for mixing with donor polymers and thereby promoting compatibility in all-PSCs devices. Overall, both the batch and continuous flow synthesized polymers demonstrated similar photophysical properties, which is significant for their potential applications in energy-related fields.

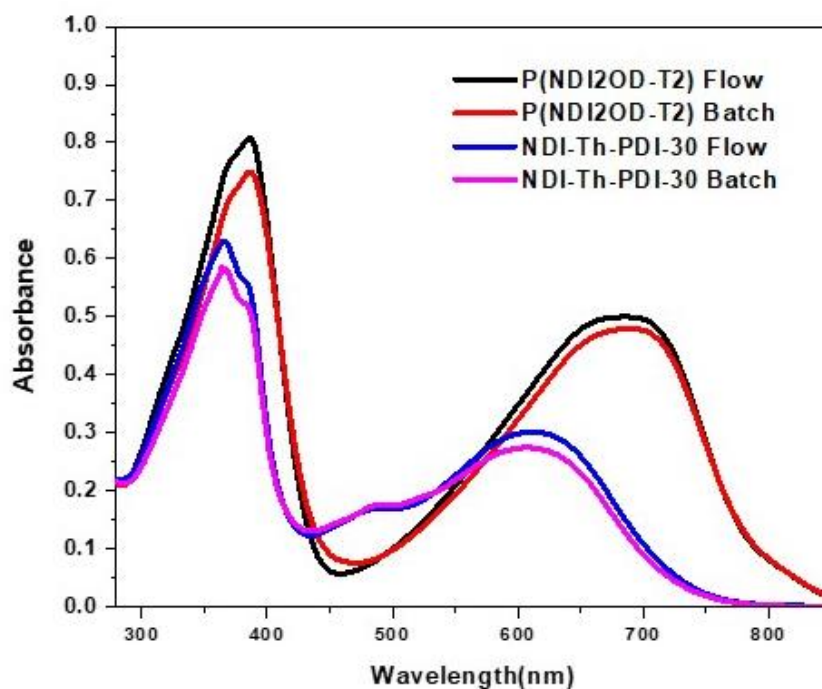


Figure 4.5 Represents the UV-vis absorption spectra of the polymers.

4.9.3 Thermal Properties

The thermal characteristics of the polymer were examined using TGA and DSC studies. The TGA data is depicted in **Figure 4.8**, demonstrating the high thermal stability of the polymers, which remained stable up to 450 °C. The Td (10%) values are given in **Table 4.3**. All DSC thermograms for all the polymers acquired during the 2nd heating and 1st cooling cycles, when they were heated in an environment of nitrogen from -50 °C to 330 °C at a rate of 10 °C/min. Plots depicting these curves are provided in **Figure 4.9**. The melting features of polymers are affected by their crystallinity, which is determined by factors such as molecular weight and dispersity of molar mass.⁴⁰⁻⁴² The melting temperature (T_m) and enthalpy (ΔH_m) derived from DSC provide crucial insights into the degree of crystallinity exhibited by the polymer sample. The P(NDI2OD-T2) synthesized via batch process displayed a wide thermal transition, featuring an endothermic peak (T_m) at 311 °C, with a corresponding ΔH_m of 9.93 J/g. The P(NDI2OD-T2) synthesized via continuous flow showed a T_m of 318 °C and ΔH_m of 13.39 J/g. The NDI-Th-PDI-30 batch synthesized random copolymer exhibited a melting transition at 266 °C with ΔH_m of 2.88 J/g. The NDI-Th-PDI-30 random copolymer synthesized by continuous flow process exhibited a melting transition at 282 °C with ΔH_m of 4.59 J/g. The melting enthalpy (ΔH_m) acquired from the melting transition is associated with the polymer's crystallinity and also serves as an indicator of its defect-free nature. The incorporation of

perylene in NDI-Th-PDI-30 resulted in lower the melting the temperatures and enthalpies compared it with that of P(NDI2OD-T2) polymer. This suggests a reduction in the planarity of the polymer backbone and a reduction in interchain aggregation.

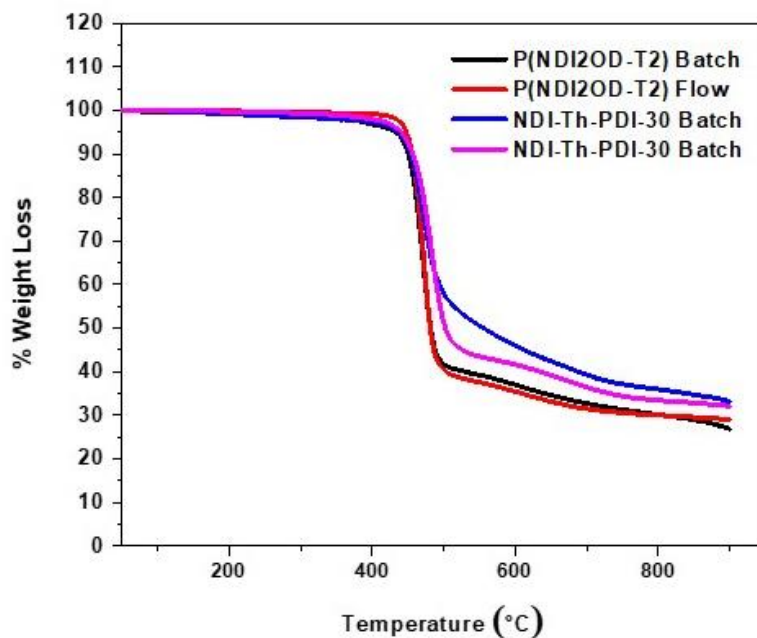


Figure 4.8 Thermogravimetric Analysis (TGA) of polymers.

The flow synthesized P(NDI2OD-T2) polymer exhibited high melting temperature and enthalpy compared with batch synthesized polymer as the former are associated with higher molecule weights. This indicates that continuous flow approach could provide a defect free polymer. The flow synthesized NDI-Th-PDI-30 random copolymer exhibited higher value of melting temperature and melting enthalpy compared with batch synthesized NDI-Th-PDI-30 copolymer. These findings could be attributed to the elevated molecular weight of the polymer and reduced polydispersity. This observation reinforces the theory of better polymer structural ordering achieved through the continuous flow polymerization compared with batch synthesis.⁴³⁻⁴⁴

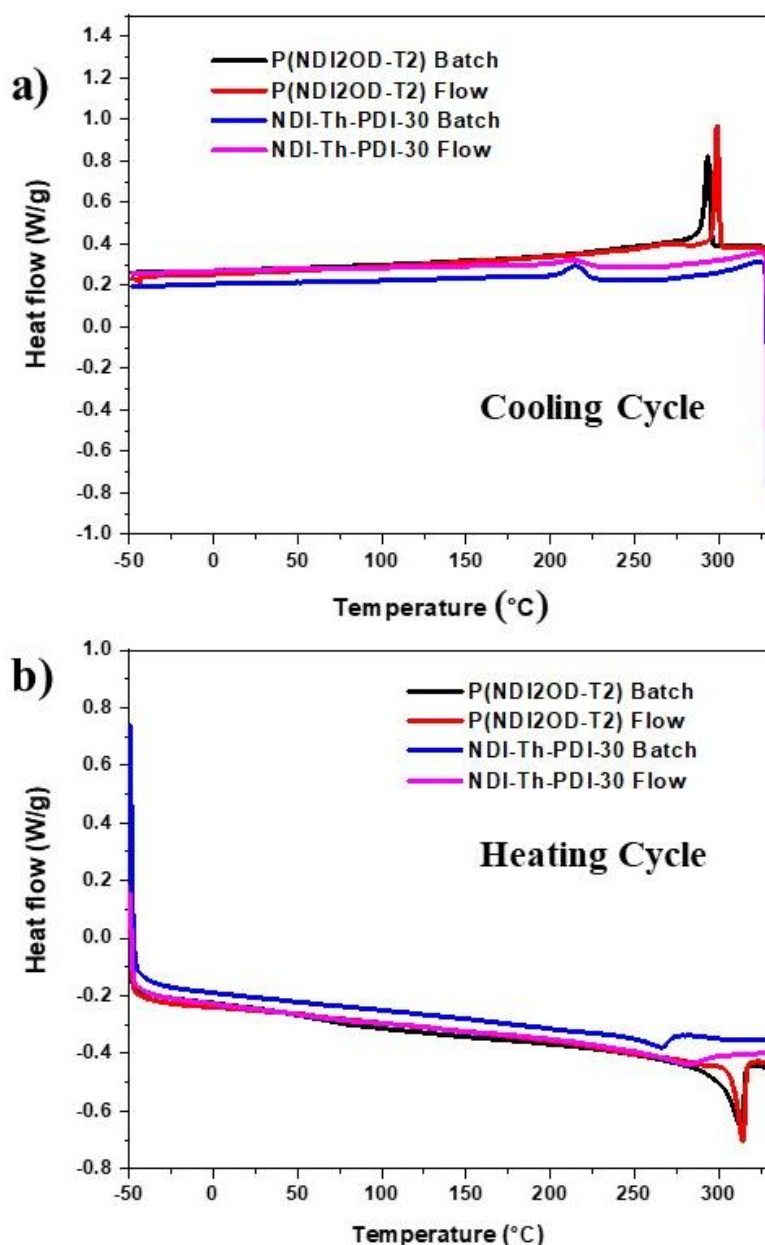


Figure 4.9 Differential Scanning Calorimetry (DSC) of polymers.

4.10 Conclusion

In this chapter, the synthesis of rylenebisimide based donor-acceptor conjugated polymers were accomplished by stille polymerization in batch, microwave and continuous flow polymerization methods. We have sucessfully synthesized P(NDI2OD-T2) donor acceptor polymer within 30 minutes time by Microwave Synthesis and achieved benefits in terms of reaction time reduction by energy efficient technique. Further, high molecular weight P(NDI2OD-T2) polymer and comparable molecular weight of NDI-Th-PDI-30 polymer were

synthesized in batch method by using high boiling 4-tertiary butyl toluene as solvent, which promises to be an efficient solvent for this type of polymerization. Consequently, 4-tertiary butyl toluene was used in scalable and highly efficient continuous flow technique for stille polymerization. P(NDI2OD-T2) polymer was synthesized using 4-tertiary butyl toluene solvent in continuous flow polymerization method and obtained a number average molecular weight (M_n) of 61000 g/mol with low polydispersity of 1.6. This polymer was synthesized within very short time of 104 min where as it requires around 3 days of reaction time generally.³²⁻³⁵ Similarly, perylene incorporated NDI-Th-PDI-30 random copolymer was also successfully synthesized using Continuous Flow method. This polymerization can provide advantages in terms of reduction of reaction time, reproducible molecular weight and dispersity for commercialized and scalable approach. We have successfully incorporated perylene (PDI) molecule in random copolymer NDI-Th-PDI-30 by both batch and continuous flow method. The percentage incorporation of PDI core was calculated to be 28 % by using ^1H NMR spectroscopy. The perylene incorporation decreases the planarity of the polymer backbone and mitigated interchain aggregation. This decreased aggregation provides benefits while mixing with donor polymers and thereby promoting compatibility in all-PSCs devices.

The P(NDI2OD-T2) synthesized via continuous flow exhibited a notably higher melting temperature (T_m) of 318 °C, coupled with a melting enthalpy (ΔH_m) of 13.39 J/g. This value is significantly higher than that observed for the batch synthesized polymer and closely approaches the highest reported value of 14.46 J/g (melting transition T_m at 314.80 °C).³⁵ The NDI-Th-PDI-30 random copolymer synthesized via continuous flow showed a melting transition at 282 °C, with a ΔH_m of 4.59 J/g. This value is higher than that of the batch synthesized polymer, which exhibited a melting transition peak observed at 266 °C, with a ΔH_m of 2.88 J/g. The thermal study proved that the polymers synthesized via continuous flow polymerization provided a better ordered structure and defect-free polymer. In summary, this study presents a better synthetic approach like Microwave and continuous flow for donor-acceptor conjugated polymers synthesis via Stille polymerization. This method offers advantages such as the ability to achieve high molecular weight polymers within a short reaction time, reproducibility in molecular weight and polydispersity, scalability, commercialization potential, and enhanced structural order.

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CHAPTER 5

Conclusion and Future Prospective

5.1 CONCLUSION

Meeting the escalating global energy demand necessitates substantial progress in tapping into renewable energy sources, alongside the imperative for robust energy storage solutions. Donor-acceptor conjugated polymers serve as efficient materials crucial for applications in organic light-emitting diodes (OLEDs), organic polymer solar cells, batteries, and supercapacitors. These polymers are widely employed in organic electronic and optoelectronic applications owing to their favorable characteristics, such as high charge carrier mobilities, straightforward processability, broad absorption across the entire visible spectrum, lightweight nature, and facile synthesis. Among the various donor-acceptor conjugated polymers, rylenebisimide based donor-acceptor conjugated polymers are promising materials for a wide range of energy applications. Despite the considerable potential exhibited by existing donor-acceptor conjugated polymers, the synthesis of novel polymers and the study of existing ones remain essential for further progress in energy applications. By enabling the development and study of tailored materials with improved performance, addressing existing limitations, fostering innovation, and ensuring sustainability and cost-effectiveness in energy technologies, we can advance our understanding and create more efficient solutions. In this context the present thesis titled as **“Batch and Continuous flow synthesis of Rylenebisimide polymers and their application in Energy Storage”** focused on synthesis of perylene and naphthalene-based D-A conjugated polymers for energy application. We have synthesized perylene and naphthalene-based D-A conjugated polymers and their composites with carbon nanotube and employed as efficient electrode material for supercapacitor energy storage. Additionally, we have also focused on the synthesis of highly efficient D-A (n-type) conjugated polymers by a beneficial technique such as Microwave and Continuous flow polymerization methods.

In chapter 2, we synthesized perylenebisimide-based donor-acceptor conjugated polymer P(PDI2OD-T2) and its composites via optimized Stille polymerization, reducing the synthesis time. By incorporating multiwalled carbon nanotubes (MWCNT) into the polymer matrix *in-situ*, we notably enhanced the conductivity of the composite polymer, designated as P-2. The improved surface area and pore structure facilitated electrolyte ion movement, crucial for supercapacitor electrode application. Various characterization techniques were employed to evaluate the material. The donor-acceptor composite polymer P-2 exhibited impressive capacitance values, reaching 93 F g^{-1} at a current density of 0.5 A g^{-1} . When configured into a symmetric supercapacitor with both liquid organic (LE--P-2||P-2) and quasi-solid gel (QE-P-2||P-2) electrolytes, the device maintained excellent capacitance - 85.4 F g^{-1} and 84.2 F g^{-1}

respectively at a current rate of 0.25 A g^{-1} and an operational voltage window of 3.1 V, with robust cycle stability. The energy and power densities of the device were impressive with values of 112.4 Wh kg^{-1} and 18600 W kg^{-1} respectively. A practical demonstration using an LED light bulb further showcased the device's capabilities. This study represents a significant advancement in synthetic techniques for developing donor-acceptor conjugated polymers for high-performance supercapacitors, offering extensive potential ranges and significant power densities.

In Chapter 3, we developed a straightforward synthesis protocol for P(NDI2OD-T2) (P-0) polymer with high molecular weight within a short period (2h) using the modified Stille polymerization method for the first time. The incorporation of MWCNT during the polymerization reaction significantly improved the physicochemical properties of the composite material compared to the pristine polymer. Specifically, the composite sample prepared with 35% MWCNT content (C-3) using the *in-situ* approach exhibited an 80 mAh g^{-1} (polymer) discharge capacity, substantially higher than that of the pristine polymer and the composite prepared by physically mixing MWCNT with the same quantity (Ex C-30). The C-3 polymer composite was further utilized for fabricating a high-voltage (2.4 V) hybrid supercapacitor, employing the C-3 composite as a negative electrode (battery-type) and activated carbon (AC, capacitive electrode) as the positive electrode material. The electrochemical performance of the AC||C-3 device was evaluated in 1M LiClO_4/PC liquid electrolyte (LS-HSC) and PMMA/PC/ LiClO_4 polymer gel electrolyte (QSS-HSC). Both devices exhibited comparable performance, attributed to the porous morphological architecture of the C-3 composite, facilitating intimate contact of the polymer with the MWCNT conducting framework. This study presents new avenues for designing robust electrode materials based on conducting polymers for non-aqueous hybrid supercapacitors.

Thesis chapters 2 and 3 mainly focused on the batch synthesis of rylenebisimide-based donor-acceptor (D-A) conjugated polymers and their composites for application as electrode materials in supercapacitors. While batch polymerization is a widely used method for synthesizing D-A conjugated polymers, it comes with inherent limitations. These limitations include prolonged reaction times and limited scalability due to variations in molecular weight and polydispersity from one batch to another. Therefore, the development of innovative synthetic approaches to address the reproducibility issue represents a significant advancement toward the commercialization and wider adoption of these materials in high-performance organic electronic devices.

In Chapter 4, we demonstrated the synthesis of rylenebisimide-based donor-acceptor conjugated polymers using Stille polymerization in batch, microwave, and continuous flow methods. Initially, we successfully synthesized the P(NDI2OD-T2) donor-acceptor polymer within 30 minutes using Microwave Synthesis, benefiting from reduced reaction time and energy efficiency. Subsequently, high molecular weight P(NDI2OD-T2) and NDI-Th-PDI-30 copolymers were synthesized in batch mode using 4-tertiary butyl toluene as a solvent, providing an efficient medium for this type of polymerization. Continuing, we employed the same high boiling solvent in a scalable and highly efficient continuous flow technique for Stille polymerization. The P(NDI2OD-T2) polymer synthesized in continuous flow exhibited a significantly reduced reaction time of 104 minutes compared to the approximately 3 days required for batch synthesis, achieving a molecular weight (M_n) of 61,000 g/mol with low polydispersity (1.6). Likewise, the NDI-Th-PDI-30 random copolymer incorporating perylene was effectively synthesized via the continuous flow method, offering advantages in terms of reaction time reduction, reproducible molecular weight, and dispersity for commercialized and scalable production.

Furthermore, we successfully incorporated perylene (PDI) molecules in the NDI-Th-PDI-30 random copolymer using both batch and continuous flow methods, with the percentage incorporation calculated to be 28% using ^1H NMR spectroscopy. This perylene incorporation contributed to decreasing the planarity of the polymer backbone and mitigating interchain aggregation, enhancing compatibility in all-PSCs devices. In terms of thermal properties, the polymers synthesized via continuous flow exhibited higher melting temperatures (T_m) and melting enthalpies (ΔH_m) compared to batch-synthesized polymers. This suggests that continuous flow synthesis resulted in better ordered structures and defect-free polymers. In summary, our study highlights the efficacy of Microwave and continuous flow methods for synthesizing donor-acceptor conjugated polymers via Stille polymerization. These methods offer advantages such as the ability to achieve high molecular weight polymers within a short reaction time, reproducibility in molecular weight and polydispersity, scalability, commercialization potential, and enhanced structural order.

5.2 FUTURE PROSPECTIVE

Supercapacitors (SCs) have emerged as promising candidates for energy storage, with electrode materials playing a crucial role in determining their performance. Conjugated polymers, particularly D-A conjugated polymers, have garnered attention for their numerous advantages. Incorporating conducting or conjugated polymers with carbon materials like carbon nanotubes (CNTs), graphene, activated carbons, and carbon aerogels enhances mechanical stability, conductivity, and surface area, thereby improving charge retention and capacitive behavior. Among various synthesis methods, *in-situ* synthesis of polymer-CNT composites has shown exceptional performance. This thesis explores the *in-situ* synthesis approach for rylenebisimide-based D-A conjugated polymers. While Stille polymerization is commonly used for synthesizing D-A polymers, it suffers from drawbacks like the use of toxic tin (Sn) metal and high cost. Direct (Hetero)arylation Polymerization (DHAP) offers advantages such as atom-economy, mild reaction conditions, substrate versatility, and reduced waste generation, making it an attractive alternative for synthesizing polymer composites, particularly for supercapacitor electrode applications. **Figure 6.1** illustrates the envisioned setup for *in-situ* polymerization with MWCNT using Direct (Hetero)arylation Polymerization.

Figure 6.1 illustrates the conventional Stille polymerization process, which necessitates a monomer tin compound to eliminate hazardous byproducts and requires pre-functionalization of monomers. In contrast, DHAP polymerization does not require prefunctionalization of monomers and does not generate toxic byproducts. Our objective is to develop a rylenebisimide based D-A conjugated polymer composite with MWCNT *in-situ* using the environmentally friendly DHAP approach. This method offers several advantages including atom-economy, mild reaction conditions, reduced generation of hazardous waste, and environmental friendliness.

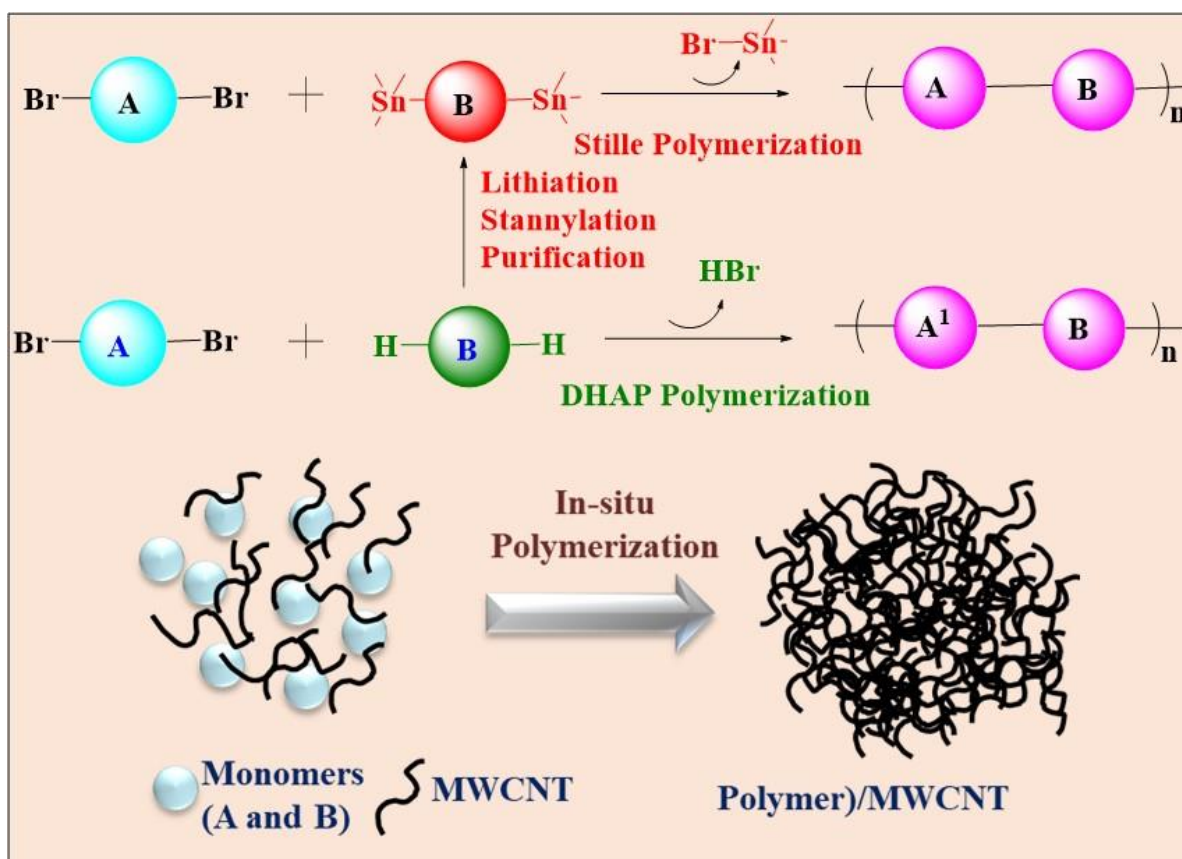


Figure 6.1 The proposed configuration for the *In-situ* polymerization with MWCNT by Direct (Hetero)arylation Polymerization.

ABSTRACT

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Faculty of Study: Chemical Science **Year of Submission:** 2024
AcSIR academic center/CSIR Lab: CSIR-National Chemical Laboratory, Pune **Name of the Supervisors:** Dr. Asha S. K.
Title of the thesis: Batch and Continuous flow synthesis of Rylenebisimide polymers and their application in Energy Storage

Addressing the global energy demand requires advances in renewable energy utilization and reliable storage solutions. Donor-acceptor conjugated polymers are pivotal in OLEDs, organic solar cells, batteries, and supercapacitors due to their broad visible absorption and mobility. Despite their potential, synthesizing and studying new and existing polymers is crucial for energy progress. The primary objective of this thesis is to synthesize donor-acceptor conjugated polymers derived from Rylene bisimides and assess their applicability as electrode materials in supercapacitors. Furthermore, the thesis aims to synthesis of these polymers by utilizing efficient and scalable synthetic techniques.

Chapter 2 focuses on synthesizing P(PDI2OD-T2) polymer and its composite with MWCNTs, utilized as electrodes for high-voltage symmetric supercapacitors, achieving a specific capacitance of 84.2 F g^{-1} at 0.25 A g^{-1} with excellent cycle stability, a high voltage window of 3.10 V , and a notable power density of 18600 W kg^{-1} in quasi-solid devices. In Chapter 3, P(NDI2OD-T2) and its composites, exhibiting high molecular weights ($M_n/M_w = 188/597 \text{ kDa}$, yield = 95%) within 2 hours and utilized as efficient negative electrode material for high-voltage (2.4 V) asymmetric hybrid supercapacitor. Chapter 4 showcases the synthesis of rylenebisimide-based polymers via Stille polymerization in batch, microwave, and continuous flow methods. Microwave synthesis of P(NDI2OD-T2) polymer was achieved in just 30 minutes. The continuous flow polymerization yielded high molecular weight P(NDI2OD-T2) ($M_n = 61,000 \text{ g/mol}$) and NDI-Th-PDI-30 ($M_n = 29,000 \text{ g/mol}$) copolymers within 104 minutes, offering advantages such as rapid polymerization, reproducibility, scalability, and enhanced structural order. This thesis primarily focused on synthesizing polymer composites for use as efficient electrode materials in supercapacitors, alongside the synthesis of donor-acceptor (D-A) conjugated polymers via microwave and continuous flow efficient methods.

List of Publications Emanating from the Thesis Work

1. **Bhaiyyasaheb(Aryan) A. Wavhal**, M. Ghosh, S. Sharma, S. Kurungot and S. K. Asha, A high-voltage non-aqueous hybrid supercapacitor based on the N2200 polymer supported over multiwalled carbon nanotubes. *Nanoscale*, **2021**, *13*, 12314–12326.
2. **Aryan A. Wavhal**, S. Dilwale, N. R. Kakde, P. P. Puthiyaveetil, M. Prakash, S. Kurungot and S. K. Asha, High-Voltage Symmetric Supercapacitor Electrodes Via In Situ Synthesized Multiwalled Carbon Nanotube-Doped Perylenebisimide-Based Donor–Acceptor Conjugate Polymer P(PDI2OD-T2). *J. Phys. Chem. C* **2024**, *128*, 12808–12821.
3. Navnath R. Kakde, H. J. Bharathkumar, **Bhaiyyasaheb(Aryan) A. Wavhal**, A. Nikam, S. Patil, S. R. Dash, K. Vanka, K. Krishnamoorthy, A. Kulkarni and Asha S K, Direct (Hetero)Arylation (DHAP) Polymerization of Conjugated Polymers – New A–B–A Monomer Design for P(NDI2OD-T2) & the Challenges of Adopting DHAP for Continuous Flow Processes. *J. Mater. Chem. C*, **2022**, *10*, 13025–13039.
4. Navnath R. Kakde, **Aryan A. Wavhal** and Asha S K, P(NDI2OD-T2) Polymer Synthesized by Stille Coupling in Batch and Continuous Flow Method. (Manuscript under preparation).

List of Posters Presented with Details

SPSI MACRO Poster Presentation International Conference on Polymer Science and Technology IISER Pune (India) (December **2018**).

Title: Continuous Flow Synthesis of High-Performance n-type Polymers based on Naphthalene and Perylene diimide.

Abstracts: Polyera Activink or N2200 or P(NDI-2OD-T2) is an n-type polymer that has found wide application in the field of all-polymer solar cells (PSCs) and OFET because of its desirable semiconducting and photo-physical properties. This polymer exhibits good solution processability, high crystalline nature and broad absorption in IR and near visible region. The properties of P(NDI-2OD-T2) polymer were tuned by random incorporation of PDI as a co-acceptor. Generally, these polymers were synthesized via Stille polycondensation reaction in batch reactors. The batch-to-batch variability in molecular weight characteristics developed by batch process is a hindrance to reproducible device performance in photovoltaic applications. The continuous flow method of developing conjugated polymers affords a reproducible and scalable method to develop high performance materials that can exhibit enhanced efficiencies in photovoltaic device applications. P(NDI-2OD-T2) was synthesized in the lab by batch process and varying amounts of the higher analogue perylene diimide was introduced into the polymer, which resulted in enhanced all-polymer solar cell device performance due to better blend morphology. Here we report the synthesis of these polymers (P(NDI-2OD-T2) and NDI-Th-PDI-30) by Stille polymerization with continuous flow process. P(NDI-2OD-T2) showed very high molecular weight $M_n=61000$, $M_w=102000$, PDI=1.6 and NDI-Th-PDI-30 polymer exhibit molecular weight $M_n=28900$ g/mol within very short reaction time.

National Science Day 2019 Poster presentation at CSIR-National Chemical Laboratory, Pune, (India). (February **2019**)

Title: Continuous Flow Synthesis of High-Performance n-type Polymers based on Naphthalene and Perylene diimide.

Abstract: Polyera Activink or N2200 or P(NDI-2OD-T2) is an n-type polymer that has found wide application in the field of all-polymer solar cells (PSCs) and OFET because of its desirable semiconducting and photo-physical properties. This polymer exhibits good solution processability, high crystalline nature and broad absorption in IR and near visible region. The

properties of P(NDI2OD-T2) polymer were tuned by random incorporation of PDI as a co-acceptor. Generally, these polymers were synthesized via Stille polycondensation reaction in batch reactors. The batch-to-batch variability in molecular weight characteristics developed by batch process is a hindrance to reproducible device performance in photovoltaic applications. The continuous flow method of developing conjugated polymers affords a reproducible and scalable method to develop high performance materials that can exhibit enhanced efficiencies in photovoltaic device applications. P(NDI2OD-T2) was synthesized in the lab by batch process and varying amounts of the higher analogue perylene diimide was introduced into the polymer, which resulted in enhanced all-polymer solar cell device performance due to better blend morphology. Here we report the synthesis of these polymers (P(NDI2OD-T2) and NDI-Th-PDI-30) by stille polymerization by continuous flow process. P(NDI2OD-T2) showed very high molecular weight $M_n=61000$, $M_w=102000$, $PDI=1.6$ within short reaction time compared to reported batch synthesize one of $M_n=26400$, $PDI=5.7$. Further optimization is ongoing.

List of Conference Attended with Details

Workshop on “FlexibleElectronics” at Samtel Center for Display Technogies, Indian Institute of Technology Kanpur, U.P, India. **2018**.

SPSI MACRO International Conference on Polymer Science and Technology IISER Pune (India). **2018**.

SPSI MACRO International conference on Science and Technology of Polymers and Advanced Materials CSIR-NCL, Pune (India). **2022**.

ABOUT THE AUTHOR



Mr. Aryan Anurath Wavhal was born to Shri. Anurath and Smt. Asha in 1992 at Asola, a small village in the Dharur taluka, Beed district of Maharashtra (India). The author started his primary schooling at Z. P School in the same village and completed secondary school from Gurudev Vidyalaya, Ambajogai. Afterwards, moved to Vasant Junior College, Kaij, and completed higher secondary education in 2010 and graduated from the Yogeshwari College, Ambajogai in 2014. The author pursued his Master's degree in Chemistry (Organic Chemistry) from the Milind College of Science, Sambhajinagar (Aurangabad), Dr. Babasaheb Ambedkar Marathwada University, Sambhajinagar (Aurangabad), (Maharashtra). After qualifying CSIR-UGC National Eligibility Test (NET-JRF) examination in December 2016, GATE in February 2017 and SET-MHT in April 2017. He joined for Ph.D in August 2017 under the supervision of Prof. Dr. S. K. Asha, Chief Scientist of the Polymer Science and Engineering (PSE) Division of CSIR-National Chemical Laboratory, Pune, India, as a Junior Research Fellow (JRF). He has received a research fellowship (JRF and SRF) from the University Grants Commission (UGC), New Delhi, India, to carry out the Ph.D. thesis work. The author is currently working as a Senior Lab Officer-Quality Control in Indian Oil Corporation Limited at Central Laboratory, Sewree, Mumbai.

PAPER

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Cite this: *Nanoscale*, 2021, **13**, 12314

A high-voltage non-aqueous hybrid supercapacitor based on the N2200 polymer supported over multiwalled carbon nanotubes†

 Bhaiyyasaheb Anurath Wavhal,^{‡a,b} Meena Ghosh,^{‡b,c} Sandeep Sharma,^{§a}
 Sreekumar Kurungot ^{*c} and Asha SK ^{*a,b}

P(NDI2OD-T2), also known as Polyera ActivInk N2200, is a widely accepted non-fullerene acceptor polymer that is used prominently in the energy harvesting application due to its ease of synthesis, high electron mobility, and other desirable semiconducting properties. With its recent foray into energy storage applications, there is tremendous potential for developing composites of N2200 with carbon nanotubes (CNTs) to improve its electrical properties and extend its applicability. Here we report a facile synthesis of an N2200 composite with multiwalled carbon nanotubes (MWCNTs) following an *in situ* approach to include MWCNTs into the polymer matrix, improving its electrochemical performance in an organic electrolyte (1 M LiClO₄/propylene carbonate). The composite material with an optimum MWCNT content exhibits prominent redox behavior delivering a specific capacity of 80 mA h g⁻¹_(polymer) in a standard three-electrode cell. Moreover, the N2200/MWCNT composite material showing a battery-type electrochemical signature could perform as an efficient negative electrode in a high-voltage (2.4 V) hybrid supercapacitor device comprising capacitive activated carbon as the positive electrode.

Received 4th March 2021

Accepted 17th June 2021

DOI: 10.1039/d1nr01422f

rsc.li/nanoscale

Introduction

Poly{[*N,N'*-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-*alt*-5,5'-(2,2'-bithiophene)} or P(NDI2OD-T2) also known as Polyera ActivInk N2200 is a nonfullerene acceptor polymer that has found wide acceptance due to its desirable semiconducting properties along with remarkable stability under ambient conditions. The main application of N2200 has been as an acceptor polymer in all-polymer solar cells, where high power conversion efficiencies have been achieved in combination with suitable donor polymers under well-controlled device fabrication conditions.^{1–7} The first demonstration of this

polymer as a charge storage material for rechargeable Li batteries was reported in 2015 in which the authors took advantage of both the electron transport pathway and highly reversible doping characteristics of the polymer.⁸ Our group reported the application of P(NDI2OD-T2) and its derivatives containing naphthalene diimide (NDI) as an acceptor and thiophene-terminated phenylenevinylene as a donor as electrode materials in a supercapacitor, which showed exceptional cycling stability.⁹

The most commonly used conjugated polymers as supercapacitor electrode materials are poly(3,4-ethylenedioxythiophene), polypyrrole, polyaniline, *etc.*, which are all p-type (electron-rich) materials with good charge-storage properties.^{10–14} In supercapacitor applications, these p-type polymers are usually used as electrodes for either type I or type II devices, where the electrodes are both symmetric or asymmetric, respectively. While reports on type I and type II supercapacitor devices using conjugated polymers abound in the literature, devices using electron poor or donor-acceptor type π -conjugated polymers are not very common. Like p-type polymers, donor-acceptor polymers also show pseudocapacitive behavior due to their intrinsic redox properties.^{8,15,16} However, their performance as supercapacitor electrode materials has been rarely explored in the literature. There are only one or two other reports on supercapacitors, which use rylenebisimides (perylene or naphthalene) as the electrode material.^{9,15,17} In our earlier work, we demonstrated the electrochemical per-

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†Electronic supplementary information (ESI) available: Synthesis scheme of monomers, ¹H NMR, GPC, TGA, DSC, and UV analyses, BET isotherms, pore size distribution profiles, supporting electrochemical data, a comparison table and a demonstration video. See DOI: 10.1039/d1nr01422f

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formance of supercapacitors based on rylenebisimides with excellent stability over long cycles (>4000 cycles), indicating the potential of donor–acceptor polymers as efficient electrode materials. Hence, further research towards improving the performance of such polymer materials is indeed essential.

Another intriguing characteristic of donor–acceptor polymers is their ability to withstand high-voltage windows when used as an electrode material in electrochemical energy storage devices (EESDs). High-voltage electrodes provide the opportunity to make use of organic electrolytes for realizing high-voltage supercapacitor devices instead of the traditional aqueous electrolyte,¹⁸ which suffers from low voltage stability due to the inevitable water oxidation at a high voltage. As the energy density (E) of a supercapacitor follows the relationship $E = \frac{1}{2}CV^2$, where C is the capacitance and V is the operating voltage, a small increase in the voltage results in a significant improvement in the energy density of the device.¹⁹ Therefore, exploring donor–acceptor polymers as electrode materials in combination with organic electrolytes is pertinent towards developing high energy supercapacitors.

Despite their advantages, organic electrolytes suffer from low ionic conductivity inciting high internal resistance and often leads to inferior electrochemical performance. Therefore, improving the conductivity of the electrode material and the interface between the electrode and electrolyte is an essential requirement to compensate for the electrolyte resistance in organic electrolyte-based supercapacitors. The conductivity of polymers can be often enhanced by mixing with various carbon materials like carbon nanotubes (CNTs) or graphene.^{20–26} Multiwalled CNTs (MWCNTs) are also an excellent conducting additive for electrode fabrication due to their high surface area, low electrical resistivity, and nano-porous structure.²⁷ Conjugated polymers can involve in π – π interactions with CNTs resulting in the unbundling of the CNT aggregates.^{28,29} Composite electrodes usually have a porous structure, which enables good accessibility of the electrolyte to the inner surface of the electrode resulting in an improved

electrode–electrolyte interface.^{30,31} Compared to the various strategies adopted for mixing CNTs with conjugated polymers, the *in situ* addition of CNTs during the polymerization reaction is a better way to achieve uniform mixing of the polymer with the conductive material, which leads to better electrochemical performance of the material. There are several reports on the application of polyaniline composites with *in situ* addition of carbon nanotubes or graphene as the electrode material in supercapacitors.^{32–37} These nanocomposites exhibited better charge-storage properties and stability as compared to pristine polyaniline. Similarly, polypyrrole *in situ* polymerized with carbon nanotubes,^{38,39} RGO (reduced graphene oxide),⁴⁰ molybdenum disulfide (MoS_2),⁴¹ and copper sulfide (CuS)⁴² have also shown improved charge-storage performance compared to pristine polypyrrole. Recently, Smirnov *et al.* reported the *in situ* synthesis of polypyrrole in the presence of cellulose nanofibers grown over graphene, which showed an enhanced specific capacitance (810 F g^{-1}) compared to the externally mixed sample (371 F g^{-1}).⁴³ *In situ* synthesized poly(3-hexylthiophene)/graphene composites also have shown a better capacitance value than *ex situ* mixed composites.⁴⁴ However, as already mentioned, these composites are tested in an aqueous electrolyte, thereby limiting the operating voltage of the devices to 1.2 V.^{45,46} Therefore, extending the strategy of the *in situ* incorporation of conducting additives to pseudo-capacitive/battery-type conducting polymers for designing suitable electrode materials for organic electrolyte-based high energy supercapacitors and hybrid supercapacitors is of great importance, yet challenging. As far as the authors are aware, there have been no reports in the literature on the synthesis of n-type polymer composites with carbon nanotubes or any conductive materials following the *in situ* approach.

In this work, P(NDI2OD-T2) or N2200 based polymer composites were synthesized by *in situ* addition of MWCNTs with various weight ratios following a modified Stille polymerization procedure. The generally reported procedure for the synthesis of P(NDI2OD-T2) by the Stille polymerization takes a

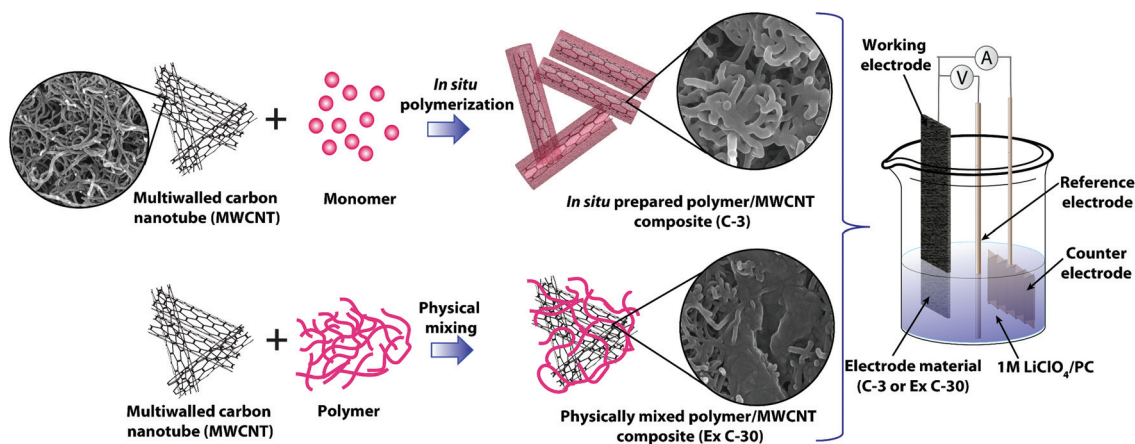


Fig. 1 Schematic representation summarizing the polymerization of P(NDI2OD-T2) supported over MWCNTs following *in situ* and physical mixing approaches, and their electrochemical analysis in a three-electrode cell.

long time (3 days) to complete.^{3,47–49} In our report, the synthesis of P(NDI2OD-T2) and its composites was carried out using modified Stille polymerization conditions, which resulted in high molecular weight polymers with good yields in very short reaction periods. To our knowledge, this is the first report where high molecular weight P(NDI2OD-T2)-based polymers were developed within 2 hours of the polymerization time. The electrochemical performance of the composite materials was tested in an organic electrolyte (1 M LiClO₄/propylene carbonate) in a standard three-electrode configuration. The *in situ* prepared polymer composites delivered 80 mA h g^{−1}_(polymer) specific capacity (considering the loading of the polymer in the working electrode), a value substantially higher compared to that of the pristine polymer and the physically mixed polymer/MWCNT composite. Moreover, the *in situ* prepared composite showed promising performance as a negative electrode coupled with an activated carbon positive electrode in a hybrid supercapacitor (HSC) cell. The preparation and electrochemical characterization of the *in situ* and physically mixed polymer/MWCNT composites are schematically summarized in Fig. 1.

Experimental section

Materials

1,4,5,8-Naphthalenetetracarboxylic dianhydride (NTCDA), 2-octyldodecanol, and 2-ethylhexyl bromide were purchased from TCI chemicals and used without further purification. 5,5'-Bis(trimethylstannyl)-2,2'-bithiophene, bis(triphenylphosphine)palladium(II) dichloride (Pd(PPh₃)₂Cl₂), multiwalled carbon nanotubes (MWCNTs) and propylene carbonate (PC) were purchased from Sigma-Aldrich and used without further purification. 4-Tertiary butyl toluene was purchased from Sigma-Aldrich and used after drying.

Measurements. ¹H NMR spectra of the monomer and polymers were recorded on a Bruker 200 and 400 MHz NMR spectrophotometer in deuterated chloroform solution with TMS as the reference. The molecular weight of the polymers was determined using size exclusion chromatography (SEC) having a Viscotek VE 1122 solvent delivery system at room temperature in tetrahydrofuran (THF) at a flow rate of 1 mL min^{−1} as an eluent and with the help of a Viscotek VE 3580 refractive index (RI) detector. The analyses were carried out using polystyrene as the standard. Absorption spectra of the polymers were recorded using a double beam PerkinElmer lambda-35 UV/Vis spectrometer with deuterium and tungsten lamps as the source. TGA (thermogravimetric analysis) was performed with the help of a PerkinElmer STA (Simultaneous Thermal Analyzer) 6000 thermogravimetric analyzer. Samples were run at a heating rate of 10 °C min^{−1} from 40 to 800 °C under a nitrogen atmosphere. TEM images were obtained with the help of a JEOL JEM-F200 HR-TEM instrument with an energy dispersive X-ray (EDX) detector for EDX analysis. FE-SEM images were recorded using an FEI NOVA SEM 450 FESEM instrument.

Sample preparation. UV-vis absorption spectra were recorded in the solution state by dissolving the polymer in chloroform at different concentrations. To calculate the concentration of MWCNTs in the C-X polymer composites, the solution was prepared at a concentration of 1 mg/50 mL in chloroform. For FE-SEM and TEM sample preparation, the polymer was dispersed in methanol as the solvent (1 mg of polymer in 2 mL of methanol). The dispersion was then drop-cast over mica for SEM and a copper grid for TEM analyses.

Electrode fabrication. For fabricating the electrodes, a homogeneous slurry was prepared by dispersing 4.75 mg of the desired sample (P-0, C-1, C-2, C-3, or Ex C-30) with 0.25 mg of polyvinylidene fluoride (PVDF) binder in 500 μL of N-methyl pyrrolidone (NMP). 100 μL of the slurry was coated on 1 cm² area of carbon fiber paper to obtain a total loading of 1.0 mg cm^{−2}. The electrodes were then dried in an oven at 60 °C overnight. For comparison, an electrode coated with MWCNTs was also prepared with 0.33 mg cm^{−2} loading.

Electrochemical measurements. All the electrochemical tests were carried out using a BioLogic VMP3 instrument. To check the electrochemical performance of the samples, three-electrode cells were assembled using the carbon fiber paper coated with the desired sample as the working electrode, a platinum mesh as the counter electrode, and Ag/Ag⁺ as the reference electrode in 1 M LiClO₄/PC electrolyte. The potential window was fixed from −0.2 to −1.4 V vs. Ag/Ag⁺. The discharge capacities of the samples were measured by the galvanostatic charge-discharge (GCD) experiment at different current rates of 0.5, 1.0, 2.5, and 5.0 A g^{−1}. The discharge capacity values of the MWCNT sample were recorded at 1.5, 3.0, and 7.5 A g^{−1} current rates. Here, the current rates are given, considering the total loading of the electrode material in the working electrode. The discharge capacities of the samples measured in the three-electrode cell assembly are reported in the units of mA h g^{−1}_(polymer) and mA h g^{−1}. mA h g^{−1}_(polymer) indicates that the capacity values are normalized exclusively by considering the loading of the P(NDI2OD-T2) polymer in the working electrode (e.g., 0.6 mg for C-3; see Section S3 in the ESI† for the polymer content in other samples). On the other hand, the unit of mA h g^{−1} represents the discharge capacity value normalized by considering the cumulative mass loading of the working electrode, which includes the polymer, MWCNTs, and PVDF binder (mass loading of 1 mg for P-0, C-1, C-2, and C-3 electrodes). Cyclic voltammetry (CV) analysis was carried out at scan rates of 5, 10, 20, 50, and 100 mV s^{−1}.

The performance of symmetric and hybrid supercapacitor (HSC) devices was first analyzed in 1 M LiClO₄/PC liquid electrolyte. Henceforth, HSC devices fabricated using the above-mentioned liquid electrolytes are termed LS-HSC, where 'LS' stands for the liquid-state electrolyte. For the symmetric device, an electrochemical cell was prepared by dipping two electrodes coated with the C-3 sample (1.0 mg cm^{−2} loading) in a beaker filled with 1 M LiClO₄/PC electrolyte, and the electrochemical cell (device) is marked as C-3||C-3. The device was characterized by CV analysis at 50 mV s^{−1} scan rate within the 0 to 1.4 V voltage window. A HSC was fabricated using

carbon paper coated with C-3 and activated carbon (AC) as the negative and positive electrodes, respectively. The AC electrode was characterized by CV analysis at 50 mV s⁻¹ scan rate in 1 M LiClO₄/PC liquid electrolyte within the voltage range of -0.2 to 1.0 V vs. Ag/Ag⁺ in the three-electrode configuration. To balance the loading to the two electrodes, the charge storage capacity of the AC sample was determined by GCD analysis at 0.5 A g⁻¹ current rate. The ratio of the positive and negative electrode loadings was optimized to be 1.5 : 1 (calculation is given in Section S3, ESI†). The CV data of the LS-HSC device were recorded at scan rates of 10, 20, 50, and 100 mV s⁻¹, and GCD data were recorded at current rates of 2.0, 1.0, 0.4, and 0.2 A g⁻¹ within the voltage window of 0 to 2.4 V. Here, the current rates are normalized with respect to the total loading of both the positive and negative electrodes. Hence, the specific capacities are represented in the unit of mA h g⁻¹_(total), where 'total' represents the specific capacity normalized by considering the total mass loading of the electrode material loaded at the positive and negative electrodes.

For fabricating a quasi-solid-state HSC (QSS-HSC) device, a polymer gel electrolyte made of LiClO₄/PC dissolved in a polymethylmethacrylate polymer matrix (PMMA/LiClO₄/PC) was used, and the required amount of electrode materials (1 mg of C-3 and 1.5 mg of AC) was coated over 1 cm² area of the Grafoil current collector. The CV data for the QSS-HSC device were analyzed at 50, 100, and 200 mV s⁻¹ scan rates and GCD data were recorded at current rates of 3.0, 2.0, 1.0, and 0.4 A g⁻¹. The application of the QSS-HSC device was demonstrated by lighting a red LED bulb.

BET experimental setup. The pore size distribution and nitrogen adsorption/desorption isotherms of MWCNT, P-0, and C-3 composite polymers were analyzed at 77 K using a Quantachrome Quadrasorb SI (automatic surface area and pore size analyzer). The surface area of the samples was determined according to the Brunauer-Emmett-Teller (BET) method at 77 K bath temperature, and nitrogen was used as the adsorption gas. The pore size distribution plots were calculated according to density functional theory (DFT), with N₂ as a model at 77 K on carbon (slit pore, NLDFT equilibrium model).

Synthesis of P(NDI2OD-T2) (P-0). The monomer NDI-2OD-Br₂ was synthesized following the previous reports for the same from our group.⁴⁷ NDI-2OD-Br₂ (0.200 g, 0.203 mmole) and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (0.099 g, 0.203 mmol) were weighed accurately into a dry Schlenk tube containing a magnetic stir bar, and 10 ml of dry 4-ter-butyl toluene was added to it. This was followed by nitrogen purging for half an hour with constant stirring at room temperature. Bis(triphenylphosphine)palladium(II) dichloride (Pd(Ph₃)₂Cl₂) (5.84 mg, 0.005075 mmol) was added to the above solution under a nitrogen atmosphere and again kept for nitrogen purging for half an hour; subsequently, the Schlenk tube was transferred into a preheated oil bath at 160 °C and stirring was continued for 2 hours. Afterward, it was cooled to room temperature and directly precipitated in methanol and filtered through a Büchner funnel. The polymer

was purified *via* Soxhlet extraction in methanol (24 hours) followed by acetone. It was then dried in a vacuum oven at 60 °C. Yield (191 mg, 95%). ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.83–8.52 (br, 2H aromatic), 7.34 (br, 4H), 4.12 (br, 4H), 1.99 (br, 2H), 1.26 (br, 64H), 0.86 (br, 12 H). *M*_n: 188 000, *M*_w: 59 7000, *D*_M: 3.18.

Synthesis of the polymer composite C-X. MWCNT and P(NDI2OD-T2) polymer composites (named C-X) were synthesized using the same procedure as that for P(NDI2OD-T2), except for the addition of the required amount of MWCNTs. For instance, for C-1, NDI-2OD-Br₂ (0.200 g, 0.203 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (0.099 g, 0.203 mmol) and 30 mg of MWCNTs were taken in a dry Schlenk tube and 10 ml of dry 4-ter-butyl toluene was added to it. Pd(Ph₃)₂Cl₂ (5.84 mg, 0.005075 mmol) was added as the catalyst, and then the same procedure as given for P(NDI2OD-T2) was followed. After cooling to room temperature, the polymer was directly precipitated in methanol (dissolution of the polymer in THF before precipitation into methanol was avoided to retain the MWCNT incorporated polymer network obtained during the *in situ* polymerization) and filtered through a Büchner funnel. Yield (224 mg–30 mg MWCNT = 194 mg, 96%). ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.84–8.55 (br, 2H aromatic), 7.36 (br, 4H), 4.15 (br, 4H), 2.0 (br, 2H), 1.29 (br, 64H), 0.89 (br, 12 H). *M*_n: 144 000, *M*_w: 351 000, *D*_M: 2.44.

Synthesis of the polymer composite C-2. C-2 was synthesized following the same procedure as given for C-1, but using 60 mg of MWCNTs. Yield (253 mg–60 mg MWCNTs = 193 mg, 96%). ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.84–8.55 (br, 2H aromatic), 7.36 (br, 4H), 4.15 (br, 4H), 2.0 (br, 2H), 1.29 (br, 64H), 0.89 (br, 12 H). *M*_n: 189 000, *M*_w: 465 000, *D*_M: 2.46.

Synthesis of the polymer composite C-3. C-3 was synthesized following the same procedure as given for C-1, but using 100 mg MWCNTs. Yield (289 mg–100 mg MWCNTs = 189 mg, 94.0%). ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.84–8.55 (br, 2H aromatic), 7.36 (br, 4H), 4.15 (br, 4H), 2.0 (br, 2H), 1.29 (br, 64H), 0.89 (br, 12 H). *M*_n: 123 000, *M*_w: 320 000, *D*_M: 2.60.

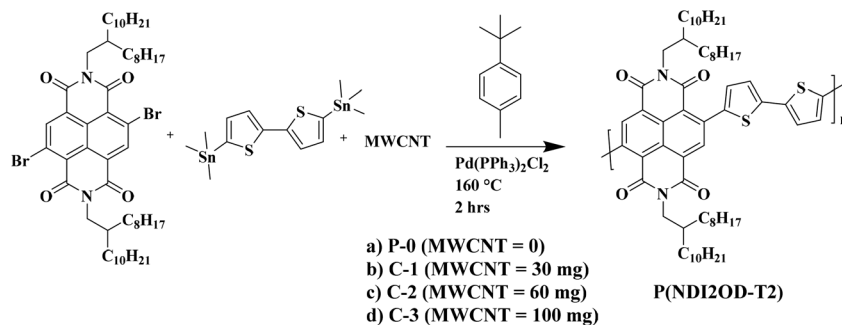
Ex C-30 polymer composite. For the purpose of comparison, an externally mixed MWCNT polymer composite was also prepared by mixing 30 mg of MWCNTs with the P(NDI2OD-T2) polymer, and the composite is marked as Ex C-30, where the 'Ex' indicates externally mixed.

Results and discussion

Synthesis and characterization

NDI-2OD-Br₂ was synthesized using a previously reported procedure in the literature.^{47–49} The synthetic scheme and characterization of NDI-2OD-Br₂ are given in ESI, Section S1.† Scheme 1 shows the synthesis of P(NDI-2OD-T2) and its composites with MWCNTs following the *in situ* strategy.

The commonly adopted procedure for the synthesis of P(NDI-2OD-T2) takes a long time (3 days) using the Stille polymerization, as reported in the literature.^{3,47–49} The polymerization is usually carried out in toluene at a tempera-



Scheme 1 Synthetic scheme for the P(NDI2OD-T2) (P-0) polymer and its composites with MWCNTs (C-X).

ture of around 90 °C for 72 h, resulting in a moderate molecular weight of ~ 50 000. In this work, we have adopted some modifications in the reaction conditions like the use of the high boiling solvent 4-ter-butyl toluene and also conducting the polymerization at a higher temperature of 160 °C. Interestingly, the polymerization was completed in a very short time of two hours. The pristine polymer P(NDI2OD-T2) synthesized by this modified procedure is referred to as P-0 in this manuscript. The composites of P(NDI2OD-T2) with MWCNTs were synthesized *via in situ* polymerization by taking various amounts of MWCNTs along with the reactants at the start of the polymerization. These composites are named C-X, where $x = 1, 2$, and 3 represent the three composites with increasing MWCNT content in the feed. The polymers were directly precipitated into methanol (instead of the traditional method of dissolving in THF and precipitating into methanol and repeating this a couple of times) to avoid the loss of the incorporated MWCNTs. The probable weight percentage incorporation of MWCNTs in the three composites was calculated by dividing the feed weight of the MWCNTs with the final total yield obtained after drying the precipitate from methanol. Thus, the weight percent incorporation of MWCNTs was calculated to be 13.4%, 23.7%, and 34.6% for C-1, C-2, and C-3, respectively.

The polymers were structurally characterized by proton NMR spectroscopy, and the molecular weight was determined using GPC (gel permeation chromatography) in THF after filtering the samples using filter paper followed by polytetrafluoroethylene (PTFE) filters to remove the MWCNTs. The atomic composition of P(NDI2OD-T2) and its composites

was characterized by energy dispersive X-ray (EDX) analysis. The EDX data indicate the presence of carbon and oxygen as the main elements and sulfur as a trace element as summarized in Table S1.† The characterization details are provided in the ESI (Fig. S1–S4†). The composite polymers exhibited good solubility in tetrahydrofuran (THF) and chloroform; they were sparingly soluble in dichloromethane (DCM) and chlorobenzene and insoluble in dimethylformamide (DMF). In all the solvents, the MWCNTs remained insoluble. The molecular weight data are given in Table 1. The polymers exhibited high molecular weights with M_n ranging from 123 000 to 189 000 and M_w in the range of 320 000–597 000.

The thermal characterization of the polymer and composites was performed by thermogravimetric analysis (TGA) under a nitrogen atmosphere. Fig. 2 shows the TGA plots of the P-0 and C-X samples along with that of pristine MWCNTs. The polymers exhibited good thermal stability with the onset decomposition temperature (T_d) greater than >450 °C. The TGA curves were also used to determine the incorporation of MWCNTs in each of the polymer composites using the formula given below.⁵⁰

% of MWCNT incorporated = % remaining pristine

$$\text{MWCNT} = \left(\frac{\% \text{ loss of composite}}{\% \text{ loss of pure polymer}} \times 100 \right)$$

The mass loss was taken as the vertical distance between the two tangential lines drawn on the mass loss curve, as shown in Fig. S5.†⁵¹ The % remaining for pristine MWCNTs was 96.44, and the % loss of the pure polymer (P-0) was 62.43.

Table 1 Molecular weight and thermal characterization of the P(NDI2OD-T2) polymer (P-0) and C-X composites

Sr. no	Polymer	M_n^a (kDa)	M_w^a (kDa)	D_M^b	% Yield	% Weight of MWCNTs in feed ^c	% Weight of MWCNTs from TGA	% Weight of MWCNTs from absorption spectroscopy ^d
1	P-0	188	597	3.18	95	0	0	0
2	C-1	144	351	2.44	96	13.4	13.91	16.0
3	C-2	189	465	2.46	95	23.7	24.06	27.3
4	C-3	123	320	2.60	92	34.6	35.08	38.8

^a M_n and M_w are number average and weight average molecular weights, respectively, determined by SEC using THF as the eluent and PS as a standard. ^b D_M is the dispersity of the polymers. ^c Determined with respect to the obtained total yield. ^d Determined by dissolving 1.0 mg of the composite polymer in 50 ml of chloroform.

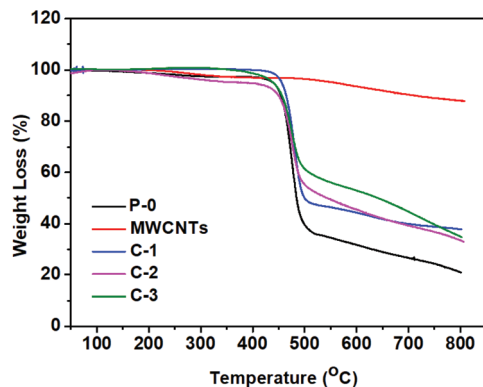


Fig. 2 TGA data of P-0, MWCNT, and the C-X samples taken in the temperature range of 40–800 °C at a heating rate of 10 °C min⁻¹ under nitrogen.

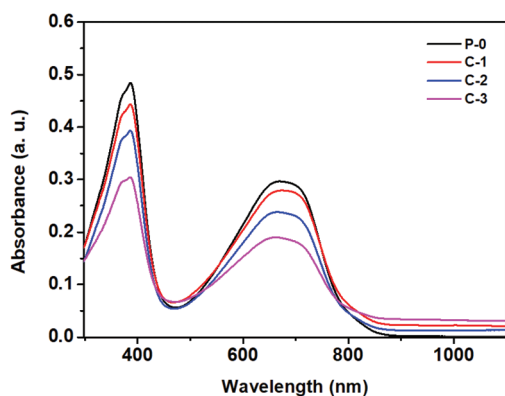


Fig. 3 UV-vis absorption spectra of P-0, C-1, C-2, and C-3 polymers recorded in chloroform at a concentration of 1 mg 50 ml⁻¹.

The percentage of MWCNT incorporation in the three composites C-1, C-2, and C-3 was determined to be 13.91, 24.06, and 34.81%, respectively.

Quantification of the polymer (and thereby MWCNTs) can also be done using absorption spectroscopy. Fig. 3 shows the absorption spectra of the pristine polymer P-0 and the composite polymers C-X recorded in chloroform. P-0 shows two absorption bands in the spectra corresponding to the π - π^* transition (300 nm to 450 nm) and the intramolecular charge transfer (ICT) band between 500 and 800 nm.⁴⁹ The molar extinction coefficient (ϵ) of P-0 was estimated to be 35 954 L M⁻¹ cm⁻¹ using the Beer-Lambert Law (Fig. S6†). Applying this value of ϵ , the concentration of the polymer in the composites C-X was calculated as detailed in ESI, Section S2.† The % MWCNTs estimated from the absorption spectra is tabulated in Table 1. Compared to the % incorporation of MWCNTs obtained from the TGA analysis, these values obtained from the absorption spectra are on the higher side for all the C-X samples. One reason for this variation could be the scattering of incident light due to the presence of the MWCNTs observed in the composites compared to the P-0 sample.

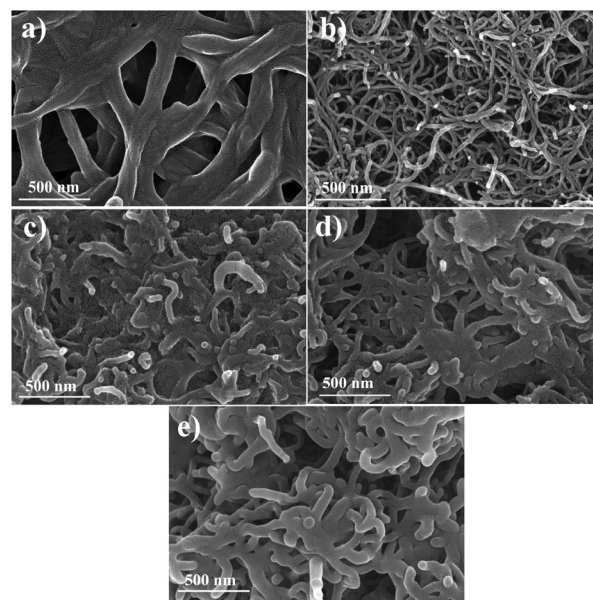


Fig. 4 FE-SEM images of (a) pristine P-0, (b) neat MWCNTs, (c) C-1, (d) C-2 and (e) C-3.

Morphology. The morphology of all the samples under study was characterized by FE-SEM and TEM analyses. As shown in Fig. 4, the FE-SEM image of P-0 (Fig. 4a) shows ribbon-like structures of the polymer, whereas the MWCNTs (Fig. 4b) possess an entangled tubular network structure. Fig. 4c–e compare the morphology of the composite polymers with increasing loading of MWCNTs. The uniform growth of the polymer layer over the *in situ* incorporated MWCNTs can be evidenced from the FESEM images. The entangled porous network of the pristine MWCNTs is also retained in all the polymer composites, and no bulk or agglomerated growth of the polymer is observed, indicating the maximum contact of the polymer layer with the carbon support. However, compared to C-1 (Fig. 4c), the morphology of the C-2 (Fig. 4d) and C-3 (Fig. 4e) samples appears to be more porous, which suggests that a higher percentage of MWCNTs results in better dispersion of the polymer during the course of the polymerization reaction.

The samples were further characterized by TEM. Fig. 5a shows the ribbon-like morphology of the polymer, as observed in the FE-SEM image (Fig. 4a). The tubular structure of MWCNTs with an average diameter of 8–15 nm is shown in Fig. 5b. The TEM images of the composite polymers (Fig. 5c–e) further confirm the uniform dispersion of the polymer over the carbon nanotubes. An overall increase in the average diameter of the tubular structure to 30–50 nm is clearly observed (in contrast to 8–15 nm for the pristine MWCNTs), which further confirms the uniform growth of the polymer along the MWCNTs in the C-X samples. In order to bring out the contrast between the *in situ* MWCNT incorporation *versus* the physical mixing of MWCNTs with the polymer, carbon nanotubes were externally mixed with the polymer. 30 wt% of

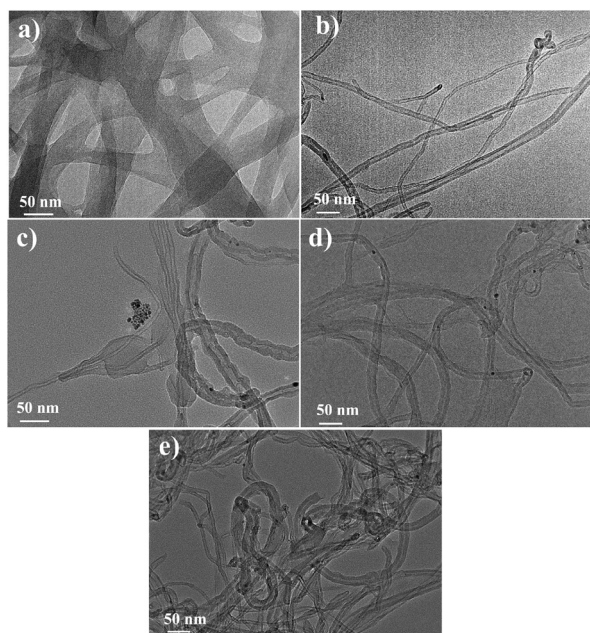


Fig. 5 TEM images of (a) pristine P-0, (b) neat MWCNTs, (c) C-1, (d) C-2 and (e) C-3.

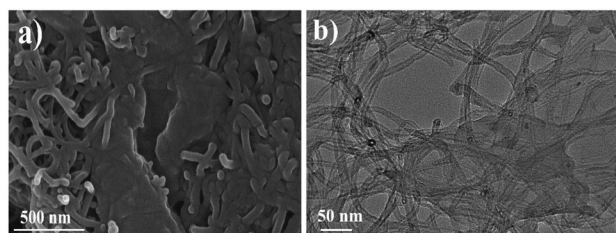


Fig. 6 (a) FE-SEM and (b) TEM images of the Ex C-30 sample.

MWCNTs in P-0 (Ex C-30) was prepared by dispersing them together in methanol and drop-casting on a silicon wafer or TEM grid for FE-SEM and TEM imaging, respectively.

The agglomerated deposition of the polymer on the MWCNTs is clearly visible in the FE-SEM image (Fig. 6a) of the Ex C-30 composite. The TEM image in Fig. 6b shows that the polymer is spread over the MWCNT network as a layer. Such

inhomogeneous distribution and undesired agglomeration were absent in the polymer composite samples prepared by the *in situ* process. The microscopy images prove the effectiveness of the *in situ* mixing of MWCNTs with the monomers prior to polymerization. The uniform distribution of the polymer chains on the MWCNT network is expected to enhance the electrochemical performance of the C-X composites compared to the pristine polymer and physically mixed polymer/MWCNT composite.

Surface area and pore size. The surface area and nature of porosity in the MWCNT, P-0, and C-3 composites were determined by nitrogen adsorption/desorption measurements at 77 K. Fig. 7 shows the pore size distribution (Fig. 7a) and nitrogen adsorption/desorption isotherms (Fig. 7b) of the C-3 composite polymer. Similar plots for MWCNTs and P-0 are given in Fig. S7a–d.† MWCNTs and C-3 composites exhibit a characteristic type III isotherm. The specific surface area values calculated using the Brunauer–Emmett–Teller (BET) model for the samples were: MWCNTs ($200.7 \text{ m}^2 \text{ g}^{-1}$), P-0 ($81.1 \text{ m}^2 \text{ g}^{-1}$), and C-3 ($224.8 \text{ m}^2 \text{ g}^{-1}$). The BET data signify that the *in situ* incorporation of MWCNTs improves the surface area of the C-3 composite compared to the pristine polymer, which is in line with the FESEM data of the respective samples.

The pore size distribution profiles for the MWCNTs (Fig. S7b†), P-0 (Fig. S7a†), and C-3 (Fig. 7a) show that MWCNTs exhibits both the microporous and mesoporous nature with more percentage of the latter. The pore size distribution of the pristine polymer is mostly in the microporous domain. On the other hand, in the composite (C-3), the pores are distributed in both microporous and mesoporous regimes. The average pore diameter of MWCNTs was $\sim 12 \text{ nm}$, while that for the polymers was in the range of $\sim 3 \text{ nm}$, as calculated using a density functional theory (DFT) desorption model. Fig. 7a shows that with the inclusion of MWCNTs, the number of pores in the mesoporous region increases compared to the P-0 sample (Fig. S7a†). The difference between the C-3 composite and the P-0 polymer originates from the morphological contrast between them. As evidenced in the FE-SEM and TEM analyses, in C-3, the polymer layer is grown in a thin and homogeneous manner over the MWCNTs without blocking the void space created by the entangled MWCNTs. As a consequence, the porous architecture of MWCNTs containing both micropores and mesopores is retained in the C-3 composite. It

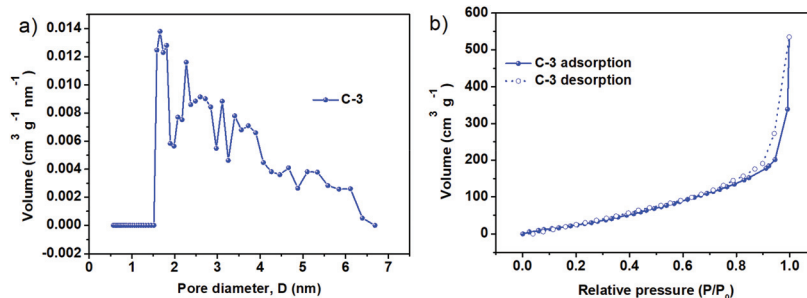


Fig. 7 (a) Pore size distribution profile and (b) nitrogen adsorption/desorption isotherm of the C-3 sample.

is anticipated that such a mesoporous framework could facilitate the electrolyte's infiltration when the sample is employed as the electrode material in EESDs.

Electrochemical characterization. The electrochemical performance of all the samples was investigated by cyclic voltammetry (CV) analysis carried out in a three-electrode cell in 1 M LiClO₄/PC electrolyte.¹⁷ Fig. 8a compares the CV profiles for the P-0, C-X, and Ex C-30 samples recorded at a scan rate of 10 mV s⁻¹. The CV profiles show the prominent redox peaks during the cathodic and anodic scans in all the cases. Compared to P-0, all the samples exhibit high current, signifying the augmented charge storage capacity of the polymer composites with MWCNTs. However, the increase in the current response (and redox behavior) is much more prominent in the C-X samples than in the Ex C-30 sample. The CV plots of MWCNTs in Fig. S8† show a nearly rectangular feature which is associated with the electric double-layer capacitor (EDLC). Furthermore, the current response observed in the CV plots of MWCNTs is significantly low compared to that of the

C-X samples. The EDLC behavior of MWCNTs confirms that the MWCNTs do not take part in the redox reactions; instead, the presence of MWCNTs in the polymer composites eases the transport of electrons by providing a conducting network. Therefore, it is reasonable to say that the observed enhancement in the faradaic current of the composite samples originates exclusively from the intrinsic redox activity of the P(NDI2OD-T2) polymer.

The position of the redox peaks (−0.9/−1.2 V and −0.65/−1.04 V vs. Ag/Ag⁺) was found to be more or less similar in all the composites (Fig. 8a), implying that the mode of MWCNT incorporation does not affect the redox properties of the samples. However, compared to the physical mixing, the inclusion of MWCNTs following the *in situ* strategy allows more number of redox-active centers being exposed for participating in the faradaic reactions and enhances the redox activity of the polymer in the C-X composites. To validate this, electrochemical impedance spectroscopy (EIS) analysis of the samples was carried out. Fig. 8b compares the Nyquist plots

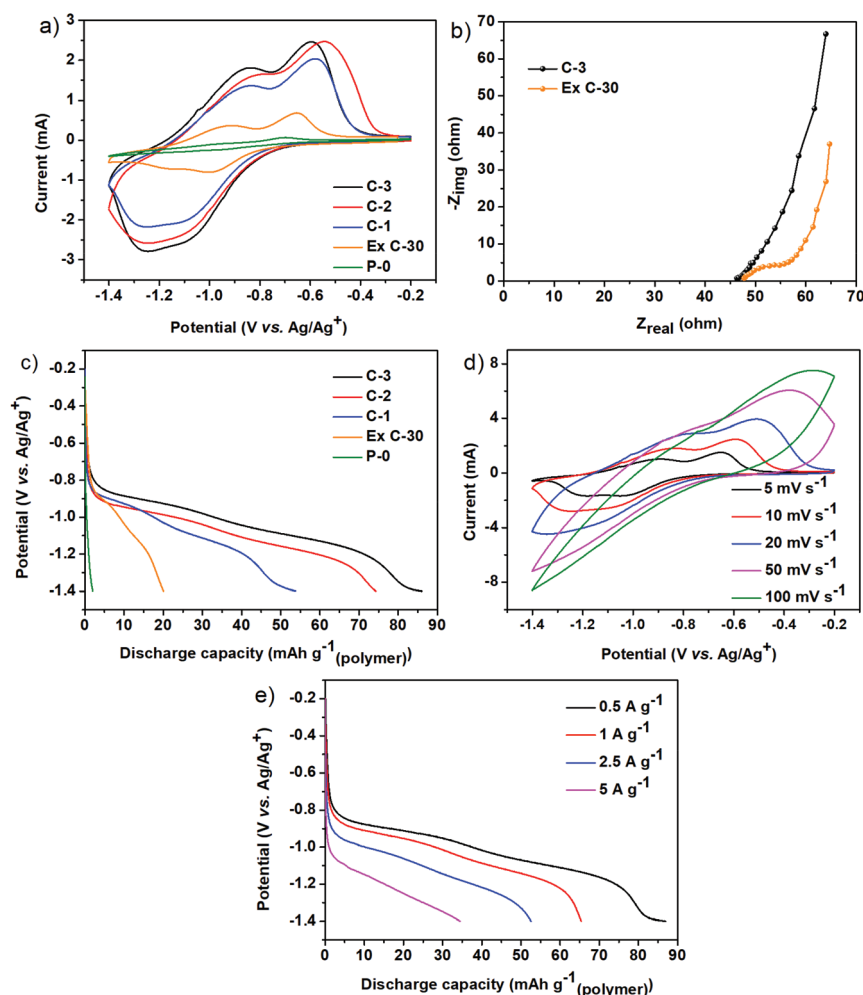


Fig. 8 (a) CV profiles for the P-0, C-1, C-2, C-3, and Ex C-30 samples recorded at 10 mV s⁻¹ scan rate; (b) Nyquist plots recorded for the C-3 and Ex C-30 samples; (c) discharge profiles for the P-0, C-1, C-2, C-3, and Ex C-30 samples plotted at a current rate of 0.5 A g⁻¹; (d) CV data of the C-3 sample recorded at different scan rates; and (e) discharge profiles plotted at different current rates for the C-3 sample.

corresponding to the C-3 and Ex C-30 samples (Nyquist plots for the other samples are given in Fig. S9†). The equivalent series resistance (ESR) of the C-3 sample was found to be $47\ \Omega$, which is comparable to that of all the other samples under study. Interestingly, despite the similar ESR value, the Nyquist plot for the Ex C-30 sample shows a small semicircle in a higher frequency region, signifying the charge transfer resistance (R_{ct}) at the electrode–electrolyte interface, which is not noticed in the case of the other samples. This observation suggests that MWCNTs present in the C-X composites could facilitate the electron transfer more effectively than in Ex C-30, revealing the advantage of the *in situ* strategy for the inclusion of MWCNTs into the P(NDI2OD-T2) polymer.

Fig. 8c compares the discharge capacity of all the samples evaluated from the galvanostatic charge–discharge (GCD) experiment at a current rate of $0.50\ \text{A g}^{-1}$. It can be noted that the discharge curves of the polymer composites appear with an apparent voltage plateau, consistent with the distinct reduction peak observed in the respective voltammogram profiles. Hence, the nature of the CV and galvanostatic discharge profiles of the polymer composites points out the battery-type behavior of the materials; therefore, in this work, the performance of the composite materials is quantified in terms of capacity rather than capacitance.^{52,53} On the other hand, MWCNTs exhibit a linear voltage response during the GCD process (Fig. S11a†), which is the characteristic of capacitor-like charge storage behavior, and the corresponding electrochemical performance is quantified as capacitance.

As evident in Fig. 8c, the average discharge capacities obtained for the C-X samples are considerably higher than those of the P-0 and Ex C-30 samples, which is in line with their CV data (Fig. 8a). The specific capacities obtained for the P-0 and Ex C-30 samples are 2 and $20\ \text{mA h g}^{-1}_{(\text{polymer})}$, respectively, at a current rate of $0.50\ \text{A g}^{-1}$. The reason behind the incredibly low capacity of the P-0 sample is that the sample does not contain any conducting additives. Therefore, the active centers could not participate in the faradaic processes due to the lack of facile transport of electrons throughout the electrode. This indicates the necessity of conducting additives in the electrode to achieve the desired electrochemical performance. The C-3 sample delivers a discharge capacity of $80\ \text{mA h g}^{-1}_{(\text{polymer})}$, which is the highest among all the C-X samples (54 and $74\ \text{mA h g}^{-1}_{(\text{polymer})}$ for C-1 and C-2, respectively). It must be noted that the capacity values given in Fig. 8c are normalized with respect to the loading of the active material (*i.e.*, P(NDI2OD-T2)) in the working electrode owing to the negligible contribution from the MWCNT additive (Fig. S11a†) to the total capacity of the composite electrode. Moreover, the capacity values considering the total loading of the electrodes (Fig. S11b†) also highlight the superior performance of the polymer composites prepared using the *in situ* method. Additionally, the discharge performance of the C-X composites is found to improve at a higher content of MWCNTs.

The C-X samples' improved capacity values could be attributed to their porous morphology with a uniform coating of the

polymer layer over the MWCNT network, as observed in the FE-SEM and TEM images (Fig. 4c–e and 5c–e). As a result, the exposed redox-active moieties could readily access the electrons traveling through the MWCNT network. Moreover, the porous architecture and improved surface area favor the electrolyte infiltration into the bulk of the electrode material and facilitate the diffusion of the electrolyte ions. Therefore, the short diffusion path for the electrons and electrolyte ions offers maximum participation of the redox-active centers during the charge/discharge process. On the other hand, in the case of the Ex C-30 sample, the inhomogeneous distribution of the agglomerated polymer layer over the MWCNT network (Fig. 6a and b) blocks the transport of the charge carriers. Therefore, only a fraction of the redox-active centers could participate in the electrochemical reactions as reflected in the low discharge capacity (Fig. 8c) and high R_{ct} value (Fig. 8b) of the Ex C-30 sample.

The CV data recorded at various scan rates for the C-3 sample are given in Fig. 8d (similar plots for the other samples are shown in Fig. S10a–d†). Fig. 8d shows that the peak current during the anodic and cathodic scans gradually increases with an increase in the scan rate from $5\ \text{mV s}^{-1}$ to $50\ \text{mV s}^{-1}$. However, at a higher scan rate ($>50\ \text{mV s}^{-1}$), the shape of the CV curve shows significant deviation, and the prominent redox peaks are found to disappear. This could be due to the low ionic conductivity of the organic electrolyte, which impedes the access of electrolyte ions to the redox centers of the electrode material at a higher scan rate. The discharge profiles of the polymer composites at different current rates are also recorded. As shown in Fig. 8e, the C-3 sample exhibits 40% retention of capacity when the current rate increases from $0.50\ \text{A g}^{-1}$ to $5\ \text{A g}^{-1}$. The discharge profiles at different current rates for the other samples are given in Fig. S11c–f.†

After the electrochemical characterization in the three-electrode configuration, the polymer composite C-3 was taken forward to demonstrate its performance in a real device. At first, a device in the symmetric configuration (C-3||C-3) was fabricated in $1\ \text{M LiClO}_4/\text{PC}$ electrolyte using two electrodes coated with C-3 composite materials. Surprisingly, no significant redox behavior was observed during the CV analysis at a scan rate of $50\ \text{mV s}^{-1}$ (Fig. S12a†). Nevertheless, the current response was found to be very small even at a working voltage window of $1.4\ \text{V}$, which is slightly higher than the potential used during the electrochemical analysis in the three-electrode cell (*i.e.*, $1.2\ \text{V vs. Ag/Ag}^+$).

The device-level performance of the C-3 polymer composite was further explored by fabricating an asymmetric device (AC||C-3)⁵⁴ using the C-3 sample as the negative electrode and activated carbon (AC) as the positive electrode material in $1\ \text{M LiClO}_4/\text{PC}$ electrolyte. The asymmetric configuration enables expanding the voltage window of the device without hampering the electrode and electrolyte stability. Fig. S12b and c† compare the electrochemical performance of the positive electrode (-0.2 to $1.0\ \text{V vs. Ag/Ag}^+$) and the negative electrode (-1.4 to $-0.2\ \text{V vs. Ag/Ag}^+$) obtained from the CV and GCD experiments within the corresponding voltage range. The ratio of the

active material loading in the positive and negative electrodes is 1.5 : 1 (AC: C-3), which was calculated by considering the capacity of the individual electrodes measured from the three-electrode study. The details of the calculation are given in the ESI (Section S3†).

As the asymmetric configuration demonstrated in this study contains two electrodes with different charge storage mechanisms, *i.e.*, one EDLC type (AC) and the other battery-type (C-3 composite), the devices are called hybrid capacitors/supercapacitors.^{55,56} The electrochemical performance of the AC||C-3 hybrid supercapacitor device containing 1 M LiClO₄/PC liquid electrolyte (LS-HSC) was analyzed within the extended voltage range of 0 to 2.4 V (Fig. S12d†). In contrast to the C-3||C-3 device, the feature of the CV plot in the LS-HSC device (Fig. S12d†) indicates the involvement of faradaic reactions during the anodic and cathodic scans. Besides, a remarkable improvement in the current response was achieved with the LS-HSC compared to that in the symmetric (C-3||C-3) device (Fig. S12d†). These observations suggest that the high

working voltage (2.4 V) of the LS-HSC device helps in accomplishing the redox activity of the C-3 composite in the two-electrode cell assembly. The CV and GCD profiles of the LS-HSC device are given in Fig. S13a and b.† As observed from Fig. S13b,† the LS-HSC device delivers 8.5 mA h g⁻¹_(total) and 7.0 mA h g⁻¹_(total) of specific capacity at the current rate of 0.2 A g⁻¹ and 2.0 A g⁻¹, respectively (current rate and capacity values are normalized for the total mass loading at the positive and negative electrodes). In the Nyquist plot (Fig. S13c†), the equivalent series resistance (ESR) for the LS-HSC device is 65 Ω. During the cycling stability experiment of the LS-HSC device (Fig. S13d†), the device's capacity increases gradually during the initial cycles and reaches the maximum value of 11 mA h g⁻¹_(total) after 1000 cycles. Owing to the initial increase in capacity during the prolonged cycling of the device, the capacity recorded at 1.0 A g⁻¹ current rate after 1000 cycles is close to the value obtained at 0.2 A g⁻¹. The improvement in the capacity during the cycling stability test is possibly due to the enhanced electrochemical activity of the material during

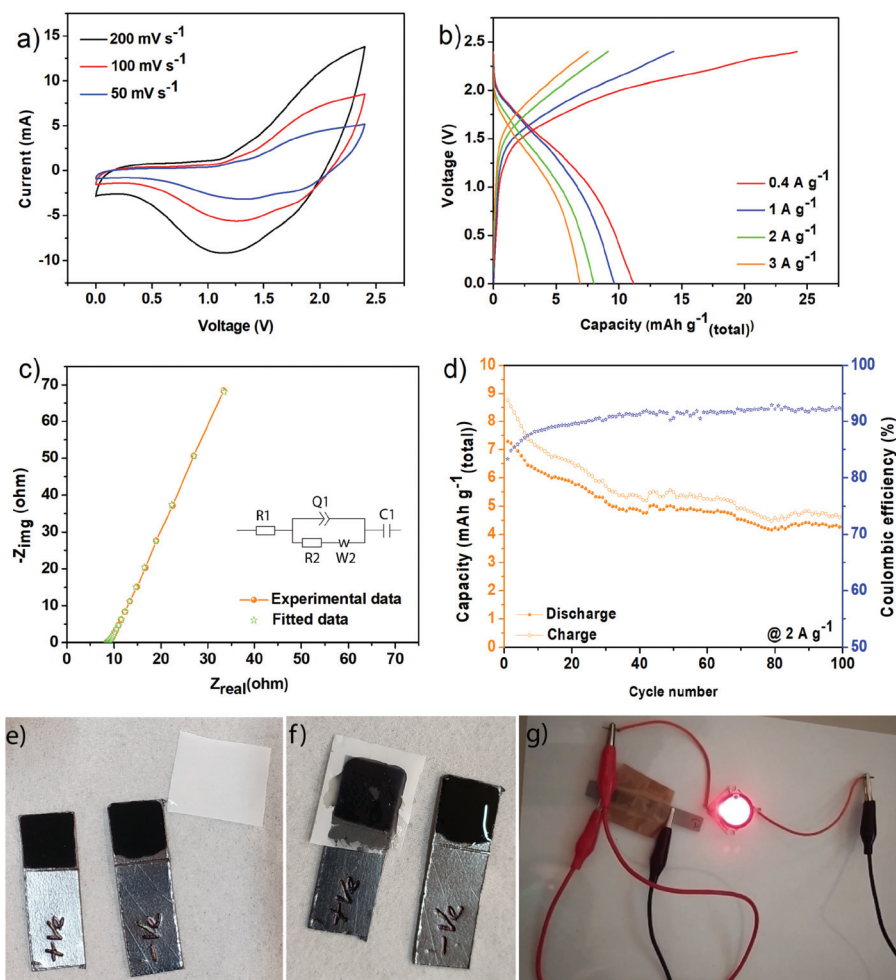


Fig. 9 (a) CV profiles recorded at different scan rates, (b) GCD profiles recorded at different current rates, (c) Nyquist plot, and (d) cycling stability data recorded at a current rate of 2.0 A g⁻¹ for the QSS-HSC device; photographs of the QSS-HSC device fabrication: (e) photograph of the positive and negative electrodes and the separator, (f) electrodes coated with the PMMA/PC/LiClO₄ polymer gel electrolyte, and (g) demonstration of the QSS-HSC device used for lighting an LED.

cycling. However, in the subsequent cycles, the device's capacity drops gradually, showing 80% retention of the maximum capacity after 2500 cycles with 92% coulombic efficiency.

Later, a QSS-HSC device (quasi-solid-state AC||C-3) was fabricated using the PMMA/PC/LiClO₄ polymer gel electrolyte. The CV profiles recorded at various scan rates for the QSS-HSC device are given in Fig. 9a. The device exhibits 11 mA h g⁻¹_(total) discharge capacity at a current rate of 0.4 A g⁻¹ (Fig. 9b). Also, it retains 6.9 mA h g⁻¹_(total) of the specific capacity even at 3.0 A g⁻¹, indicating the good rate capability of the system. It is observed that the charging capacity values of the device at 0.4 and 1.0 A g⁻¹ are higher compared to the corresponding discharge capacities resulting in low coulombic efficiency of the device at lower current rates. However, the device could perform better at higher current rates with more than 95% coulombic efficiency. The resistance of the QSS-HSC device is measured from the EIS analysis, and the corresponding Nyquist plot is given in Fig. 9c. The device exhibits an ESR of 8.8 Ω without a prominent semicircle feature in the high-frequency region of the Nyquist plot. It is worth mentioning that the overall resistance observed for QSS-HSC is much lower than that of many of the organic electrolyte-based supercapacitors reported earlier.^{57–59} The low resistance of QSS-HSC is attributed to a seamless pathway for the transport of charge carrier species throughout the electrode, which is achieved by creating a uniform and intimate contact of the polymer layer with the MWCNT backbone in the C-3 polymer composite, as already explained in the previous sections.

The cycling stability of the QSS-HSC device was analyzed at a current rate of 2.0 A g⁻¹. As seen in Fig. 9d, the device could retain 60% of the initial capacity after 100 cycles. The overall electrochemical performance of the C-3 composite-based LS-HSC and QSS-HSC devices indeed highlights that the faradaic charge storage properties of the P(NDI2OD-T2) polymer are improved by means of *in situ* inclusion of MWCNTs into the polymer matrix. The electrochemical performance of the C-3 composite in the three-electrode cell and the QSS-HSC device is compared with that of some of the previously reported redox-active polymers used as active electrode materials in supercapacitors (Table S2†). Furthermore, for demonstrating the device-level application, a 2.4 V QSS-HSC device is used for lighting a red LED bulb. The photographs of the various steps involved in the device fabrication are presented in Fig. 9e and f. A photograph of the glowing LED bulb powered with the QSS-HSC device is given in Fig. 9g, and a demonstration video is also attached with the ESI.†

Conclusions

In summary, we have developed a facile synthesis protocol for the P(NDI2OD-T2) (P-0) polymer with a high molecular weight within a short period of time (2 h) for the first time by means of the modified Stille polymerization method. The inclusion of MWCNTs during the polymerization reaction was found to

improve the physicochemical properties of the composite material compared to that of the pristine polymer. As a result, the composite sample prepared with 35% MWCNT content (C-3) following the *in situ* approach exhibited an 80 mA h g⁻¹_(polymer) discharge capacity, which is substantially higher than those of the pristine polymer and the composite prepared by physically mixing MWCNTs with the same quantity (Ex C-30). The C-3 polymer composite was further used for fabricating a high-voltage (2.4 V) hybrid supercapacitor taking the C-3 composite as a negative electrode (battery-type) and activated carbon (AC, capacitive electrode) as a positive electrode material. The electrochemical performance of the AC||C-3 device was analyzed in 1 M LiClO₄/PC liquid electrolyte (LS-HSC) and a PMMA/PC/LiClO₄ polymer gel electrolyte (QSS-HSC). Both devices show comparable performance, which is attributed to the porous morphological architecture of the C-3 composite showing intimate contact of the polymer with the MWCNT conducting framework. This work provides new opportunities toward the design of conducting polymer-based robust electrode materials for non-aqueous hybrid supercapacitors.

Author contributions

Bhaiyyasaheb Anurath Wavhal: Development of the methodology, conceptualization, formal analysis, writing – the original draft, writing – review and editing, investigation, and visualization; Meena Gosh: Development of the methodology, conceptualization, formal analysis, writing – the original draft, writing – review and editing, investigation, and visualization; Sandeep Sharma: Conceptualization; Sreekumar Kurungot: Writing – review and editing, conceptualization, resource, and supervision; Asha SK: Conceptualization, formal analysis, investigation, writing – the original draft, writing – review and editing, resource, and supervision.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was financially supported by the SERB project EMR/2017/001656. B. A. Wavhal and M. Ghosh acknowledge UGC, New Delhi, India and CSIR, New Delhi, India, respectively, for the research fellowship.

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High-Voltage Symmetric Supercapacitor Electrodes Via *In Situ* Synthesized Multiwalled Carbon Nanotube-Doped Perylenebisimide-Based Donor–Acceptor Conjugate Polymer P(PDI2OD-T2)

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Cite This: <https://doi.org/10.1021/acs.jpcc.4c02345>



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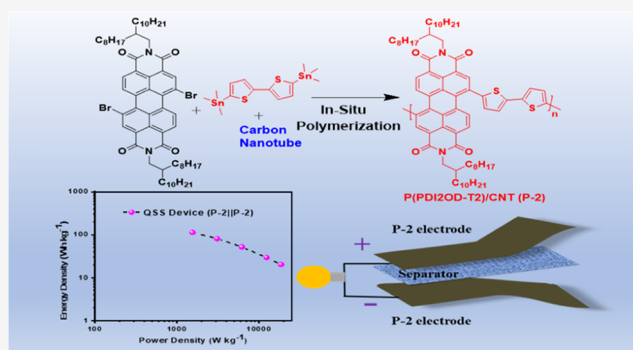


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Supporting Information

ABSTRACT: This study presents the design and synthesis of a donor–acceptor π -conjugated polymer composite P(PDI2OD-T2)/MWCNT tailored for high-voltage symmetric supercapacitor applications. The synthesis of P(PDI2OD-T2)/MWCNT was expedited by adopting a novel *in situ* polymerization technique that modifies the traditional Stille polymerization process. Incorporating approximately 33% by weight of multiwalled carbon nanotubes (MWCNT) into the polymer matrix, referred to as P-2, significantly enhances its conductivity, surface area, and porosity. These improvements in the material properties contribute to the superior electrochemical performance of the composites by promoting efficient electrolyte ion transport across the electrode–electrolyte interfaces. The symmetric supercapacitor devices fabricated with P-2 electrodes employing both liquid organic (LE-P-2||P-2) and quasi-solid-state gel (QSS- P-2||P-2) electrolytes demonstrate capacitance values of 85.4 and 84.2 F g^{−1}, respectively, at a current density of 0.25 A g^{−1}, while operating at a high-voltage window of 3.1 V. Moreover, these devices exhibit robust cycling stability, maintaining approximately 70% of their initial capacitance over 45,000 cycles with a coulombic efficiency of 96%. The successful demonstration of a quasi-solid-state symmetric supercapacitor underscores the potential of flexible energy storage solutions, as evidenced by a PMMA LiClO₄ gel electrolyte prototype. This flexible device not only maintains structural integrity but also achieves an impressive power density of 18,600 W kg^{−1} and an energy density of 112.4 Wh kg^{−1}, indicating its practical viability for real-world applications.



INTRODUCTION

Supercapacitors (SC) have demonstrated significant ability in the energy storage field due to their high power density, stability of devices, excellent reversibility, and quick charging/discharging capabilities.^{1–5} Electrode materials are the central components of these energy storage devices and perform an important function in determining their overall efficiency.^{6,7} In energy-storing devices, conjugated polymers are commonly used as prominent electrode materials due to several advantages as compared to costly metal oxide and carbon materials.^{8–13} Conjugated polymers exhibit advantages in terms of low cost, good conductivity, flexibility, rich color variations, simple synthetic procedures, and controllable structures.^{8,14–16} Energy density is one of the key parameters for developing efficient supercapacitor devices and meeting the needs of various applications of energy storage. However, the supercapacitor's energy density is directly dependent on the specific capacitance C and the square of the operating voltage.^{17,18} The energy density of the device is significantly

enhanced even by a slight voltage increase. In general, for energy storage applications, electron-rich or p-type conjugated polymers are used with aqueous electrolytes, which limit their voltage window.^{19,20} Donor–acceptor conjugated polymers are efficient materials for obtaining a higher operating voltage window by storing energy in both positive and negative electrodes. Their application in combination with organic electrolytes is an important aspect of developing a high-energy supercapacitor.^{17,21}

The use of organic electrolytes offers a higher voltage window,²² however, they have limitations such as limited ionic conductivity, higher internal resistance, and poor electrode

Received: April 10, 2024

Revised: July 4, 2024

Accepted: July 11, 2024

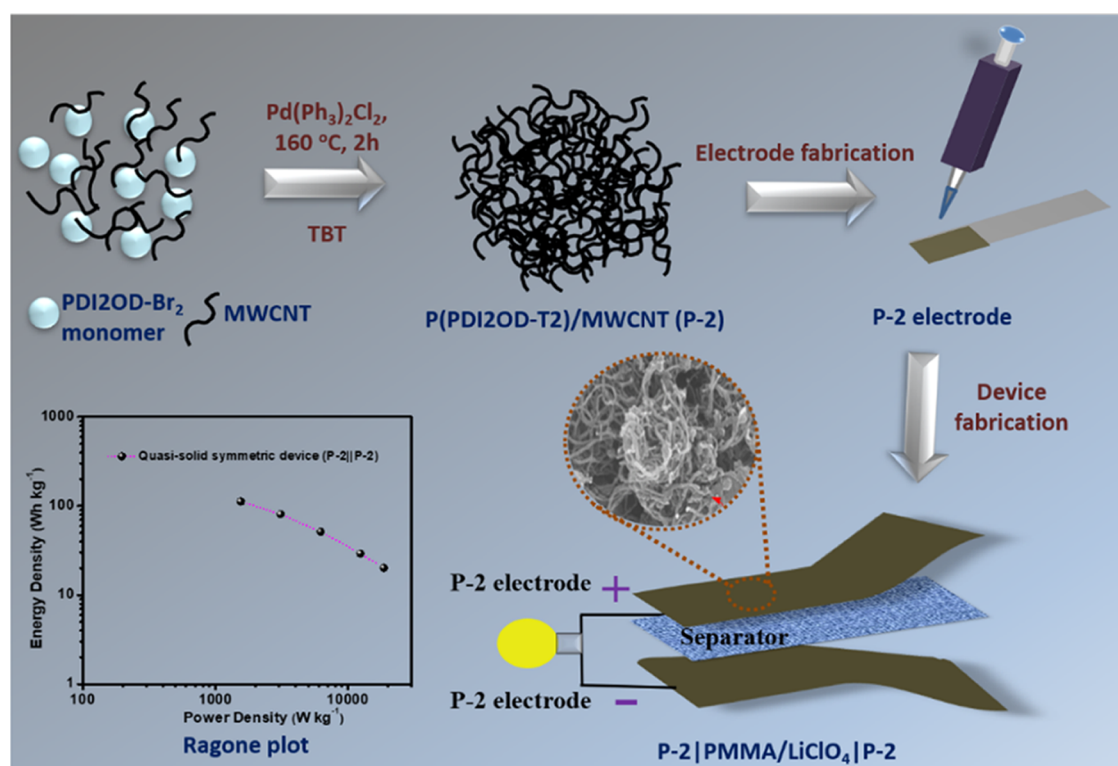


Figure 1. Schematic diagram summarizing the *in situ* polymerization of P(PDI2OD-T2) with MWCNTs along with their electrochemical analysis in a quasi-solid-state symmetric supercapacitor device.

electrolyte interaction. A polymer electrode with a rigid structure offers poor contact with electrolytes, low counter-anion diffusion, and low conductivity due to the unexposed surface of the electrode, all of which lower the performance.^{4,23} Consequently, it is observed that the donor–acceptor conjugated polymers show a significantly low performance compared to the theoretically predicted results.²⁴ In recent studies, researchers have tried to address this problem by synthesizing electrode materials with suitable structural modifications. A few such reports are presented in this section. Luscombe et al. synthesized a series of three hyperbranched donor–acceptor polymers from triphenylamine (TPA) and naphthalene diimide (NDI) monomers with varying thiophene spacers for application as a cathode material of supercapacitor.²⁵ Meng et al. described a porous P(DEBT/TETPA) copolymer electrode, where TETPA possessed a tetrahedral structure to induce porosity and DEBT performed as a carrier.²⁶ Recently, Zhang et al. synthesized donor–acceptor conjugated polymers using anthraquinone and nitrobenzene acceptors with EDOT–carbazole–EDOT donor and applied them as electrode materials for supercapacitors.²⁷ This study explored the effect of the incorporation of electron-withdrawing groups into conducting polymers and its impact on hole injection, which in turn affects the key electrochemical properties such as capacitance and cycling stability. Despite these approaches, so far, the donor–acceptor polymers suffer from poor energy density, large equivalent series resistance, limited capacitance, and restricted cyclability.^{17,21,28} Therefore, the development and synthesis of electrode materials that increase the surface area and expose the reaction centers is crucial for enhancing the performance of supercapacitors.²⁹

One of the approaches for enhancing the surface area of the polymers is to mix porous conducting carbon-based additives like graphene, carbon nanotubes (CNTs), carbon nanofiber, and carbon black with conjugated polymers.^{30–36} Carbon nanotubes (CNTs), a class of conducting carbon materials, are distinguished by their exceptional properties, including high electrical conductivity, extensive surface area, robust thermal stability, and notable flexibility.³⁷ Different strategies have been exploited to develop composites of conjugated polymers with single-walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs).³⁸ Among these approaches, the *in situ* synthesis has been reported to be effective for p-type polymers, for example, polypyrrole,^{39–41} poly(3-hexylthiophene),⁴² PEDOT,⁴³ polythiophene,⁴⁴ and polyaniline.^{45–49} It has been shown that *in situ* mixing of CNT with conjugated polymers exhibits better electrochemical performance compared to the external mixing of pristine polymers and neat CNT due to their uniform mixing, high surface area, better morphology control, and improved conductivity in the former case. Recently, we reported n-type P(NDI2OD-T2) or N2200 donor–acceptor polymer and their *in situ* synthesized composites with MWCNT that worked in a 2.4 V operating voltage window, which exhibited better capacitance in comparison with pristine polymer as well as externally mixed polymer carbon nanotube composites.⁵⁰ The P(NDI2OD-T2)/MWCNT composites performed as positive electrodes.

Herein, we present the first report of a perylenebisimide-based donor–acceptor π -conjugated polymer P(PDI2OD-T2) and its *in situ* composite with MWCNTs, which exhibited potential as both positive and negative electrode materials for supercapacitor applications. The P(PDI2OD-T2) or poly-{[N,N'-bis(2-octyldodecyl)-3,4,9,10-peryleneedicarboximide-(1,7&1,6)-diyl]-alt-5,5'-(2,2'-bithiophene)} donor–acceptor

conjugated polymer and their *in situ* composites with MWCNT were synthesized by a modified Stille polymerization reaction within a short interval of time (2 h), where it is normally reported to take long reaction times of 12–72 h.^{51–53} The composites of the P(PDI2OD-T2) polymers were synthesized through the *in situ* incorporation of different weight percentages of multiwalled carbon nanotubes (MWCNTs) such as 25% (P-1) and 33.0% (P-2) during the polymerization. The *in situ* addition of the MWCNT serves a dual role in offering a high surface area, wide pore distribution, and exposure of the active reaction centers of the polymer, which improves the movement of electrolyte ions at the electrode/electrolyte interface. The electrochemical performance of the pristine polymer P-0 and polymer composites (P-1 and P-2) was investigated in a conventional three-electrode arrangement in an organic electrolytic solution. The *in situ* generated polymer composite (P-2) exhibited a specific capacitance of 93 F g⁻¹ (at 0.5 A g⁻¹), which was significantly higher compared to that of P-0. Furthermore, the *in situ* prepared composite polymer P-2 was explored for both positive and negative electrodes with a symmetric supercapacitor device (SC), which was able to achieve a high operating voltage (3.1 V). Additionally, a solid-state (flexible) device was efficiently fabricated using the P-2 polymer, which showed equally good performance with a high-voltage window. The *in situ* polymerization of polymer/MWCNT composites with MWCNT and their electrochemical characterization are schematically summarized in Figure 1.

■ EXPERIMENTAL SECTION

Materials. The following substances were purchased from TCI Chemicals and employed without further purifications: 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA), potassium phthalimide, 2-molecular bromine (Br₂), triphenylphosphine, Iodine (I₂), octyl-1-dodecanol, and hydrazine hydrate. Bis(triphenylphosphine)palladium(II) dichloride (Pd-(Ph₃)₂Cl₂), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene, methanol, dichloromethane, chloroform, deuterated chloroform, acetone, glacial acetic acid, sulfuric acid (H₂SO₄), propylene carbonate (PC), multiwalled carbon nanotubes (MWCNTs), lithium perchlorate (LiClO₄), poly(methyl methacrylate) (PMMA), celgard (polypropylene), *N*-methyl pyrrolidone (NMP), and poly(vinylidene fluoride) (PVDF), were purchased from Sigma-Aldrich. 4-Tertiary butyl toluene, *N,N*-dimethylformamide (DMF), and 1,2,4-trichlorobenzene were also obtained from Sigma-Aldrich and dried prior to use.

Measurements. The ¹H NMR spectra of the monomers and polymers were examined in deuterated chloroform solvent with TMS as the reference on a Bruker 200 and 400 MHz NMR spectrophotometer. The molecular weights of the polymers were determined by gel permeation chromatography (GPC) utilizing a high-temperature Agilent PL-GPC 220 system equipped with an RI detector. The eluent used was 1,2,4-trichlorobenzene (TCB) at a flow rate of 1 mL min⁻¹ at 140 °C. A 2 mg sample was dissolved in 2 mL of TCB, and the solution was filtered through a 0.45 μm PVDF filter. The UV–vis absorption spectra of the polymers were obtained using a PerkinElmer lambda-35 UV/vis spectrometer with deuterium and tungsten lamps as sources. A PerkinElmer STA (Simultaneous Thermal Analyzer) 6000 thermogravimetric analyzer was used to perform thermogravimetric analysis (TGA). The samples were heated from 50 to 700 °C at a rate of 10 °C min⁻¹ under a nitrogen atmosphere. Thermogravi-

metric analysis (TGA) and differential thermogravimetric analysis (DTGA) were performed of sample P-0 from 50 to 900 °C at a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere. The high-resolution transmission electron microscopy (HR-TEM) images were obtained using a JEOL JEM-F200 HR-TEM device. The field emission scanning electron microscopy (FE-SEM) images were obtained using an FEI NOVASEM 450 FE-SEM instrument.

The ζ-potential was determined using the dynamic light scattering (DLS) using a Zetasizer Nano Series, Nano ZS90, and a size range for ζ-potential (diameter) of 3.8 nm to 100 μm and a 90° scattering detector angle. X-ray photoelectron spectroscopy (XPS) was performed using a Thermo K-Alpha⁺ X-ray spectrometer. Raman analysis of the samples was conducted with a Tech-noS IndiRAM CTR 500C Micro Raman Spectrometer.

Sample Preparation. UV–vis absorption measurements were performed in the solution state in chloroform at various concentrations. The solution was prepared at a concentration of 1 mg per 50 mL in chloroform to calculate the concentration of MWCNTs in the polymer composites (C-X). For FE-SEM and HR-TEM sample preparation, methanol was used as the solvent to disperse the polymer sample (1 mg of polymer in 2 mL of methanol). After that, the dispersion was drop-cast over mica for SEM and a copper grid for TEM analysis. ζ-Potential measurements using dynamic light scattering (DLS) were carried out in methanol as the solvent in a quartz cuvette.

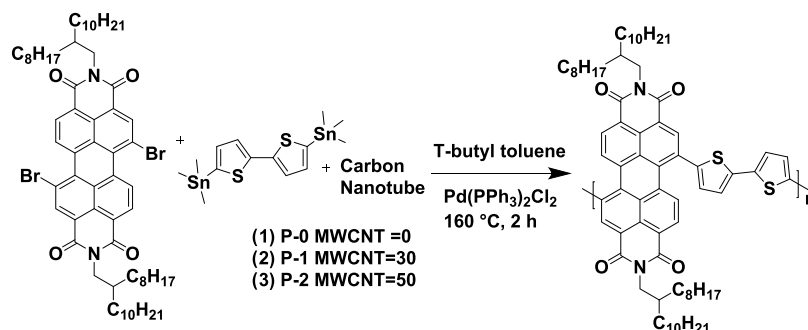
BET Experimental Setup. The pore size distribution and nitrogen adsorption/desorption isotherms of the MWCNT, P-0, and P-2 composite polymers were evaluated at 77 K using a Quantachrome Quadrasorb SI Analyzer (automatic surface area and pore size analyzer). The surface areas of the samples were measured using the Brunauer–Emmett–Teller (BET) method, with nitrogen as the adsorption gas at a 77 K bath temperature. The pore size distribution plots were produced using density functional theory (DFT) at 77 K on carbon with N₂ as the model (slit pore, NLDFT equilibrium model).

Electrode Preparation for the Three-Electrode Studies. Carbon fiber paper was used as the support or current collector for the active material. A homogeneous slurry was prepared by dispersing 4.75 mg of the desired sample (P-1 and P-2) and 0.25 mg of poly(vinylidene fluoride) (PVDF) binder in 500 μL of *N*-methyl pyrrolidone (NMP). The slurry was sonicated for 4–6 h for better dispersion of the material, and 100 μL of this slurry was cast over a piece of carbon fiber paper to achieve a loading of 1 mg cm⁻². However, the P-0 electrode was prepared using an 80:15:5 ratio of the active material (pristine polymer P-0), multiwalled carbon nanotubes, and PVDF using a similar process of slurry preparation and coating. After that, the electrodes were allowed to dry overnight in an oven at 60 °C.

Flexible Electrode for the Device. The flexible electrode was supported on flexible Scotch grafoil tape. A slurry of the active material was prepared at the above-mentioned ratio in 200 μL of NMP. The homogeneously dispersed slurry was cast over peeled grafoil scotch in a 2 cm² area to get an active material loading of 0.64 mg cm⁻² (P-2 electrode). The coated electrodes were dried overnight in an oven at 60 °C. This electrode was further used for quasi-solid-state device fabrication and electrochemical characterization.

Quasi-Electrolyte Preparation. A nonaqueous quasi-solid polymer electrolyte was prepared for the fabrication of quasi-

Scheme 1. Synthesis of P(PDI2OD-T2) (P-0) Polymer and Their Composites P-1 and P-2 with MWCNTs



solid-state flexible supercapacitor devices. For gel formation, 1.6 g of poly(methyl methacrylate) (PMMA) was dissolved in 5 mL of 3 M LiClO₄ in propylene carbonate (PC) and heated at 115 °C with constant stirring for 1 h.

Electrochemical Measurements. BioLogic VMP3 was used to conduct all electrochemical tests. Three-electrode cells were assembled using carbon fiber paper coated with the active material as the working electrode, a platinum mesh as the counter electrode, and Ag/Ag⁺ as the reference electrode in a 1 M LiClO₄/PC electrolyte. The potential window was set at −0.2 to −1.4 V vs Ag/Ag⁺. Cyclic voltammetry (CV) was performed at scan rates of 5, 6, 7, 8, 9, 10, 20, 50, and 100 mV s^{−1}. For the computation of capacitances, galvanostatic charge–discharge measurements were performed at current densities of 0.5, 1, and 2.5 A g^{−1}. The device-level performance and the electrochemical characteristics of the liquid organic and nonaqueous quasi-solid-state devices were also measured using the same instrument as that used for the three-electrode system. Electrochemical studies of the device were performed in 0.2–3.3 V of a potential window.

Quasi-Solid-State Device Fabrication. The electrode supported over a thin layer of grafoil-peeled scotch tape was coated with a thin layer of quasi-solid-state (PMMA LiClO₄) electrolyte. The separator cell guard membrane (polypropylene) was weighed with a thin electrolyte layer, and the device was assembled and packed with the help of transparent scotch tape. This symmetric device was used both as a supercapacitor and a flexible supercapacitor.

Synthesis of Polymer P(PDI2OD-T2) (P-0). The details of the synthesis and characterization of the monomer PDI2OD-Br₂ are provided in Supporting Information, Section S1. The PDI2OD-Br₂ (200 mg, 0.179 mmol) and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (88 mg, 0.179 mmol) monomers were placed in a Schlenk tube equipped with a stirring magnet. Dry 4-*tert*-butyl toluene solvent (10 mL) was poured into the reaction mixture and nitrogen-purged at an ambient temperature for 30 min. Under a nitrogen environment, 6.53 mg (0.009308 mmol) of bis(triphenylphosphine)palladium(II) dichloride (Pd(PPh₃)₂Cl₂) was added to the aforesaid solution, purged with nitrogen for 30 min, and the Schlenk tube was heated at 160 °C in an oil bath for 2 h with continuous stirring. After completion of polymerization, the reaction mixture was cooled to ambient temperature, and the polymer was dissolved in chloroform, reprecipitated using methanol, and filtered using a Büchner funnel. The polymer was purified by Soxhlet extraction in methanol for 24 h followed by *n*-hexane and acetone. Finally, the polymer was dried at 60 °C in a vacuum oven. Yield: 142 mg, 85%. ¹H NMR spectrum (400 MHz, CDCl₃) δ ppm: 8.75–8.74 (br, 2H

aromatic), 8.41 (br, 4H aromatic) 7.32–7.24 (br, 4H), 4.14–4.13 (br, 4H), 2.02 (br, 2H), 1.34–1.22 (br, 64H), 0.85–0.82 (br, 12 H). *M_n*: 17,100, *M_w*: 31,600, and *Đ_M*: 1.8.

Synthesis of Polymer Composites P-1 and P-2. The composite polymer synthesis followed a synthetic procedure similar to that mentioned above for the P(PDI2OD-T2) (P-0) polymer, except that a multiwalled carbon nanotube (MWCNT) was added along with the monomer for *in situ* polymerization to obtain the polymer MWCNT composites. A detailed synthesis is provided below.

Synthesis of Polymer Composite P-1. The monomers PDI2OD-Br₂ (200 mg, 0.179 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (88 mg, 0.179 mmol), and 60 mg of MWCNTs were placed in a Schlenk tube equipped with a stirring magnet; 4-*tert*-butyl toluene solvent (10 mL) was poured into the reaction mixture. After the addition of 6.53 mg (0.009308 mmol) of bis(triphenylphosphine)palladium(II) dichloride (Pd(PPh₃)₂Cl₂) as the catalyst, the solution was subjected to nitrogen purging for 30 min. Similar steps were followed, as described for the P(PDI2OD-T2) (P-0) polymer. For workup, the reaction mixture was cooled to ambient temperature and precipitated in methanol (chloroform dissolution was avoided in order to preserve the MWCNT-incorporated polymeric networks produced by *in situ* polymerization). Yield: 250–60 mg MWCNTs = 190 mg, 95%. ¹H NMR spectrum (400 MHz, CDCl₃) δ ppm: 8.75 (br, 2H aromatic), 8.41 (br, 4H aromatic), 7.32–7.24 (br, 4H), 4.14 (br, 4H), 2.02 (br, 2H), 1.34–1.12 (br, 64H), 0.85–0.82 (br, 12 H). *M_n*: 12,500, *M_w*: 19,600, and *Đ_M*: 1.5.

Synthesis of Polymer Composite P-2. The monomers PDI2OD-Br₂ (200 mg, 0.179 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (88 mg, 0.179 mmol), and 100 mg of MWCNT were placed in a Schlenk tube. 4-*tert*-butyl toluene solvent (10 mL) was injected into the reaction mixture. 6.53 mg (0.009308 mmol) of the bis(triphenylphosphine)palladium(II) dichloride (Pd(PPh₃)₂Cl₂) catalyst was added and the same procedure was followed as described for P-0 and P-1 polymer. Yield: 270–100 mg MWCNTs = 171 mg, 86%. ¹H NMR spectrum (400 MHz, CDCl₃) δ ppm: 8.74 (br, 2H aromatic), 8.41 (br, 4H aromatic), 7.32–7.24 (br, 4H), 4.14 (br, 4H), 2.02 (br, 2H), 1.34–1.22 (br, 64H), 0.85–0.82 (br, 12 H). *M_n*: 20,400, *M_w*: 28,400, and *Đ_M*: 1.4.

RESULTS AND DISCUSSION

Synthesis and Characterization. PDI2OD-Br₂ was synthesized by brominating 3,4,9,10-perylene-tetracarboxylic dianhydride, followed by imidization with 2-octyl-1-dodecyl-

amine. The details of the synthesis of the monomer PDI2OD-Br₂ are given in Supporting Information, Section S1. The structural characterization of the monomer PDI2OD-Br₂ using ¹H and ¹³C NMR spectroscopy is shown in Figures S1 and S2. Scheme 1 shows the synthesis of the P(PDI2OD-T2) (P-0) polymer and its *in situ* synthesized composites (P-1 and P-2) with MWCNT.

Stille polymerization was used to synthesize the P(PDI2OD-T2) (P-0) polymer and its composites with MWCNT (P-1 and P-2). The P(PDI2OD-T2) polymer is commonly synthesized by Stille or Suzuki polymerization and it requires a reaction time of around 12–72 h.^{51–53} Here, the PDI2OD-Br₂ monomer was reacted with 5,5'-bis(trimethylstannyl)-2,2'-bithiophene at 160 °C and the Pd(Ph₃)₂Cl₂ catalyst was utilized with 4-*tert*-butyl toluene as the high boiling solvent, which yielded the P(PDI2OD-T2) polymer within 2 h of reaction time. In this study, the pristine P(PDI2OD-T2) polymer is named P-0. The polymer composites P-1 and P-2 were polymerized with the *in situ* inclusion of different doses of MWCNTs (60 and 100 mg) along with the monomers, respectively. The polymers were precipitated directly in methanol (rather than the typical approach of dissolution of the polymer in chloroform and reprecipitation in methanol) to prevent the loss of MWCNTs incorporated by *in situ* polymerization. Using methanol, *n*-hexane and acetone, polymer P-0 and its composites were purified using Soxhlet extraction. The probable weight percentages of MWCNT as feed weight percent incorporation in polymer composites P-1 and P-2 were determined (the amount of MWCNT fed divided by the total yield) to be 23.0 and 36.9%, respectively. The polymers were soluble in chloroform and 1,2,4-trichlorobenzene, and insoluble in DMF and THF. ¹H NMR spectroscopy was used to confirm the structure of the polymers, as shown in Figures S3–S5. The polymer solution in chloroform was filtered first with filter paper and then with a poly(tetrafluoroethylene) (PTFE) filter to remove the MWCNTs, which were then used for ¹H NMR spectroscopy and gel permeation chromatography (GPC) analysis. The number and weight-average molecular weights and the polydispersity (*Đ*) for the polymers were investigated by gel permeation chromatography (GPC) with 1,2,4-trichlorobenzene as an eluent at 140 °C, and its chromatogram is shown in Figure 2. The number-average molecular weight of the polymers ranged from *M_n* 12,500 to 20,500 kg mol^{−1} and the dispersity (*Đ*) from 1.4 to 1.8, as shown in Table 1.

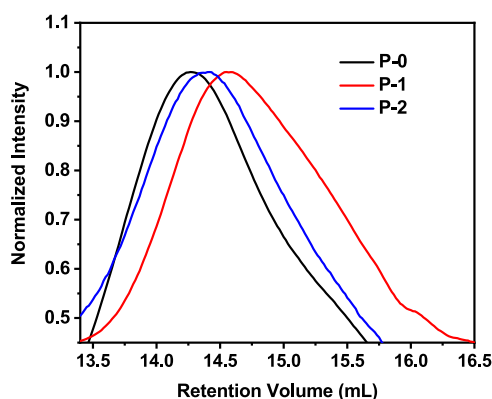


Figure 2. Gel permeation chromatogram (GPC) of P(PDI2OD-T2) (P-0), P-1, and P-2 polymers.

Thermogravimetric analysis (TGA) in a nitrogen environment was performed to determine the thermal properties of the polymers and composites. The TGA curves in Figure 3 demonstrate the high thermal stability of the polymers up to 400 °C. The following formula was utilized to calculate the percentage incorporation of MWCNT for composite samples from the TGA curves.⁵⁴

$$\begin{aligned} &\% \text{ of MWCNT incorporated} \\ &= \% \text{ remaining pristine MWCNT} \\ &\quad - \left(\frac{\% \text{ loss of composite}}{\% \text{ loss of pure polymer}} \times 100 \right) \end{aligned}$$

As illustrated in Figure S6, the mass loss was calculated by measuring the vertical separation between the two tangent lines formed on the weight loss plot. The percentage of pristine MWCNT remaining was 97.61%. The MWCNT incorporation percentages were calculated as 24.8 and 33.0% for the composites P-1, and P-2, respectively.

In order to understand the degradation profile of the polymer, differential thermogravimetric analysis (DTGA) was performed for P(PDI2OD-T2) (P-0) from 50 to 900 °C. TGA measures the weight loss as a function of temperature, while DTGA shows the rate of weight loss, as depicted in Figure S7. Thermogravimetric analysis shows that a sharp significant weight loss starts at around 400 °C and continues until about 520 °C, indicating the breakdown of the polymer structure. After the primary degradation, the slower weight loss of up to 900 °C likely represents the degradation of the more stable perylenebisimide (PBI) aromatic moieties.⁵⁵ The DTGA curve (Figure S7) shows a peak at 380–550 °C, corresponding to the primary degradation phase, and additional peaks at 600–900 °C, indicating further degradation of the stable PBI fragments.

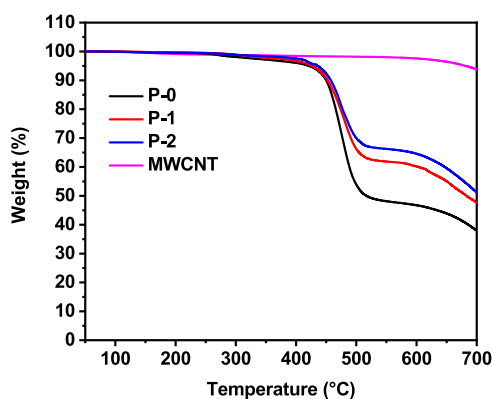
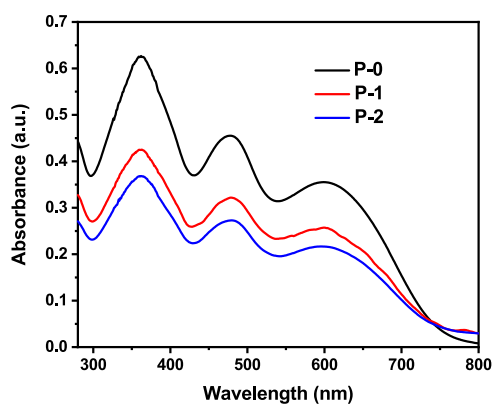
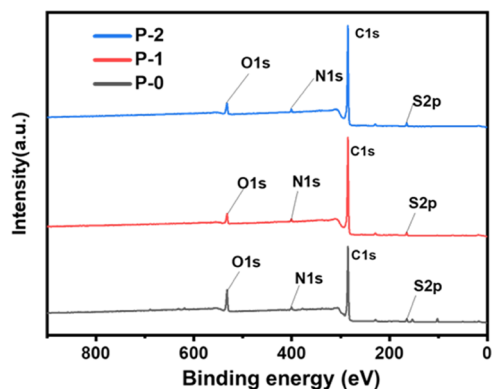
The percentage of MWCNTs in the polymer composites was also calculated using absorption spectroscopy. The absorption spectra of the polymers were measured in chloroform, and are shown in Figure 4. The absorption band between 300 and 430 nm indicates a π – π^* transition. The bands occurring between 430 and 535 nm and 535 and 720 nm correspond to the S0–S2 and S0–S1 electronic transitions, respectively.⁵¹ Using the Beer–Lambert law, the molar extinction coefficient (ϵ) for polymer P-0 was calculated as 31931 L M^{−1} cm^{−1} based on the absorption spectra of P-0 recorded at different concentrations in chloroform (Figure S8a,b). The percentages of polymer and MWCNT in polymer composites were calculated using the molar extinction coefficient (ϵ), and the detailed calculations are described in Supporting Information, Section S2. The percentages of MWCNTs in the polymer composites P-1 and P-2 were determined to be 26 and 35.8%, respectively. The percentage MWCNT incorporation calculated from the UV–vis absorption spectra matched very well with the feed ratio and the percentage MWCNT calculated from TGA, and are listed in Table 1.

X-ray photoelectron spectroscopy (XPS) analysis was carried out to obtain a comprehensive understanding of the interaction between the MWCNTs and P(PDI2OD-T2) polymer. The XPS analysis shown in Figure 5 indicates that the polymers were mainly composed of carbon, nitrogen, sulfur, and oxygen.⁵⁶

Table 1. Polymerization Yield, Molecular Weights, and MWCNT % Incorporation Determined By Feed, TGA, and UV-Vis Spectroscopic Analysis for Polymer P-0 and Its Composites P-1 and P-2

sr. no	polymer	M_n^a (kg mol ⁻¹)	M_w^{aa} (kg mol ⁻¹)	$\bar{D}_M^b$	% yield	% weight of MWCNT in the feed ^c	% weight of MWCNT from TGA	% weight of MWCNT from absorption spectroscopy
1	P-0	17.2	31.5	1.8	85	0	0	0
2	P-1	12.5	19.5	1.5	90	23.1	24.8	26.0
3	P-2	20.5	28.5	1.4	86	36.9	33.0	35.8

^a M_n and M_w were measured by GPC using 1,2,4-trichlorobenzene as the eluent and PS as the standard. ^b $\bar{D}_M$ is polydispersity. ^cMWCNT incorporation in the feed was determined based on the overall yield.

**Figure 3.** Thermogravimetric analysis performed for the P-0, MWCNT, and P-1 and P-2 samples.**Figure 4.** UV-vis absorption spectra of P-0, P-1, and P-2 polymers were measured in chloroform.**Figure 5.** XPS survey spectra analysis of the P-0, P-1, and P-2 samples.

Detailed analysis of the C 1s, N 1s, and S 2p peaks was conducted to analyze the interactions at the molecular level. The C 1s spectra depicted in Figure 6a exhibit a peak at

approximately 284.8 eV, which is indicative of the sp^2 carbon atoms present in the polymer backbone and MWCNTs. Meanwhile, Figure 6b shows N 1s peaks at 400 eV, with a noticeable shift toward the left for the P-1 and P-2 samples, suggesting altered electronic environments resulting from nitrogen–MWCNT interactions, potentially involving electron acceptance. Figure 6c illustrates the S 2p spectra featuring characteristic spin–orbit coupling peaks around 163–165 eV. The observed shifts and intensity variations in P-1 and P-2 compared to P-0 imply robust sulfur–MWCNT interactions, likely encompassing charge transfer or bonding mechanisms that impact the electronic environment of the sulfur atoms. In short, the XPS analysis highlights substantial interactions between the polymer and MWCNTs in P-1 and P-2 composites, affecting the electronic environment of nitrogen and sulfur atoms and potentially enhancing structural and electronic properties.

The dispersion properties of the polymer composites were analyzed by ζ -potential measurements using dynamic light scattering (DLS). The ζ -potential values for the MWCNT, P-0, P-1, and P-2 were -0.0598 , -0.138 , -0.382 , and -0.853 , respectively, as detailed in Table S1 and Figure S9. The increased ζ -potential observed in the polymer composites (P-1 and P-2) suggests a more uniform distribution and prevention of carbon nanotube agglomeration within the polymer matrix. This change indicates the adsorption of polymer chains onto the surface of MWCNT, which affects the overall properties of the composite.^{57,58} Conductivity measurements demonstrate that higher ζ -potential values are associated with well-dispersed MWCNTs, leading to improved electrical properties,⁵⁹ while lower values indicate aggregation and reduced conductivity.

Morphology. FE-SEM and HR-TEM techniques were used to determine the morphology of the all-polymer samples and MWCNT. Figure 7a shows that the P-0 polymer exhibits a spherical morphology with interconnected spherical particles of varying diameters (Figure S10a). On the other hand, the MWCNT exhibited an entangled tubular morphology (Figure 7b) with a highly porous interconnected network of carbon tubes (Figure S10b). Uniform dispersion and wrapping of MWCNT over the polymer were observed for P-1 and P-2 with an enhancement of the porous network (Figure 7c,d). The FE-SEM images show a better interaction of the polymer with MWCNT during *in situ* polymerization, as shown in Figure 7. Compared with P-1, composite P-2 showed well-wrapped structures with MWCNT along with a very good porous architecture. This uniform networking of the MWCNT over the composite polymers is expected to enable the exposure of active sites and act as a direct pathway for electron transport. FE-SEM images at a higher magnification of 5 μ m are shown in Figure S10. This also indicates a maximum contact between the MWCNT with the polymer, where no bulk growth was observed.

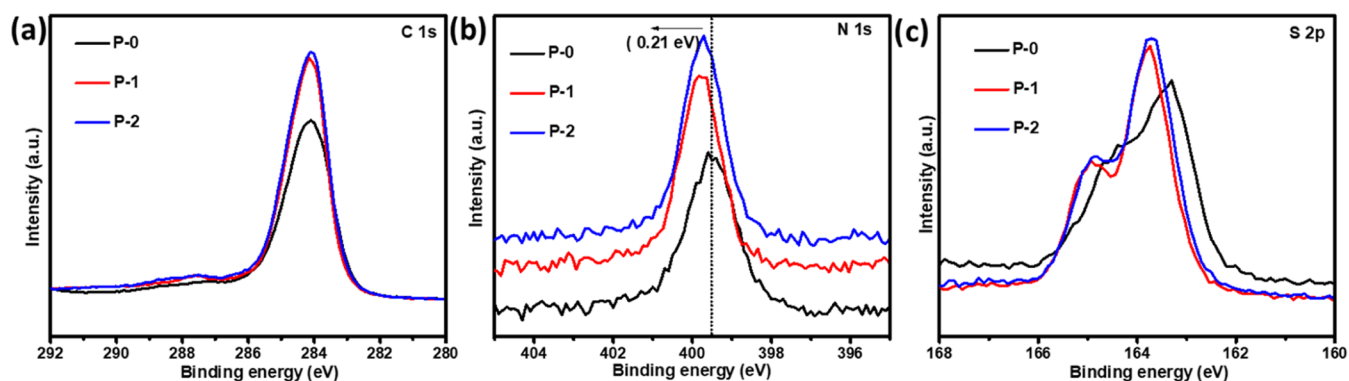


Figure 6. (a–c) X-ray photoelectron spectroscopy (XPS) analysis of P-0 (PDI2OD-T2), P-1, and P-2.

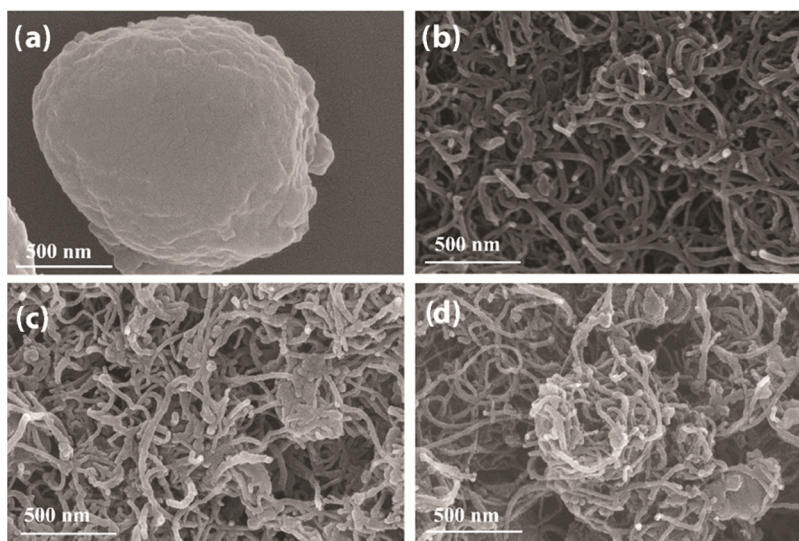


Figure 7. FE-SEM images of (a) P-0, (b) neat MWCNTs, (c) P-1, and (d) P-2 at a resolution of 500 nm.

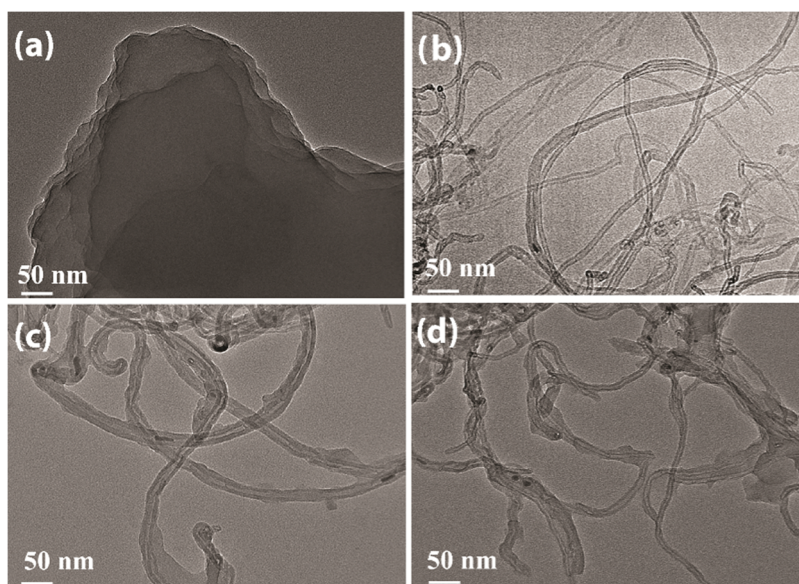


Figure 8. HR-TEM images of (a) pristine P-0, (b) neat MWCNT, (c) P-1, and (d) P-2 at 50 nm.

The samples were also analyzed by HR-TEM. The neat polymer P-0 (Figure 8a) and MWCNT (Figure 8b) showed spherical and tubular morphologies, respectively, which confirmed the FE-SEM observations (Figure 7a,b). Figure

8c,d shows the overall increase in the diameter of the MWCNT, and the polymer layer was spread on the surface of the MWCNT. HR-TEM images confirm the lack of unwanted agglomeration and the presence of a homogeneous

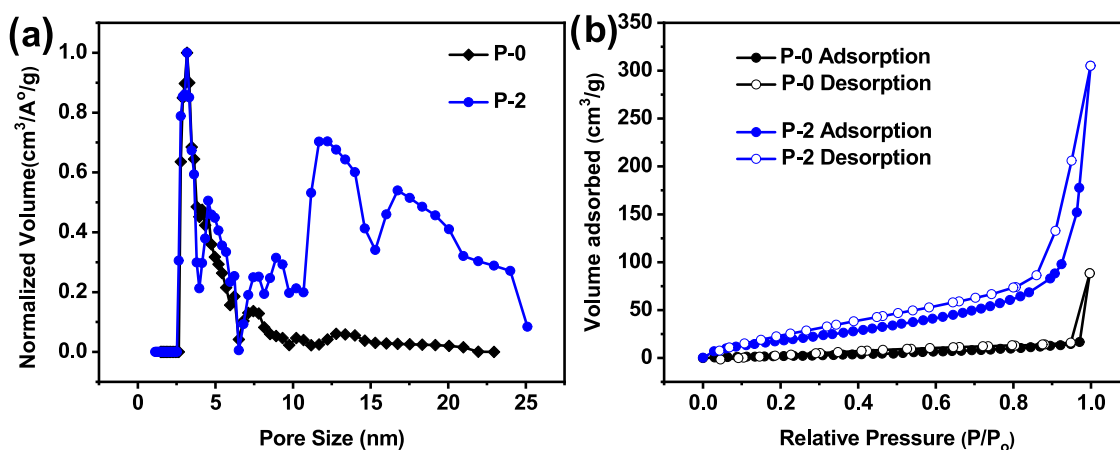


Figure 9. (a) Pore size distribution profiles and (b) nitrogen adsorption/desorption isotherms of P-0 and P-2 samples.

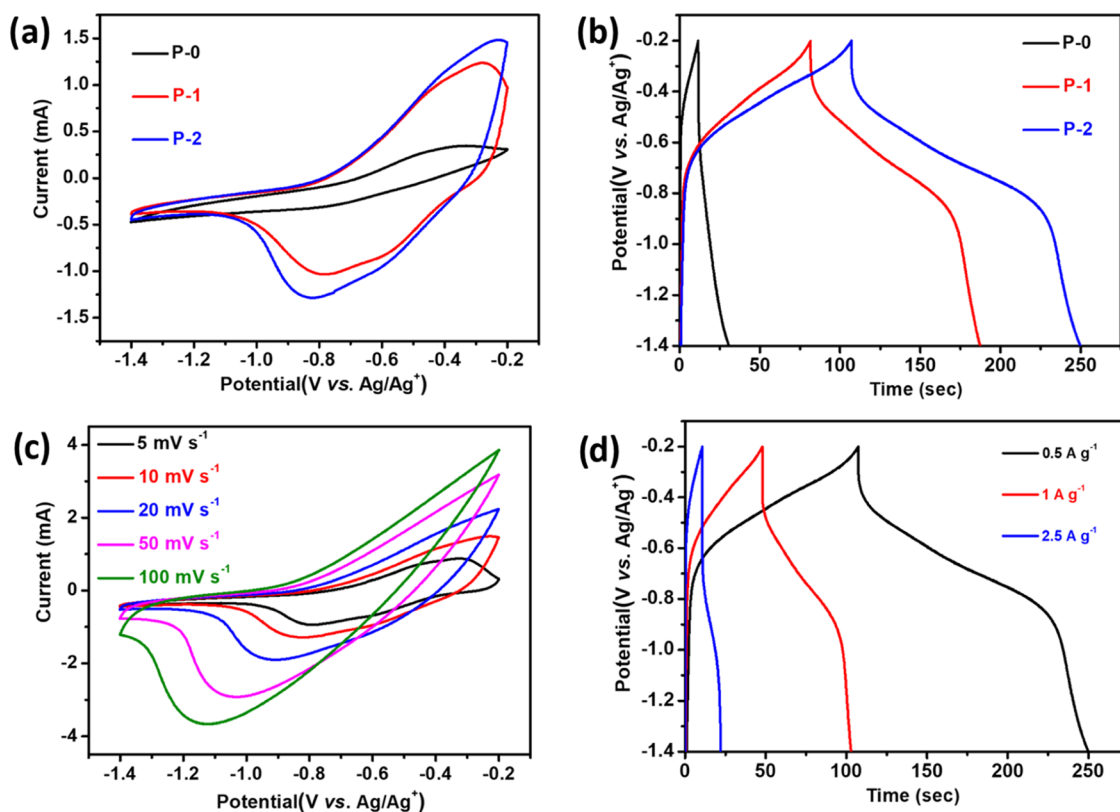


Figure 10. (a) CV profiles of the P-0, P-1, and P-2 samples measured at a scan rate of 10 mV s⁻¹. (b) Galvanostatic charge–discharge (GCD) of the P-0, P-1, and P-2 samples recorded at a current rate of 0.5 A g⁻¹. (c) CV scans at various scan rates from 5 to 100 mV s⁻¹ for the P-2 sample, and (d) the GCD profile recorded at various currents of 0.5, 1.0, and 2.5 A g⁻¹ for P-2.

distribution in *in situ* synthesized samples. FE-SEM and HR-TEM images prove the uniform polymeric network with the MWCNT and the absence of bulk networks in the *in situ* polymerized samples. This is expected to enhance the electrochemical performance of the composites.

Surface Area and Pore Size. The nitrogen adsorption/desorption isotherms and pore size distributions of the P-0 and P-2 polymer samples are shown in Figure 9a,b. P-0 showed a predominantly microporous pore size distribution (Figure 9a), whereas MWCNT exhibited both micro- and meso-pore distribution, as shown in Figure S11. As the MWCNT content increased, the number of pores across the mesoporous area increased in the composite polymer P-2 compared to P-0, as

shown in Figure 9a. The pore size distribution profile of the composite polymer was similar to that of MWCNT. The density functional theory (DFT) desorption model indicated that the average pore width for polymers was around 3 nm, whereas that for the MWCNTs was 14 nm. The polymer samples P-0, P-2, and MWCNT exhibited Type III isotherms, as shown in Figures 9b and S11b. The specific surface area values were determined to be 206.0 m² g⁻¹ for MWCNT, 11.3 m² g⁻¹ for P-0, and 84.2 m² g⁻¹ for P-2 using the BET model. The BET results show that the *in situ* MWCNT inclusion increases the surface area of the P-2 composites compared to that of the polymer P-0, which is consistent with the FE-SEM results. The difference in the pore size between the polymer

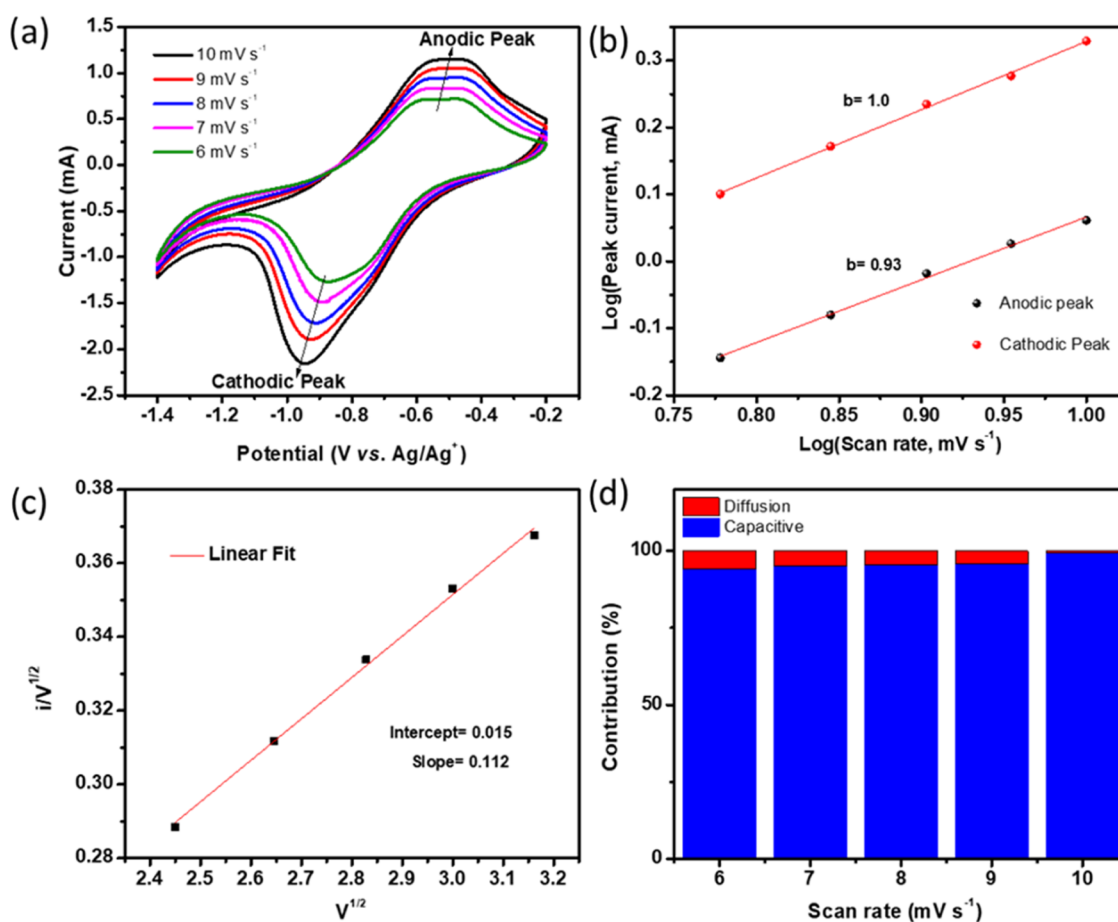


Figure 11. (a) The CV profile of P-2 measured at a scan rate of 6–10 mV s⁻¹, (b) the log (peak current, mA) vs log (scan rate, mV s⁻¹) plot, (c) $i/V^{1/2}$ vs $V^{1/2}$ relationship, and (d) capacitive contribution of P-2 at different scan rates calculated for the oxidation peak at -0.53 V vs Ag/Ag⁺.

composites P-2 and P-0 is attributed to their morphologies. As demonstrated by FE-SEM and HR-TEM analysis, the polymer layer in the P-2 polymer composites was coated thinly and homogeneously on the surface of the MWCNT. The main objective of such a hierarchical porous and high surface morphology is to easily transport electrolyte ions when the material is utilized as an electrode, thereby increasing the overall capacity for charge storage.

The *in situ* synthesized polymer composites demonstrated superior morphological characteristics and increased surface area, as indicated by FE-SEM (Figure 7), HR-TEM (Figure 8), and BET analysis (Figure 9). The uniform dispersion of the polymer and carbon nanotube in the composites, as observed in the analysis, is in line with the ζ -potential and XPS results. Polymer P-0 exhibits a less porous network due to the nature of spherical particles with varying diameters, as confirmed by FE-SEM and HR-TEM analyses (Figures 7a and 8a). On the other hand, polymer P-2 shows thin and homogeneous polymer layer growth over the MWCNTs, as revealed by the HR-TEM images. The incorporation of *in situ* MWCNTs enhances the surface area of the P-2 composite compared to that of P-0, which is consistent with the FE-SEM results. This hierarchical porous morphology is beneficial for efficient electrolyte ion transport when the material is used as an electrode, thereby improving the overall charge storage capacity.

ELECTROCHEMICAL CHARACTERIZATION

The electrochemical efficiencies of all electrodes (P-0, P-1, and P-2) were analyzed in a three-electrode assembly using a 1 M LiClO₄/PC electrolyte, where Ag/Ag⁺ was used as the reference, the platinum mesh was used as the counter, and polymer-coated toray carbon was used as the working electrode. As shown in Figure 10a, P-0, P-1, and P-2 were initially examined using cyclic voltammetry at a scan rate of 10 mV s⁻¹. The composite polymers P-1 and P-2 exhibited reversible redox peaks, indicating pseudocapacitive charge storage behavior. The significant increase in the current response of P-1 and P-2 compared to that of the neat polymer P-0 mainly arises from the exposure and utilization of the maximum active sites upon MWCNT addition (Figure 10a). For comparison, the CV of the MWCNT was measured at varying scan rates from 5 to 100 mV s⁻¹ (Figure S12a), showing a rectangular feature that depicted the EDLC type of charge storage. The lower current response of the MWCNT at a scan rate of 10 mV s⁻¹ indicated the absence of MWCNT participation in the redox reactions. Furthermore, the GCD of the MWCNT well matched the CV profile and did not show any redox properties during charge–discharge. However, its inclusion in the polymer (P(PDI2OD-T2)) creates a conducting network for the facile passage of electrons. P-2 out-performed P-1, as an improvement in the current response was observed from CV, which could be due to the higher MWCNT content in the former and also the uniform wrapping

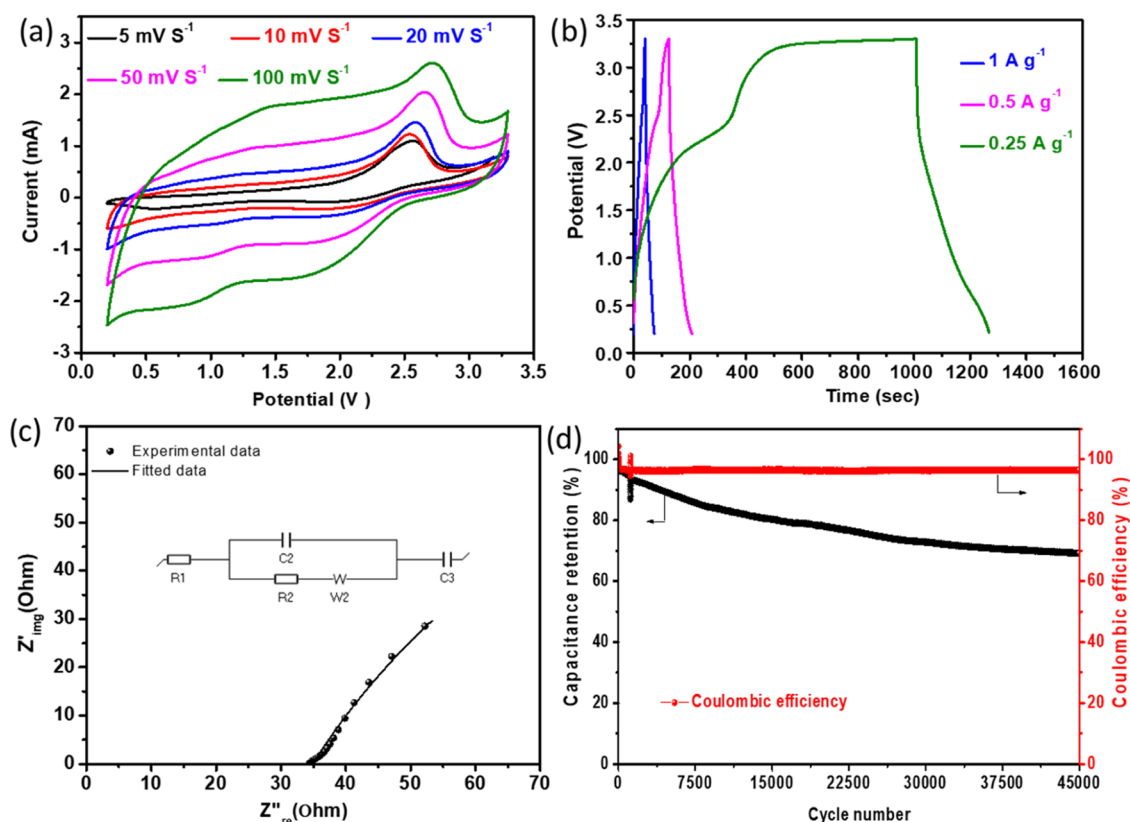


Figure 12. Full cell device characterization in the liquid electrolyte (LE-P-2||P-2): (a) CV profile of the symmetric device at various scan rates, (b) galvanostatic charge–discharge (GCD) at various current rates, (c) electrochemical impedance spectroscopy (EIS) measurement of the LE-P-2||P-2 symmetric device, and (d) cycle stability at a current density of 2.0 A g^{-1} .

of the MWCNT network over the polymer. The CV profiles of P-0 and P-1 are shown in Figure S13a,b.

The galvanostatic charge–discharge (GCD) investigation for P-0, P-1, and P-2 in a three-electrode assembly is shown in Figure 10b. The observed GCD profile was in good agreement with that of the CV curves. Furthermore, the capacitances were calculated for P-0, P-1, and P-2 using eq no. E1 (Supporting Information, Section S3). The discharge capacitances of P-0, P-1, and P-2 were 10.0, 61.6, and 92.9 F g^{-1} , respectively, at a current rate of 0.5 A g^{-1} . The comparatively high capacitance value associated with the P-2 composite is mainly attributed to the active participation of faradaic processes enabled by the high MWCNT content. This emphasizes the significance of the donor–acceptor polymer modification technique using the *in situ* MWCNT addition approach. It is worth noting that the elevated surface area and altered porosity of the composites facilitate electron transport in charge storage by providing a highly accessible surface area and conducting network in the composite samples.

Figure 10c shows the CV profile of composite P-2 at scan rates of 5, 10, 20, 50, and 100 mV s^{-1} . The polymer shows reversible peaks at $-0.4/-0.9 \text{ V}$ vs Ag/Ag^+ , in 5 mV s^{-1} , and a more or less similar feature was observed throughout all the scan rates, highlighting the good reversibility of the polymer P-2. Figure 10d compares the GCD profile of P-2 at current rates of 0.5, 1.0, and 2.5 A g^{-1} . The capacitances obtained were 92.9, 70.7, and 37.4 F g^{-1} , respectively. Similarly, the GCD profiles were recorded for P-0 and P-1, as shown in Figure S13c,d. The discharge capacitances obtained for P-0 and P-1 were 10, 2.2,

and 0.6 F g^{-1} , and 61.6, 48.3, and 28.5 F g^{-1} at current rates of 0.5, 1.0, and 2.5 A g^{-1} respectively.

Cyclic voltammetry (CV) measurements were conducted on the P-2 electrode to investigate the charge storage mechanism. The test was carried out using a three-electrode setup in a 1 M LiClO_4 electrolyte at scan rates of $6\text{--}10 \text{ mV s}^{-1}$. The reference electrode used was Ag/Ag^+ and the counter electrode was a platinum (pt) mesh. The CV profile displayed distinct redox peaks at all scan rates (Figure 11a). The peak current (i) for both the anodic and cathodic reactions was recorded at scan rates ranging from 6 to 10 mV s^{-1} . By using the equation, $i = av^b$, where i is the peak current, v is the scan rate, and a and b are variables, the slope of the log–log plot of the peak current (mA) against scan rate (mV s^{-1}) was determined to find the parameter b . A value of b close to 1.0 indicates the dominance of a surface-controlled or capacitive mechanism, while a value near 0.5 suggests a diffusion-controlled mechanism. The calculated b values for the anodic and cathodic peaks were 0.93 and 1.0, respectively, indicating that the capacitive mechanism governs the faradaic reactions at the peak regions (Figure 11b). The contributions of diffusion- and capacitive-controlled reactions in the total current response from the CV scans were determined using the following equation,

$$i = k_1 v + k_2 v^{1/2}$$

where k_1 and k_2 are the constant parameters, i is the current, and v is the scan rate. By plotting $i/v^{1/2}$ against $v^{1/2}$, the values of k_1 (0.112) and k_2 (0.015) were obtained as the slope and y-intercept, respectively (Figure 11c). The percentage contributions of the capacitive process at scan rates of 6, 7, 8, 9, and 10

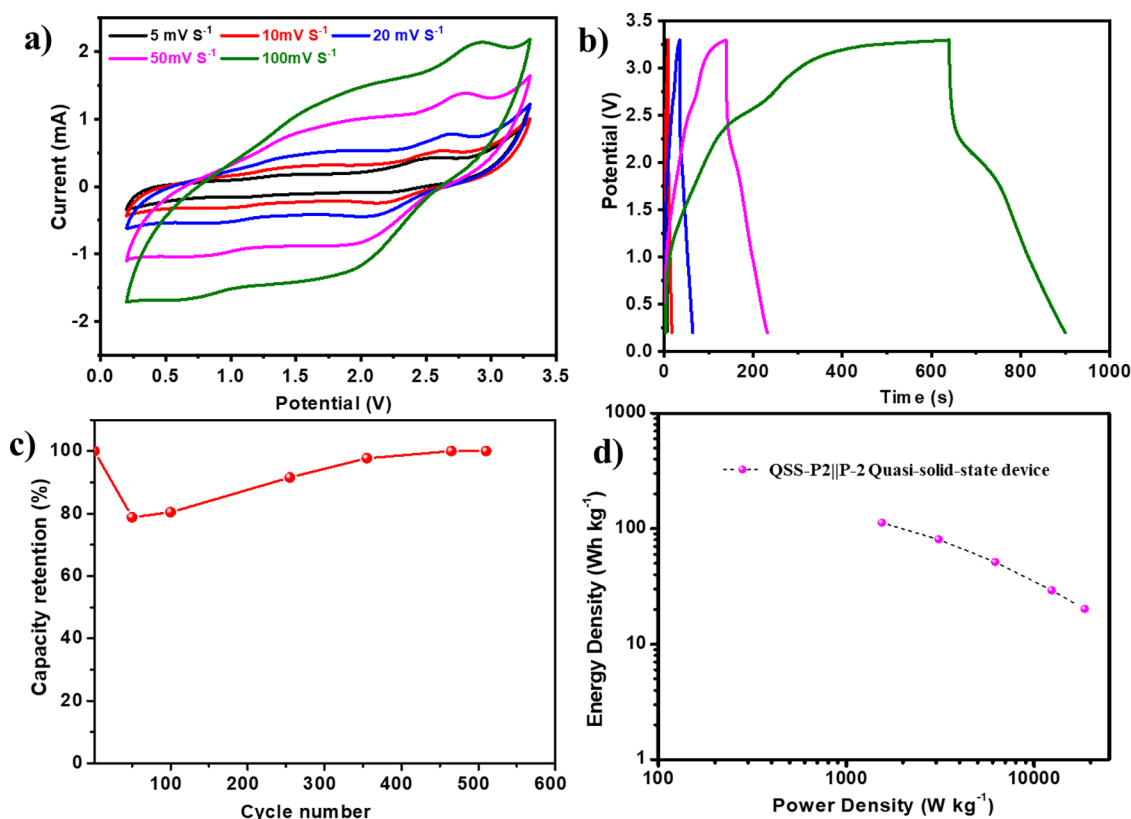


Figure 13. Flexible solid-state device and (QSS-P2||P-2) measurements: (a) CV profile at different scan rates, (b) galvanostatic charge–discharge at various current rates, (c) durability test at a current rate of 1.0 A g⁻¹, and (d) comparison of power density and energy density at different current rates.

mV s⁻¹ were found to be 94, 95.1, 95.4, 95.7, and 99.5%, respectively (Figure 11d). As the scan rate increases, the capacitive response increases, while the diffusive contribution decreases due to the limited time available for the redox reaction at higher scan rates.

The donor–acceptor polymer P-2 shows good properties as positive and negative electrodes. Therefore, the fabrication of a symmetric device in a liquid electrolyte (1 M LiClO₄ in propylene carbonate) was attempted to investigate its material properties. The CV profiles (0.2–3.3 V) at various scan rates of 5–100 mV s⁻¹ are shown in Figure 12a. The high-voltage window (3.1 V) highlights the importance and the intrinsic properties of the polymer, which are higher than or comparable to those of the previously reported donor–acceptor polymers.^{21,24–26} The reversible redox features originating from the polymer material are maintained throughout all CV scan rates. The GCD of the symmetric device LE-P-2||P-2 (LE-liquid setup) shown in Figure 12b exhibits capacitances of 85.4, 53.0, and 43.9 F g⁻¹ at current rates of 0.25, 0.5, and 1.0 A g⁻¹ given the currents of 0.32, 0.64, and 1.28 A to total Z (1.28 mg of active mass on both electrodes), respectively, calculated using eq no. E2 (Section S3). This value is higher than or comparable to that of many reported donor–acceptor polymers, as shown in Table S3.

The study of the internal resistance of electrolytes, charge transfer resistance, and ion diffusion in supercapacitor devices was conducted using electrochemical impedance spectroscopy (EIS) (Figure 12c). The values of solution resistance and charge transfer resistance were extracted by carrying out EIS fitting, with the corresponding equivalent circuit shown in the inset. The solution resistance (R_s) was determined by the

intercept on the x -axis of the Nyquist plot in the high-frequency region, observed to be 34.8 Ω , which is lower than that of the reported donor–acceptor polymer.^{13,25,26} Furthermore, a small semicircle (R_{ct}) attributed to the charge transfer resistance with a value of 0.57 Ω results in faster charge transfer at the electrode–electrolyte interface. The symmetric LE-P-2||P-2 device exhibits high cycling stability when tested at a current rate of 2 A g⁻¹, showing stability over 45,000 charge–discharge cycles. The data revealed 80% retention of capacitance while approaching 15,000 cycles and 70% capacitance retention over 45,000 cycles with a decent coulombic efficiency of 96% throughout the cycles (Figure 12d). This high cycling stability can be attributed to the material stability upon composite formation with the MWCNT and redox active material. The cycling stability of the device surpasses that in previous reports and is compared in Table S3.

Post-mortem analysis of the P-2 composite electrode was conducted after prolonged electrochemical cycling using XPS and Raman spectroscopy (Figure S14a,b). The XPS survey spectra of the P-2 electrode after electrochemical cycling (Figure S14a) revealed an increase in the intensity of the O 1s peak, indicating the formation of oxygenated species on the electrode surface. Other elements such as N, C, and S were also detected along with Li, Cl, and F from the electrolyte and binder. Changes in peak intensities suggest alterations in the surface chemistry of the P-2 electrode. The Raman spectra (Figure S14b) for the P-2 electrode exhibit prominent D, G, and G' bands before cycling, indicating a well-defined structure with a significant MWCNT content. After cycling, there is a decrease in the intensity of these bands, indicating changes in the surface chemistry, which is consistent with the XPS results.

Furthermore, a flexible quasi-solid-state device was fabricated. The fabrication of the flexible solid symmetric device followed the drop-casting method for the electrode preparation over a peeled grafoil, as detailed in the [Experimental Section](#). A thin layer of quasi-PMMA LiClO_4 electrolyte was applied to the electrodes, and the separator was carefully sealed with a QSS-P2||P-2 (QSS-quasi-solid-state device). The CV of the quasi-solid-state symmetric device is depicted in [Figure 13a](#), which exhibits reversible redox features at a scan rate of 5–100 mV s^{-1} , similar to its liquid counterpart. This indicates the retention of material activity even in the quasi-solid-state without compromising the redox activity. The GCD capacitances ([Figure 13b](#)) obtained at current rates of 0.25, 0.5, and 1.0 A g^{-1} were 84.2, 60.5, and 38.5 F g^{-1} , respectively. Furthermore, the cycle stability of the quasi-solid-state device is shown in [Figure 13c](#), which exhibited a 99% capacitance retention over 500 cycles. Finally, a demonstration of the QSS-P-2||P-2 device is presented in [Figure S15](#). The device was first charged to light a light-emitting diode (LED) bulb. The Ragone plot (power density vs energy density) of the QSS-P-2||P-2 is shown in [Figure 13d](#). The maximum energy density of the device was 112.44 Wh kg^{-1} , and the maximum power density output was 18,600 W kg^{-1} , given from [eq no. E4](#) (Section S3). A comparison of energy and power densities is presented in [Table S2](#). The comparable activity of the composite polymer P-2 in liquid and solid-state devices highlights the good intrinsic activity of the material. The good device performance could be attributed to the better interaction of the MWCNT and polymer, which provided a highly accessible surface area and improved the electron conductivity and channels for the easy transport of Li^+ -ions. [Table S3](#) compares the capacitance, voltage window, and cycling stability of the P-2 composite in a three-electrode cell and symmetric device configurations with the performance of some of the previously reported donor–acceptor (n-type) redox active polymers.

CONCLUSIONS

In summary, perylenebisimide-based donor–acceptor conjugated polymer P(PDI2OD-T2) and its composites were synthesized through optimized Stille polymerization in a reduced time frame. The *in situ* incorporation of multiwalled carbon nanotubes (MWCNTs) into the polymer matrix notably enhanced the conductivity of the composite polymer, designated as P-2. The improved surface area and pore structure of the composite facilitated the movement of electrolyte ions, which is crucial for device applications as a supercapacitor electrode. The material was thoroughly evaluated using various characterization techniques. The donor–acceptor composite polymer P-2 exhibited commendable capacitance values, reaching 93 F g^{-1} at a current density of 0.5 A g^{-1} . When configured into a symmetric supercapacitor with both liquid organic (LE-P-2||P-2) and quasi-solid-state (QSS-P-2||P-2) device, the device maintained excellent capacitances of 85.4 and 84.2 F g^{-1} , respectively, at a current rate of 0.25 A g^{-1} and an operational voltage window of 3.1 V, with robust cycle stability. Moreover, these devices exhibited robust cycling stability, maintaining approximately 70% of their initial capacitance over 45,000 cycles with a decent coulombic efficiency of 96%. The energy and power densities of the device were impressive with values of 112.4 Wh kg^{-1} and 18,600 W kg^{-1} , respectively. A practical demonstration using an LED light bulb further showed the device's capability. This

study signifies an important advancement in the use of synthetic techniques to develop donor–acceptor-conjugated polymers for high-performance supercapacitors with extensive potential ranges and significant power densities.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.4c02345>.

Synthesis of the monomers and their structural characterization using ^1H , ^{13}C NMR; characterization of the polymers using ^1H NMR, TGA, DTGA, UV–visible absorption spectroscopy, XPS, Raman, ζ -potential, BET isotherms, and pore size distribution profiles; FE-SEM images and electrochemical characterization; calculations and a comparison table (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was financially supported by the SERB project SPF/2021/000135 000135 and the Centre of Excellence (CoE) (F.No. 25014/2/2015-PC-II; FTS: 14428) supported by the Ministry of Chemical and Fertilizers, Department of Chemicals and Petrochemicals, Government of India. A.A.W. acknowledges UGC, New Delhi, India, for the research fellowship.

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