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Synthesis and Coating of Electroactive Polymers: Wet vs. Dry Processing

Dianatdar Langeroudi, Afshin

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Abbreviation

	(alphabetical order)
TPA-CH_2OH	[4-(N-phenylanilino)phenyl] methanol
NMP	1-Methyl-2-pyrrolidinone
AIBN	2,2′-Azobis(2-methylpropionitrile)
TPA-CHO	4-(Diphenylamino)benzaldehyde
TPA-Me	4-Methoxytriphenylamine
AFM	Atomic force microscopy
ALD	Atomic layer deposition
B.E.	Binding energy
CNT	Carbon nanotube
CP	Conductive polymer
CE	Counter electrode
CV	Cyclic voltammetry
DI water	Deionized water
DSC	Differential scanning calorimetry
DMA	Dynamic mechanical analysis
ECC	Effective conjugation coordinate
EDLC	Electrical double-layer capacitor
A	Electron acceptor
D	Electron donor
EDS	Energy dispersive X-ray spectroscopy
FTIR	Fourier-transform infrared spectroscopy
GCD	Galvanostatic charge-discharge
GPC	Gel permeation chromatography

T_g	Glass transition temperature
H	Hardness
HH	Head-to-head
HT	Head-to-tail
HOMO	Highest occupied molecular orbital
ITO	Indium tin oxide
IR	Infrared
ICP	Intrinsically conductive polymer
LUMO	Lowest unoccupied molecular orbital
E	Modulus of elasticity
DMF	N,N-dimethylformamide
NMR	Nuclear magnetic resonance
oCVD	Oxidative chemical vapor deposition
(poly-(EDOT-co-3-TE))	poly-(3,4-ehylenedioxythiophene-co-thiophene-3-ethanol) ethanol)
PEDOT	Poly(3,4-ethylenedioxythiophene)
Poly(EDOT-co-TAA)	Poly(3,4-ethylenedioxythiopheneco-thiophene-3-acetic acid)
PProDOT	Poly(3,4-propylenedioxythiophene)
PPP	Poly(para-phenylene)
PPV	Poly(p-phenylene vinylene)
PANI	Polyaniline
PDI	Polydispersity index
PPy	Polypyrrole
PSS	Polystyrene sulfonate
PTFE	Polytetrafluoroethylene

PTPA	Polytriphenylamine
PU	Polyurethane
PC	Propylene carbonate
RE	Reference electrode
R2R	Roll-to-roll
SEM	Scanning electron microscopy
TT	Tail-to-tail
TBAP	Tetrabutylammonium perchlorate
THF	Tetrahydrofuran
TEM	Transmittance electron microscopy
TPA	Triphenylamine
TPAA	Triphenylamine acrylate = [4-(diphenylamino)phenyl] methyl ester
VPP	Vapor phase polymerization
WE	Working electrode
XRD	X-Ray Diffraction
XPS	X-ray photoelectron spectroscopy

SUMMARY

Electroactive polymers have been of the subject of great interest in recent decades due to their ability to show metal-like conductivity while retaining polymer-like flexibility at the same time. They have found broad applications in microelectronics, medicine and energy sectors, particularly where biocompatibility is involved. This is due to their soft and flexible nature, making them suited to human interface compared to their inorganic counterparts. Since these polymers are often used in the form of a thin coating layer on an underlying substrate, widespread research has been done on their synthesis and processing. In this regard, two different techniques have been developed simultaneously with and without the use of solvent for their processing. Each of these techniques have strengths and challenges related to the type of polymer, polymer film formation, film properties, substrate choice and interfacial phenomena.

This thesis aims to first provide an overview of electroactive polymers and their processing techniques namely wet and dry routes. The merits and demerits of each route is discussed in detail based on the state-of-the-art literature. Their scientific progress and technological relevance has been critically compared. This thesis investigated each method to study different aspects of these polymers. In particular, an electroactive unit (triphenylamine) was chosen as the building block for design and synthesis of different polymer architectures and how it affects their electrochemical energy storage performance. These polymers were investigated using wet processing, since their dry processing would be extremely challenging.

In the second part of this thesis, the dry processing technique of oxidative chemical vapor deposition (oCVD) is comprehensively discussed from the early works which were less than two decades ago up to its current state-of-the-art. A unique contribution of this thesis is the synthesis of polypyrrole using oCVD with an in-depth molecular characterization to gain insight into its processing condition and thin film properties. The application for conductive coatings of polypyrrole was studied in the context of electrochemical energy storage and piezoresistive sensing devices using porous or delicate substrates.

SAMENVATTING

Elektroactieve polymeren hebben de afgelopen decennia veel belangstelling gekregen vanwege hun vermogen om metaalachtige geleidbaarheid te vertonen terwijl ze tegelijkertijd polymeerachtige flexibiliteit behouden. Ze worden vooral toegepast in de sectoren van micro-elektronica, medicijnen en energie, met name waar het gaat om biocompatibiliteit. Dit komt door hun zachte en flexibele karakter, waardoor ze geschikt zijn voor de menselijke interface in vergelijking met hun anorganische tegenhangers. Omdat deze polymeren vaak worden toegepast in de vorm van een dunne coatinglaag op een onderliggend substraat, is er veel onderzoek gedaan naar de synthese en verwerking ervan. In dit opzicht zijn er gelijktijdig twee verschillende technieken ontwikkeld met en zonder het gebruik van oplosmiddel voor hun verwerking. Elk van deze technieken brengt sterke punten en uitdagingen met betrekking tot het type polymeer, polymeerfilmvorming, filmeigenschappen, substraatkeuze en grensvlakfenomenen.

Dit proefschrift beoogt eerst een overzicht te geven van elektroactieve polymeren en hun verwerkingstechnieken, namelijk natte en droge routes. De voor- en nadelen van elke route worden in detail besproken op basis van de state-of-the-art literatuur. Hun wetenschappelijke vooruitgang en technologische relevantie zijn kritisch vergeleken. Dit proefschrift onderzocht elke methode om verschillende aspecten van deze polymeren te bestuderen. In het bijzonder werd een elektroactieve eenheid (trifenylamine) gekozen als bouwsteen voor het ontwerp en de synthese van verschillende polymeerarchitecturen en hoe dit hun elektrochemische energieopslagprestaties beïnvloedt. Deze polymeren werden onderzocht met behulp van natte verwerking, omdat hun droge verwerking een grote uitdaging zou zijn.

In het tweede deel van dit proefschrift wordt de droge verwerkingstechniek van oxidatieve chemische dampafzetting (oCVD) uitgebreid besproken vanaf de vroege werken die minder dan twee decennia geleden waren tot aan de huidige stand van de techniek. Een unieke bijdrage van dit proefschrift is de synthese van polypyrrool met behulp van oCVD met een diepgaande moleculaire karakterisering om inzicht te krijgen in de verwerkingsconditie en dunne-filmeigenschappen. De toepassing voor geleidende coatings van polypyrrool werd bestudeerd in de context van elektrochemische energieopslag en piëzoresistieve detectieapparaten die poreuze of verfijnde substraten gebruiken.

ACKNOWLEDGEMENTS

My journey is coming to an end and I am having the mixed feelings that everyone probably experienced at some point in their lives. Happy that I could step forward in my life; and sad as I should leave my memories behind, which I was never good at! I am writing this piece in order to recognize and record my appreciation and gratitude for the people who were part of this journey.

I‘d like initiate with my advisors, Prof. Ranjita Bose and Prof. Francesco Picchioni. Dear Ranjita: I am aware that selecting the first PhD student when starting as the PI was not the easiest one. Yet, you chose me and I hope that after this time, you are happy with the choice you made:). In addition to your guidance, you were patient with me growing and becoming more and more independent during time. You were always there to support me in face of challenges; and you were patient listening to my frustration time to time. But you know? It paid off! I think being the first student of a young group allowed me to experience what I wouldn't have otherwise, which made me more confident. Thank you for everything. *Ami aapnake janate chai je etir ami onek proshongsha kori.* Dear Francesco: next to directing me in the project and showing me the way to go not to get lost (and it is very easy to get lost!), our monthly meeting had an indispensable role in keeping me motivated to not give up when facing failures here and there. Every time I was talking to you, I was getting the energy to proceed. I will always look up to you and hope that at least I learned one thing or two from you, for the time that I will be in a position to lead people. *Ti ringrazio davvero per la gentilezza.*

Before proceeding, talking about advisors, I feel obligated to mention my Master's thesis supervisor, Prof. Masoud Jamshidi of Iran University of Science and Technology, who taught me the alphabets of polymers and how to do research! Definitely, I would not be in a position of obtaining the PhD scholarship without his mentorship. I want to use this opportunity for thanking him for being such a great mentor.

Next, I want to express my deep gratitude for Anna Appeldoorn, Marcel de Vries, and Rick Van der Reijd for their dedication and constant support during fabrication, installment, and maintenance of CVD reactor (which I gave myself the permission to call *Mars*). They were particularly patient and helpful whenever I need them for help. Dear Anna, Marcel, and Rick: this thesis would not have been written if it was not for your support, and I never say things if I do not mean to! In addition, I am highly thankful of Erwin Wilbers for his safety guide and technical support, Leon Rohrbach as well as Gert-Jan Boersma for training me on a wide range of analytical techniques and being patient with me forgetting how to work them frequently :). Finally, I thank Geraldine Gambier and Kim Winters for their administrative support in last few years. Dear Geraldine: I particularly recall you as someone who always had smile on her face :).

During my time in Zernike, I had the opportunity to interact and collaborate with many people from whom I learned a lot *via* our discussions and collaborations. For the start, I thank Prof. Giacomo Ruggeri of University of Pisa, who kindly reviewed our manuscript out of *chapter 2*. For the experimental part of the same chapter, I especially thank Dr. Juani Perez and Dr. Ciaran Lahive for their great discussion and teachings over organic synthesis and purification; Dr. Okan Akin for literally teaching me how to do an electrochemical experiment from the scratch, as well as contributing to the publication out of the chapter. I also thank Dr. Yefei Fan for his support and guidelines of how to work in our labs when I initially started in RUG; plus teaching me how to do freeze-thaw cycles as part of polymer synthesis procedure. Last but not the least, my thanks goes to Irene Mongatti for synthesizing part of the materials and taking care of NMR spectra, let alone that she is an amazing person and a great friend.

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Concluding on science part of this piece, I want to express my especial thanks to the assessment committee who were kind in accepting to review my thesis in spite of heavy workloads. This is particularly the case for Prof. Anna Maria Coclite, who is doing the extra effort of travelling from Austria. Also, Prof. Maria Loi as well as Prof. Giuseppe Portale, who, in addition to thesis review, kindly allowed me to go to their group for using the profilometers in last few years. At this point, the names of additional PIs for assessment has not been finalized. Yet, I thank all of you in advance and sincerely appreciate your time, effort, and input for my thesis review process and promotion event.

When I look back after these times, in addition to gezellig Groningen, I particularly miss the great friends I made who – unfortunately- I should say goodbye to for now. The unfortunate is that life taught me that the chance of cross-pathing these friends might be slim, yet I want all of you to know that you will always remain in my memory and will be missed.

I start with Giovani and Adrivit, who gave me the honor to be my paranymphs for the defense day. Giovani: I never forget our talks on a wide range of fun topics, our laughs, our lunches together, your (and your family's) kindness for hosting us (Ghazaleh and I) in beautiful Pisa in beautiful Italy. You have been and remain an amazing friend. Adrivit: you know, I just wish you had joined our group sooner; I miss you so much. Nothing more to say!

Going back in time, in the first few months of me in Groningen, the initial close friendship I had was with Malihe. Malihe: you know that there is not enough space if I want to start recognizing our unforgettable moments. I could not recall PhD time without you. Thank you for being such an amazing friend and I hope life brings you joy and success all the times :).

Felipe Orozco! Only you know why I included your family name among others :). You were my initial friend at work, bearing with my complaints about everything you could think of, and remaining a great friend throughout this journey. You were particularly good at showing me the positive aspects of things and compensating for my EQ when it was necessary :).

Jing! My first office-mate just next to me. You know you could always bring smile on my face, and you were quick in picking up “my type” of humor (which makes me trouble often). I particularly enjoyed your company and hope you all the good things in life.

It is highly probable that I am missing to mention some other friends or colleagues, who I enjoyed their company during my journey and my mind does not help me remembering them in this last-minute writing (to explain: I once wrote the acknowledgment around 6 months ago and now that I need it, I can not find it; so I am writing just before this goes to print).

At the end, I want to recognize my family and especially my beloved wife, Ghazaleh. Also, as it is a especial moment, I want to mention the names of my close friends: Shahab, Hamed, and Mohsen. Yet I do not elaborate on this line as words are failing me to describe my feelings. Just the point that you all know you are and remain in my heart!

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Belgium

Academic Output

Journal

- **A.Dianatdar**, M.Miola, O.D.Luca , P.Rudolf , F.Picchioni, R.K.Bose, *All-Dry, One-step Synthesis, Doping and Film Formation of Conductive Polypyrrole*, Journal of Materials Chemistry C, 2022, 10, 557-570.

- **A.Dianatdar**, ,O.Akin, I.Mongatti, J.Momand, G.Ruggeri, F.Picchioni, R.K.Bose, *Carbon Nanotube-Triphenylamine Polymer Composites for Energy Storage Electrodes*, RSC ADV., 2021, 11, 35187

Under preparation (Journal)

- A.Mukherjee, **A.Dianatdar**, M.Hendriksen, A.Kottapalli, Marleen Kamperman, Ranjita K. Bose, *Oxidative Chemical Vapor Deposition of Polypyrrole on Stretchable Electrospun Membranes as Highly Sensitive Piezoresisitive Strain Sensors*

- **A. Dianatdar**, F. Picchioni, R.K. Bose, *Conjugated Polymers Synthesis by Chemical Vapor Depositions: Opportunities vs. Challenges* (Review Paper)

Conference

- **A.Dianatdar**, F. Picchioni, Ranjita K. Bose, *Polypyrrole- Carbon Fiber Composite for Flexible Energy Storage Electrode,* EUROMAT 2021, virtual event (oral presentation)

- **A. Dianatdar**, F. Picchioni, R.K. Bose, *Development of Polytriphenylamine-Carbon nanotube Composite with Increased Charge Transfer*, European Material Research Society (EMRS) 2019 Spring Meeting, Nice, France (poster session)