Developments towards novel dense polymer brushes for device applications

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Developments towards novel dense polymer brushes for device applications

by

Thomas Constable

A Doctoral Thesis submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of Loughborough University

June 2015

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For Nan and Grandad
Abstract

The research project aimed to synthesise semiconducting polymer brushes (polymer chains densely grafted to a surface) utilising simple and efficient organic chemistry methods, with a view to use in molecular-level electronic applications. Conjugated polymers were initially chosen for their ability to conduct electrical charge along a polymer chain by facilitating electron transfer between π-bonds. Polymers also aimed to be "living", which could allow for further chain growth at a later point in time. This could lead to the production of various useful brush-block co-polymers, with different blocks (or layers) of polymers having different chemical, structural and electronic properties.

Initially, several syntheses towards monomers for poly(phenyl isocyanide) and poly(quinoxaline-2,3-diyl) were undertaken with limited success. Attention was turned to the synthesis of poly(thiophene)s by Kumada catalyst-transfer polymerisation (KCTP), again with varying success. After this, ring-opening metathesis polymerisation (ROMP) was explored as a possible avenue. The successful synthesis of several cyclopropenes for use as monomers was carried out. However, the ROMP of these monomers failed. ROMP of unsubstituted norbornene was successful. XPS studies suggested that vapour deposition of SAMs (Self Assembled Monolayers) gave homogenous monolayers. Solution-phase depositions appeared prone to inhomogeneous multilayer deposition. Vapour deposited SAMs gave better grafting densities at lower deposition pressures, leading to thicker polymer brushes. Finally, atom transfer radical polymerisation (ATRP) methods have been investigated. ARGET-ATRP was determined as the favoured method as it uses lower quantities of copper. Functionalised monomers for ATRP were synthesised, but homopolymers of these polyaromatic monomers have been difficult to synthesise by both copper-mediated ATRP and AIBN initiation. Polymer brushes and polymer brush diblocks of post-polymerisation modified PHEMA and PDMAEMA have been successfully grown on silicon wafers and glass slides, with a view to using the diblocks of these polymers as effective bulk heterojunction photovoltaic devices. The kinetics of the growth of both polymers by the ARGET and ATRP methods were studied to determine the degree to which each polymerisation is living; to determine if diblock growth would be possible. PHEMA brushes were successfully modified with a range of polyaromatic acid chlorides. Focussing on anthracene (which has excellent fluorescence properties, displaying a clear ability to move electrons between energy levels), this attachment was further confirmed by a range of techniques, before successfully growing a brush diblock of the unfunctionalised and functionalised polymers.
Acknowledgements

Firstly, I would like to dedicate this thesis to my late grandparents, Ronald and Edna. They would have been incredibly proud of what I have accomplished. I am also incredibly thankful to my family: Dad, Mum, Adam and Katy. I couldn’t have done this without their support and encouragement. I am also grateful to Fred, my wife-to-be, who has supported, encouraged and put faith in me over the last eight and a half years. I hope I’ve made you all proud. Thank you all for believing in me, even at times when perhaps I didn’t believe in myself.

I would also like to thank my four supervisors: Steve Christie, Steve Edmondson, George Weaver and Simon Martin for technical support and guidance throughout the project.

Ben Buckley and Marc Kimber have always been forthcoming with advice and support, usually over a beer (or seven). Thanks also to Ben for providing me with a house to live in!

I also extend my sincerest thanks to all my colleagues at Vertellus, who were very supportive and accommodating whilst I completed my research and writing – thank you Mike, Jin, Monica, Claudia, Ghislaine, Qingpu and Veronika. I hope you all enjoyed the cake! I also appreciate the support of Helen, Martin and Imi. To Oli, Rob and Terry, thanks for giving me my escape, suffering for hours in the saddle together. Your support and friendship is truly appreciated.

To Jens Voigt: Getting to ride with Jens in the New Forest, chatting about not giving up (with a guy who has ridden the Tour de France seventeen times and broken the Hour Record) helped me more than you could imagine. I hope somehow you read this Jensie.

To those who I worked with in the organic labs: Hayley, thanks for all the dinners. Claire, thanks for all the tea, and later for all the trips to the pub in Kingston. I owe you a Filet-O-Fish! Jasón, you are a phenomenal goalie. Fuchs, I’m glad we kept you amused. Awais, keep loving all the single ladies baby. Duncan, I hope you keep Slam Dunc’ing that funk. Bullous, thanks for being my trebuchet build buddy. Paul, thanks for helping me fix that sink! Trish, thanks for Warioware Smooth Moves. Sam, thanks for the dislocated shoulder. Emma, don’t let Rossi buy you shots. Rossi, keep buying Emma shots! Tash, we were in it together for the long haul. Anish, thanks for Eddie Murphy, South Park on Sky Plus and beating a group of eight year olds at Laser Quest! Noble, thanks for… ummm… thanks for… … … nope, I’ve got nothing, sorry bru!
A few people were always willing to go above and beyond for me. You'll be my friends forever.

Stephen Neary – Many nights in the pub in my first year, retro-gaming nights back at yours, inch-thick pancakes and who could forget our road trip back to Raphoe in the “Land Barge”. Although neither of us were early risers, I’m glad I had you there to keep me company late into the night. Good evenings spent: Tuxedo Crab, Stevie Time, Ruby Port, Dry Ice Mortars and all.

James Holt – You wondered why I hated you for three months until eventually getting drunk enough to ask me about it and chasing me round half of Loughborough demanding answers before you realised I didn’t hate you. I probably should have after that, but Jimmy you were always there, even when the going got tough and you were often caught between a rock and a hard place. Thanks for all your support and motivation, and (for a while) dragging me out of bed and to the gym every day. Just don’t make me do lunges… you know I have awful balance!

Andrew Capel – Picking up the almighty task of getting me into some kind of form for my triathlon, your infectious enthusiasm and willingness to ignore my athletic flaws helped me not only get round Tatton Park on that fateful Saturday, but in a very respectable time too. Although slightly bitter, I’m also glad that you’ve lead the almighty Acrylate Stanley to glories that I could only dream of. Perhaps your only downfall is your tendency to try and kill me – I’d recommend looking up the effects of drinking seven pints of water in seven minutes BEFORE goading me into taking on the challenge next time. It is still Tom 3 Food 0 by the way. Pass the arctic roll…

Nat Brown – From the moment you laid eyes on my Mohawk I knew we’d be friends for a long time. If only Fred shared your opinion on it! Thanks for following my ambulance to Leicester when my shoulder went, what an afternoon that was. Your laughter at my profanities didn’t seem to impress the nurses though! Your help organising the Stanley social calendar in the final year was invaluable. Thanks for buying me dinner too all those times I couldn’t really afford it so I didn’t have to miss out. If the other two ever want to catch a horror movie, you know where I am! Thanks to you and Capel for putting me up every time I had to come up to stay.

Darren Lee – You’ve been my best mate over the course of the last six years. Whilst I may be your temeritous trebuchet rival, there would no trebuchet without your brainchild. Thanks for Star Wars, Robot Chicken, teaching me to fish with a dropkick and a loaf of bread, hours spent playing terrible simulators, and taking me to Makro to buy ridiculous sized bottles of Tabasco sauce. Even after I’d left Loughborough to write up you’d still check up on me, making sure I’m going to submit on time. I’m glad I got there in the end; I told you I wouldn’t let you down. However, approval of your apology for the Beef Wellington is, and always will be, pending…

Finally, The Boston Shipment acknowledges Gunter, The Capelican and Fluff Bailey. Mission accomplished comrades, return to base for debrief and cocktails. VIVA LA HELLFISH.
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## List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>% wt.</td>
<td>Weight by Percentage</td>
</tr>
<tr>
<td>3EHT</td>
<td>3-(2-Ethylhexyl)thiophene</td>
</tr>
<tr>
<td>Ac</td>
<td>Acetate</td>
</tr>
<tr>
<td>acac</td>
<td>Acetylacetone (keto tautomer)</td>
</tr>
<tr>
<td>ADMET</td>
<td>Acyclic diene metathesis</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy or Microscope</td>
</tr>
<tr>
<td>AIBN</td>
<td>2,2’-Azobisbutyronitrile</td>
</tr>
<tr>
<td>AMU</td>
<td>Atomic mass units</td>
</tr>
<tr>
<td>APTES</td>
<td>(3-Aminopropyl)triethoxysilane</td>
</tr>
<tr>
<td>Ar</td>
<td>Aryl</td>
</tr>
<tr>
<td>ARGET</td>
<td>Activators Re-Generated by Electron Transfer</td>
</tr>
<tr>
<td>ATR</td>
<td>Attenuated total reflectance</td>
</tr>
<tr>
<td>ATRP</td>
<td>Atom Transfer Radical Polymerisation</td>
</tr>
<tr>
<td>BIBB</td>
<td>α-Bromoisobutyril bromide</td>
</tr>
<tr>
<td>bpy</td>
<td>2,2’-Bipyridine</td>
</tr>
<tr>
<td>COD</td>
<td>1,5-cyclooctadiene</td>
</tr>
<tr>
<td>CRP</td>
<td>Controlled radical polymerisation</td>
</tr>
<tr>
<td>Cy</td>
<td>Cyclohexyl</td>
</tr>
<tr>
<td>DBNF</td>
<td>Double bond number fraction</td>
</tr>
<tr>
<td>DCC</td>
<td>Dicyclohexylcarbodiimide</td>
</tr>
<tr>
<td>DIBAL</td>
<td>Diisobutylaluminium hydride</td>
</tr>
<tr>
<td>DMA</td>
<td>Dimethylacetamide</td>
</tr>
<tr>
<td>DMAEMA</td>
<td>2-Dimethylamino ethyl methacrylate</td>
</tr>
<tr>
<td>DMAP</td>
<td>4-Dimethylaminopyridine</td>
</tr>
<tr>
<td>DME</td>
<td>1,2-Dimethoxyethane</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N-Dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl sulfoxide</td>
</tr>
<tr>
<td>dppe</td>
<td>1,2-Bis(diphenylphosphino)ethane, or diphos</td>
</tr>
<tr>
<td>dpf</td>
<td>1,1’-Bis(diphenylphosphino)ferrocene</td>
</tr>
<tr>
<td>dppp</td>
<td>1,3-Bis(diphenylphosphino)propane</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>DTBP</td>
<td>2,6-Diterbutylpyridine</td>
</tr>
<tr>
<td>$E_b$</td>
<td>Binding energy</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>EDCI</td>
<td>1-Ethyl-3-((3-dimethylaminopropyl)carbodiimide</td>
</tr>
<tr>
<td>EGDMA</td>
<td>Ethylene glycol dimethacrylate</td>
</tr>
<tr>
<td>E_k</td>
<td>Kinetic energy</td>
</tr>
<tr>
<td>EL</td>
<td>Emitting Layer</td>
</tr>
<tr>
<td>Ellips.</td>
<td>Ellipsometry data</td>
</tr>
<tr>
<td>Et</td>
<td>Ethyl</td>
</tr>
<tr>
<td>eV</td>
<td>Electron Volt</td>
</tr>
<tr>
<td>EWG</td>
<td>Electron withdrawing group</td>
</tr>
<tr>
<td>FF</td>
<td>Fill factor</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>g</td>
<td>Grams</td>
</tr>
<tr>
<td>GD</td>
<td>Grafting density</td>
</tr>
<tr>
<td>GPC</td>
<td>Gel permeation chromatography</td>
</tr>
<tr>
<td>GRIM</td>
<td>Grignard Metathesis Polymerisation</td>
</tr>
<tr>
<td>h</td>
<td>Hours</td>
</tr>
<tr>
<td>Hacac</td>
<td>Acetylacetone (enol tautomer)</td>
</tr>
<tr>
<td>HEMA</td>
<td>2-Hydroxyethyl methacrylate</td>
</tr>
<tr>
<td>HMTETA</td>
<td>1,1,4,7,10,10-Hexamethylenetetramine</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>HTL</td>
<td>Hole Transporting Layer</td>
</tr>
<tr>
<td>i^Pr</td>
<td>Isopropyl</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>I_sc</td>
<td>Short circuit current</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium tin oxide</td>
</tr>
<tr>
<td>KCTP</td>
<td>Kumada Catalyst-Transfer Polymerisation</td>
</tr>
<tr>
<td>L</td>
<td>Ligand, or litre</td>
</tr>
<tr>
<td>LBLX</td>
<td>Layer-by-layer cross-linking</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>M</td>
<td>Molarity (mol L^{-1})</td>
</tr>
<tr>
<td>MC</td>
<td>Merocyanine</td>
</tr>
<tr>
<td>Me</td>
<td>Methyl</td>
</tr>
<tr>
<td>mg</td>
<td>Milligrams</td>
</tr>
<tr>
<td>min</td>
<td>Minutes</td>
</tr>
<tr>
<td>mL</td>
<td>Millilitres</td>
</tr>
<tr>
<td>MMA</td>
<td>Methyl methacrylate</td>
</tr>
<tr>
<td>mmol</td>
<td>Millimoles</td>
</tr>
<tr>
<td>M_n</td>
<td>Molecular weight of polymer</td>
</tr>
<tr>
<td>mol</td>
<td>Moles</td>
</tr>
<tr>
<td>MSE</td>
<td>Root Mean Square Error</td>
</tr>
<tr>
<td>N_A</td>
<td>Avogadro’s number</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>n-Bu</td>
<td>n-Butyl</td>
</tr>
<tr>
<td>NHC</td>
<td>N-Heterocyclic carbene</td>
</tr>
<tr>
<td>n-Hx</td>
<td>n-Hexyl</td>
</tr>
<tr>
<td>NMM</td>
<td>N-Methylmorpholine</td>
</tr>
<tr>
<td>NMP</td>
<td>Nitroxide Mediated Polymerisation</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>OFET</td>
<td>Organic Field Effect Transistor</td>
</tr>
<tr>
<td>OLED</td>
<td>Organic light emitting diode</td>
</tr>
<tr>
<td>P3BrHT</td>
<td>Poly(3-(6-bromohexyl)thiophene)</td>
</tr>
<tr>
<td>P3HS</td>
<td>Poly(3-hexylselenophene)</td>
</tr>
<tr>
<td>P3HT</td>
<td>Poly(3-hexylthiophene)</td>
</tr>
<tr>
<td>P3MT</td>
<td>Poly(3-methylthiophene)</td>
</tr>
<tr>
<td>PAA</td>
<td>Poly(acrylic acid)</td>
</tr>
<tr>
<td>PAnt-HEMA</td>
<td>Anthracene-functionalised PHEMA</td>
</tr>
<tr>
<td>PCBM</td>
<td>[6,6]-Phenyl-C_{61}-butyric acid methyl ester</td>
</tr>
<tr>
<td>PCE</td>
<td>Power conversion efficiency</td>
</tr>
<tr>
<td>PDMAEMA</td>
<td>Poly(2-dimethylamino ethyl methacrylate)</td>
</tr>
<tr>
<td>PDOTV</td>
<td>Poly(diocylthiopheneineylene)</td>
</tr>
<tr>
<td>PEDOT</td>
<td>Poly(3,4-ethylenedioxythiophene)</td>
</tr>
<tr>
<td>PEG</td>
<td>Poly(ethylene glycol)</td>
</tr>
<tr>
<td>PFO</td>
<td>9,9-Dioctyfluorene</td>
</tr>
<tr>
<td>PGMA</td>
<td>Poly(glycidyl methacrylate)</td>
</tr>
<tr>
<td>Ph</td>
<td>Phenyl</td>
</tr>
<tr>
<td>PHEMA</td>
<td>Poly(2-hydroxyethyl methacrylate)</td>
</tr>
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<td>PIX</td>
<td>PEDOT-initiated cross-linking</td>
</tr>
<tr>
<td>PMDETA</td>
<td>1,1,4,7,7-Pentamethyldiethylenetriamine</td>
</tr>
<tr>
<td>PMMA</td>
<td>Poly(methyl methacrylate)</td>
</tr>
<tr>
<td>PPDA</td>
<td>Poly(perylene diimide acrylate)</td>
</tr>
<tr>
<td>PRE</td>
<td>Persistent radical effect</td>
</tr>
<tr>
<td>PSS</td>
<td>Poly(styrene sulfonate)</td>
</tr>
<tr>
<td>PTPAA</td>
<td>Poly(triphenylamine acrylate)</td>
</tr>
<tr>
<td>PVTPA</td>
<td>Poly(4-vinyltriphenylamine)</td>
</tr>
<tr>
<td>PyBOP</td>
<td>(Benzotriazol-1-yloxy)tripyrrolidinophosphonium hexafluorophosphate</td>
</tr>
<tr>
<td>RAFT</td>
<td>Reversible Addition-Fragmentation Chain Transfer Polymerisation</td>
</tr>
<tr>
<td>RCA</td>
<td>Radio Corporation of America</td>
</tr>
<tr>
<td>RCA-1</td>
<td>see RCA-SC-1</td>
</tr>
<tr>
<td>RCA-SC-1</td>
<td>Radio Corporation of America Standard Clean Number 1</td>
</tr>
<tr>
<td>Rg</td>
<td>Radius of gyration</td>
</tr>
<tr>
<td>ROMP</td>
<td>Ring-Opening Metathesis Polymerisation</td>
</tr>
<tr>
<td>rpm</td>
<td>Revolutions per minute</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>rt</td>
<td>Room temperature</td>
</tr>
<tr>
<td>S</td>
<td>Siemens</td>
</tr>
<tr>
<td>SAM</td>
<td>Self-assembled monolayer</td>
</tr>
<tr>
<td>SI</td>
<td>Surface initiated</td>
</tr>
<tr>
<td>SIP</td>
<td>Surface initiated polymerisation</td>
</tr>
<tr>
<td>SOS</td>
<td>Poly(styrene b ethylene oxide-b-styrene)</td>
</tr>
<tr>
<td>SP</td>
<td>Spiropyran</td>
</tr>
<tr>
<td>SPMA</td>
<td>Spiropyran methacrylate</td>
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<tr>
<td>TBAF</td>
<td>Tetrabutylammonium fluoride</td>
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<tr>
<td>TBDMS</td>
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</tr>
<tr>
<td>t-Bu</td>
<td>tert-Butyl</td>
</tr>
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<td>Tetrahydrofuran</td>
</tr>
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<td>Thin Layer Chromatography</td>
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<td>Triphenylamine</td>
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<td>Triphenylphosphine</td>
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<tr>
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<td>Ultraviolet and visible regions</td>
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<tr>
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<td>Volume-to-volume</td>
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<td>Open circuit voltage</td>
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<td>Weight-to-Volume</td>
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<td>w/w</td>
<td>Weight-to-Weight</td>
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<td>Halogen or leaving group</td>
</tr>
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<td>X-Ray Photoelectron Spectroscopy or Spectrometer</td>
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<td>X-Ray Diffraction</td>
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<tr>
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<td>Bite angle</td>
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<tr>
<td>Δ</td>
<td>Change in phase of the incident light on reflection</td>
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<tr>
<td>θ</td>
<td>Tolman cone angle</td>
</tr>
<tr>
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<td>Micromoles</td>
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<tr>
<td>μW</td>
<td>Microwave</td>
</tr>
<tr>
<td>ρ</td>
<td>Bulk density of brush composition</td>
</tr>
<tr>
<td>Σ</td>
<td>Reduced grafting density</td>
</tr>
<tr>
<td>σ</td>
<td>Grafting density</td>
</tr>
<tr>
<td>σ</td>
<td>Conductivity</td>
</tr>
<tr>
<td>Ψ</td>
<td>Change in amplitude of the incident light waves upon reflection</td>
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The long-term aim of this research project was to synthesise semiconducting polymer brushes (polymer chains densely grafted to a surface) utilising facile and efficient organic chemistry methods, with a view to use in molecular level electronic applications. Conjugated polymers were initially chosen for their ability to conduct electrical charge along a polymer chain by facilitating electron transfer between π-bonds. Polymer brushes have been previously applied to electronic applications such as organic light-emitting diodes, transistors and photovoltaic devices (i.e. solar cells). As well as these applications, polymer brush systems have also been used in the fields of biomaterials and transition-metal catalysis, to name just a couple of examples. Although conjugated brushes would appear to be a popular and useful application, there is not much literature precedent in the field for growing this type of brush.

This project also aimed to make polymer brushes that were as close to “living” as possible; to never truly terminate the polymerisation, which could allow for further chain growth at a later point in time. This could lead to the production of various useful brush-block co-polymers, with different blocks (or layers) of polymers having different chemical, structural and electronic properties. In practice, “living” is the ideal situation, but is never truly achievable. The best we can do is “pseudo-living”, as inevitably some chains will be irreversibly terminated. We can achieve this through well-controlled radical polymerisation techniques. Over the course of this project the aim was to synthesise novel brushes by these controlled, “pseudo-living” methods, such as Atom Transfer Radical Polymerisation (ATRP), Ring-Opening Metathesis Polymerisation (ROMP) and Kumada Catalyst-Transfer Polymerisation (KCTP).

1.1. Polymer brushes

Polymer brushes can be defined as “surface-confined macromolecular architectures” such that they are polymer chains tethered to a surface. The chains are packed close enough together that the steric confinement forces the polymer to grow away from the surface to which it is bound. Suitable surfaces include, but are not limited to, materials such as silicon, gold and indium tin oxide (ITO). Silica gel, quartz fibres or the walls of nanotubes have also been used as substrates in the literature to name a few examples. Polymer brushes are widely used to modify or “tailor” the surface properties of a substrate. This will often result in
improvements to a substrate’s surface properties, such as wettability, biocompatibility, corrosion resistance, friction coefficient and colloidal stability.

Polymer brushes first came to interest in the scientific community back in the 1950s, when it was discovered that flocculation of colloidal particles could be avoided by attaching polymer chains to them. However, the term “brush” is relatively new, and only came into conventional use after Milner coined the term in 1991. Modern approaches to tethered layers of polymers are characterised as being a “brush” when a high grafting density (abbreviated GD; a measure of the number of polymer chains per unit area) is achieved. This close packing of the polymer chains presents no other option for the chain but to “stretch” as much as possible to reduce the steric interactions between neighbouring chains, giving lots of chains standing on end, like the bristles of a brush. This is known as being in the “brush regime”. When the grafting density is low (i.e. the chains are well-spread and further apart on the surface of the substrate), and the chains are therefore not forced upright, as the steric interactions are reduced, they fold over themselves, and revert to what is known as the “mushroom” (or “pancake”) regime. In between these two regimes is the transition phase. These regimes are illustrated in Figure 1.

![Figure 1: Mushroom, transition and brush regimes of surface-attached polymers](image-url)

The transition from one regime to the next is governed by the relationship between the distance separating individual chains and the radius of gyration of the equivalent untethered polymer. If the radius of gyration is far less than the distance between tethered chains, then we see polymers in the mushroom regime. As the distance between chains approaches parity to the radius of gyration, polymers move into the transition regime, and when the radius of gyration far exceeds the distance between chains, they adopt true brush form. When in the brush regime, polymers will often display different properties compared to their in-solution (untethered) equivalents, for example improved protein resistance, variations in electrical conductance.
when the polymer chains are orientated in different directions\textsuperscript{34}, as well as differing thermoresponsive\textsuperscript{35} and pH responsive\textsuperscript{36} behaviour to their solution equivalents.

The regimes above have been mathematically described by Minko and Brittain.\textsuperscript{32} They proposed the parameter “$\Sigma$”, which they term to be “reduced grafting density”. This parameter describes the ratio between the cross sectional area of the free polymer chain in solution and the area covered by the chain on a surface. $\Sigma$ can be calculated by multiplying three parameters together, as shown by Equation 1: $\sigma$ (the grafting density), $\pi$ and $R_g^2$ (the square of the radius of gyration of an untethered polymer chain of the same molecular weight).

$$
\Sigma = \sigma \pi (R_g^2)
$$

\textbf{Equation 1:} Calculation of reduced grafting density

Grafting density ($\sigma$) is dictated by the number of “anchorage points” on a surface that allow polymer chains to grow. It can be measured from the parameters in Equation 2.

$$
\sigma = \frac{h \rho N_A}{M_n} \approx \frac{1}{D^2}
$$

\textbf{Equation 2:} Calculation of grafting density – $h$ is polymer brush thickness, $\rho$ is the bulk density of the brush composition, $N_A$ is Avogadro’s constant ($6.022 \times 10^{23}$ mol$^{-1}$), $M_n$ is the average molecular weight of the polymer chains.

This equation suggests that thicker brushes (high $h$) indicate a higher grafting density, as the grafted polymer chains are closer in proximity and are forced to stretch away from the surface (i.e. exhibiting “brush” character rather than “mushroom”). Higher bulk density of the brush composition ($\rho$) indicates that the polymer chains are in close proximity. At lower average molecular weights ($M_n$) it is easier to pack polymer chains more closely, due to the reduced number steric hindrances over higher molecular weight equivalents. Grafting density can also be approximated by simply taking the reciprocal of $D^2$ (“$D^*$” is equal to the distance between the polymer chains on the surface), as illustrated in Figure 2.
Breaking down Equation 2, we can approximate that film thickness in the unsolvated state is increased by one or more of the following parameters: increasing monomer size, increased grafting density and increased molecular weight of the polymer. The addition of different solvents can actually cause polymer chains to change from one regime to another as the polymer chains swell to differing degrees in the differing solvents. Adding a good solvent to brushes will cause a decrease in the bulk density of the brushes as the chains spread apart from each other when swelling. Grafting density and molecular weight will stay the same; therefore the brush thickness will increase.

\[ \Sigma \]

\[ h \]

\[ D \]

Σ can also be considered as the transition point parameter. It effectively tells us the number of equivalent chains that would occupy an area of a free, non-overlapping polymer chain under identical conditions. If the parameter is less than one, it can be assumed that the surface-bound polymer will be in the mushroom regime. A value between one and five suggests the polymer is starting to show brush behaviour, but is essentially in transition between the two regimes, and higher than five suggests the polymer is in the “true brush regime” (Figure 3). These numbers are a general rule of thumb, and although mostly applicable they can vary between differing samples. In the opinion of Minko and Brittain, only surface-bound polymers with a Σ greater than 5 can be correctly termed “polymer brushes”, and because of this many literature examples, in their opinion, are inaccurately described as being brushes as they fall below this grafting density threshold.\(^{32}\)
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Figure 3: Changes in film thickness and regime type of surface-bound polymers with increasing grafting density (adapted from Minko and Brittain\textsuperscript{32})

Grafting density is quite clearly a critical parameter for determining the regime of surface-bound polymers. This will subsequently affect the suitability of certain polymers for brush based applications, as properties of polymers change with grafting density and in turn the regime in which they are aligned. Normally, a high grafting density is necessary to get a uniform coating that covers most of the surface with a thick layer of brushes. This is desirable for applications such as the micro-electronic devices that we targeted. However, polymers in the mushroom regime that subsequently have low grafting densities can be useful for some applications, for example when using brushes to intersperse particles in a polymer melt\textsuperscript{37}. In this instance, a lower grafting density is desirable as the brushes actually repel the polymer matrix, whereas surface-bound polymers in the mushroom regime attract the matrix. Therefore grafting density is specific to both the polymer and its intended use, and as a result of this there is not a universal value for a “good” grafting density.

1.2. Grafting to and grafting from approaches

There are two main ways to tether a polymer to an immobilised surface: by either growing the free polymer in solution and subsequently attaching it to the surface using a functionalised end group (known as grafting to), or by depositing a monolayer of a polymerisation initiator on the surface of a substrate and using the relevant monomer(s) to grow the polymer from the surface-attached initiator (termed grafting from, Figure 4\textsuperscript{25}). The grafting from technique is also referred to as “surface-initiated” polymerisation, as the initiator for the polymerisation is confined to the surface of the substrate.
The grafting to approach yields significantly lower grafting densities in comparison to the grafting from strategy. As the polymer chains are attached to the surface using the grafting to tactic, polymer chains previously tethered to the surface will sterically hinder the remaining free chains from traversing through the existing polymer layer, in turn preventing them from accessing the active binding sites on the surface of the substrate. Far superior grafting densities can be attained by employing the grafting from approach. Minko and Brittain suggest that polymers grafted to a surface perhaps cannot be considered to be polymer brushes as they do not achieve the necessary grafting density to have $\Sigma > 5$. A brush grown using the grafting from technique allows for much smaller molecules to be attached to the surface with reduced steric hindrance, leading to far greater grafting density.

Grafted from brushes consist of several components, illustrated in Figure 5. Firstly, a linker and/ or initiator must be attached to the substrate to activate it for polymerisation. The next phase is to then grow the polymer from the initiator-coated surface, synthesising the polymer from the free monomers. This is achieved by placing the activated substrate into an atmosphere of the aforementioned monomer, typically solution or vapour based. Finally, the polymer will be either terminated with a capping agent, or masked with a masking group if growing a living polymer. Succinctly, the construction of the polymer brush occurs from the surface-up, utilising small building blocks, in stages.
Due to the smaller nature of the molecules being attached with the grafting from approach, and the stepwise nature of the brush assembly, the relative steric interactions are far lower than those associated with trying to attach a pre-grown polymer to a surface. In turn, more binding sites (the initiator sites) are available to the monomers than would be available to the pre-prepared polymer. For these reasons, molecules can pack in tighter together on the surface with the grafting from approach. The steric forces are vastly reduced, but are not entirely absent, and as a result actually assist the polymers to stretch out once formed. This leads to desirable polymers in the sought-after brush regime. Brush regime polymers grown by the grafted from approach are easily capable of reaching thicknesses in excess of 100 nm, whereas polymers grafted to the surface are rarely observed at such film thicknesses.\textsuperscript{25}

A polymer attached by the grafted from methodology is also far more robust than the grafted to counterpart, as grafted from polymers are usually covalently bonded to the substrate. Grafted to polymers can be covalently bonded to the surface, however this is both difficult and largely unseen. They are typically attached to the surface by physisorption and other weak interactions. Therefore they are easily removed.\textsuperscript{15}

Deposition of grafted to polymers on a surface can be difficult if they are insoluble. This particular problem is common if the polymer is heavily cross-linked or of a high molecular weight. This is another situation where the grafting from approach is advantageous, as a monomer will be much lower in molecular weight and should be readily soluble in solvent and...
possibly even volatile enough to be used in a vapour atmosphere for the subsequent grafting from polymerisation. Cross-linkable monomers can then be used and cross-linked post-polymerisation.

### 1.3. Types of polymerisation

As polymer chemistry has developed, two types of general classification system for polymers have been introduced and are now widely used. One system, introduced by Carothers in 1929, is based on polymer structure and the difference in composition compared to the monomers from which it is synthesised. The other is determined by the polymerisation mechanism, and was first discussed by Flory in 1953.

#### 1.3.1. Carothers’ System: Addition and condensation polymers

Carothers system divides polymers into condensation and addition polymers. A polymer is classified as a condensation polymer if its synthesis involves the elimination of small molecules (such as water) when monomers that contain functional groups join together as part of the polymer chain. Examples of condensation polymers include polyamides such as Nylon, shown below in Scheme 1. Nylon is formed by combining dicarboxylic acids with diamines to eliminate water and from amide linkages between the monomers. Other common condensation polymers include polyesters (formed from dicarboxylic acids and diols) and polycarbonate (formed from bisphenol and phosgene).

\[
\begin{align*}
&\text{H}_2\text{O} + \text{H}_2\text{N}^-\text{R}^-\text{NH}_2 \\
&\rightarrow \left(\begin{array}{c} \\
\text{N}^-\text{R}^-\text{NH}_2 \\
\end{array}\right)_{n} + 2n\text{H}_2\text{O}
\end{align*}
\]

Scheme 1: General synthesis of Nylons

Some naturally occurring polymers such as cellulose, starch, wool, and silk are considered to be condensation polymers. Although their synthesis is suspected to be from certain reactants which would result in the elimination of water, this is not certain. However, cellulose can be thought of as the polyether formed when glucose is dehydrated. Carothers included such polymers in his definition of condensation polymers by stating that “polymers as those in which the formula of the repeating unit lacks certain atoms that are present in the monomer(s) from which it is formed or to which it may be degraded” to also include such systems as condensation polymers. This is further supported by the fact that the hydrolysis of cellulose yields glucose, as illustrated in Scheme 2.
Carothers also defined another class of polymers. If the monomers join together without eliminating a small molecule, it is classified as an addition polymer. As nothing is lost when the monomers are joined together, addition polymers can also be defined as those with the same composition as the monomers. This typically applies to unsaturated vinyl monomers that then become saturated as the units join together, as shown in Scheme 3. Common examples include alkenes, styrenes, acrylates and methacrylates.

Over time, with advances in polymer chemistry and the development of newer polymerisation techniques, it became clear that Carothers’ system for classification was not entirely accurate. A prominent example of the flaws of Carothers’ system can be illustrated by polyurethanes, which are typically formed from the corresponding diols and diisocyanates, but without the elimination of any small molecules (Scheme 4), suggesting an addition polymer.

Carothers’ original classification would class polyurethanes as addition polymers, as the elemental composition of the monomers is the same as that of the polymers. However, the structure of polyurethanes, with the carbamate functional groups that link the monomer units together, is more akin to the structure of a condensation polymer. For this reason, some reconsideration of the definitions of addition and condensation polymers resulted in condensation polymers being re-defined as those “polymers whose repeating units are joined together by functional units of one kind or another”. These linkages include groups such as esters, amides, carbamates, sulfides and ethers, to name a few. This classification system
therefore considers polyurethanes to be a condensation polymer, and not an addition polymer as defined by Carothers. The typical structure of condensation polymers defined in this way is shown in Figure 6.

\[ R-Z-R-Z-R-Z \]

**Figure 6:** Structure of condensation polymers. \( R \) = aliphatic or aromatic group \( Z \) = Functional link e.g. ester, ether, amide, sulfide, carbamate etc.

This updated classification however excludes some polymers that would be considered condensation polymers by Carothers’ definition. The example below in Scheme 5 of a phenol-formaldehyde based polymer is considered a condensation polymer by Carothers’ definition as water is liberated, but is excluded by the updated definition as the main backbone of the polymer does not contain a functional group.

\[
\begin{align*}
&\text{OH} + \text{OH} \\
\rightarrow &\left(\begin{array}{c}
\text{OH} \\
\end{array}\right) + n \text{H}_2\text{O}
\end{align*}
\]

**Scheme 5:** Synthesis of a polyphenol by condensation polymerisation

Although there is agreement on a polymer being a condensation polymer under these two definitions in most cases, some polymers are included under one definition and excluded under the other (as previously illustrated). Because of this, polymers are classified as condensation polymers if it falls under either definition. Therefore, if a polymer or its synthesis exhibits any of the following it is considered to be a condensation polymer: (i) the elimination of small molecules such as water during synthesis, (ii) the backbone contains functional groups, or (iii) the repeating unit lacks atoms that are present in the monomer. If a polymer does not meet any of these criteria, it is then classified as an addition polymer.

**1.3.2. Flory’s system: Chain-growth and step-growth**

The other well-used type of classification is determined by the polymerisation mechanism. This was first discussed by Flory in 1953 and polymers can be classified as being produced by either step-growth or chain-growth polymerisation. Chain and step growth polymerisation have several defining characteristics, but the most prominent are the functionalities of the molecules that react with one another and the relationship between the degree of conversion from monomer to polymer in relation to the molecular weight of the polymer.
Step-growth polymerisation occurs when the functional groups of bi-functional or multi-functional monomers react together, progressively forming dimers, which in turn react again to form trimers, tetramers and larger oligomers before eventually forming long-chain polymers. Any of these smaller units can react together to form a larger unit, as illustrated in Figure 7. The nature of this mechanism means that molecular weight increases at a fairly slow pace, and a high degree of monomer conversion is required to yield polymers of significant molecular weights.43

By contrast, chain-growth polymerisation uses an initiator to create an initiating species. This reactive initiating species can be a free radical, cation or anion. Polymerisation is then facilitated by the propagation of this reactive species from one monomer to the next in a chain reaction. This is the key difference between chain and step growth: here, the monomers can only react with the activated reactive centre; monomers cannot react with other monomers as they do in step-growth polymerisation. Dimers, trimers, tetramers etc do not react with each other as they do with step growth polymerisation. This process of chain propagation continues as the reactive centre is transferred to the newly added unit and the process repeats to incorporate hundreds or thousands of repeat units. Polymerisation will continue until the centre
is eradicated by a termination reaction (of which there may be only one or there may be several possible terminating reactions). A typical example of chain growth polymerisation of vinyl monomers is illustrated in Scheme 6.

\[ 
\begin{align*} 
R^* & \quad \text{initiation} \quad R \quad R'^* \quad \text{propagation} \quad R \quad R'^* \quad \text{termination} \\
R^* & \quad \text{initiation} \quad R \quad R'^* \quad \text{termination} 
\end{align*} 
\]

* denotes reactive species (free radical, anion, cation)

Another defining characteristic between step and chain growth polymerisation is that both show a significant difference in the relationship between the average molecular weight of the polymer chains and the percentage of the monomer that has been converted. Stopping each type of polymerisation at varying degrees of conversion and plotting against the average molecular weight yields markedly different results for the two different types of polymerisation. Chain growth polymerisation will show high-molecular-weight polymer molecules almost immediately. There are few intermediate-sized molecules in the reaction mixture, perhaps only in the earliest stages. In reality, we only observe monomer, high molecular weight polymer, and initiator species. As conversion increases, we see an increase in the number of polymer chains, rather than an increase in the molecular weight of the chains. Step-growth polymerisation however only obtains high molecular weights of polymer at high levels of conversion as the smaller oligomers join together to form polymeric chains. In this case polymer chain length and chain quantity both depend on the degree of conversion.

The classification of polymerisation by these two methods, like the addition-condensation system, is not without exceptions. Some chain-growth polymerisations show a linear increase in average molecular weight as conversion progresses. This mechanism is different to typical chain-growth polymerisation, and is identified by the combination of rapid initiation and the absence of terminating side-reactions. The living polymerisation techniques discussed later, and implemented in this project, are characterised by this type of progression. Some ring-opening polymerisations also follow this type of progression. All three types of polymerisation are illustrated by the plot in Figure 8.
A common misconception is that addition polymers and those produced by chain-growth polymerisation are one and the same, as are condensation polymers and those produced by step-growth polymerisation. Although most addition polymers are produced by chain-growth polymerisation, and most condensation polymers are produced by step-growth, neither are produced exclusively by the associated method. Ring-opening polymerisations often illustrate this point. The ring-opening polymerisation of epoxypropane to form polypropylene oxide is a good example (Scheme 7). Whilst formed by condensation (ether functionality incorporated into the backbone), it forms via a chain-growth mechanism. It should therefore be categorised as a condensation chain-growth polymer.

\[ n \text{ epoxypropane} \rightarrow \left( \text{polypropylene oxide} \right)_n \]

**Scheme 7**: Polymerisation of epoxypropane to form polypropylene oxide; an example of condensation chain-growth polymerisation.

Polymers such as Nylon-6 can be synthesised by multiple pathways, as illustrated in Scheme 8. The resultant polymer will always be considered a condensation polymer, because the backbone contains amide functionality. Polymerisation of cyclic ε-caprolactam to form Nylon-6 proceeds via a chain-growth mechanism. Polymerisation of linear 6-aminohexanoic acid also yields Nylon-6, but as a result of step-growth polymerisation. Classifying polymers only by
structure or mechanism is therefore an oversimplification. Both structure and mechanism should be stated to define a polymer type without creating uncertainty and inaccuracy.

**Scheme 8:** Synthetic pathways to Nylon-6 via mechanistically different polymerisation types

### 1.3.3. Living/controlled polymerisation

Controlled, or “living” polymerisations are an attractive proposition for the preparation of polymer brushes. A living polymerisation is one that is free from side reactions, such as chain-transfer and termination. If this is achieved, then polymers will have a well-defined architecture, be of or very close to a targeted molecular weight with low polydispersity, and have low amounts of imperfections. The control over properties such as molecular shape and composition can lead to unique properties not seen in uncontrolled equivalents. Such properties can include increased redox potential and differing solubility of identical polymers that were produced by controlled and uncontrolled methods. Traditionally, a living polymer is grown by coordination ionic polymerisation, but more recently it has been applied to radical polymerisations.

Industrially, free-radical polymerisation is a widely employed process. Its uses range from the production of acrylonitrile-butadiene rubbers for tyres to high molecular weight poly(methyl methacrylate) (marketed as Plexiglas), to name a couple of examples. Radical polymerisation is advantageous over other methods because it is relatively insensitive to impurities, reaction temperatures are moderate, and multiple polymerisation processes are available (bulk, solution, precipitation, emulsion etc.).

However, there are disadvantages. Firstly, traditional radical polymerisation exhibits an inability to control molecular weight and molecular weight distribution to a significant degree. This is due to the fact that there is no control over terminating reactions. Secondly, there are extreme difficulties in producing well-defined block copolymers as the life of propagating chains is relatively short. Finally, polymers with pre-determined tacticity are also difficult to produce due
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to this relative lack of control afforded by traditional radical polymerisation.\textsuperscript{45,57,58} These disadvantages can be avoided by employing “controlled” radical polymerisation techniques.\textsuperscript{57}

By suppressing the aforementioned termination and side reactions, the polymerisation can be controlled as desired, to yield a well-defined polymer. Because of this suppression of termination, a controlled polymerisation is also a living polymerisation, and is based on an equilibrium between the dormant and active states (Scheme 9).\textsuperscript{59}

\textbf{Scheme 9:} Catalyst control of a copper-mediated living polymerisation

Fast and simultaneous initiation is required, partnered with slow propagation to give good polydispersity.\textsuperscript{45,59} The growing chain spends most of its time in the “dormant” state (Scheme 10), and periodically will propagate. This equilibrium favours the reverse reaction, which is why living polymerisations are slow, and the chances of detrimental side reactions are reduced,\textsuperscript{58,59} although not entirely eliminated, which leads to such polymerisations being termed as “pseudo-living”.

\textbf{Scheme 10:} Basic principles of a pseudo-living polymerisation

The dormant species is usually covalently bonded with a leaving group that is inactive to side reactions but can easily be unmasked by the catalyst to give propagation of the monomer. Typical species for such a requirement are alkyl halides where the radical can be resonance stabilised by a functionality in the α-position, for example 2-bromoisobutyryl derivatives (Scheme 11). The polymer is then “capped” again to recover the dormant species.\textsuperscript{45}
Scheme 11: Resonance stabilisation of a free-radical by the α-carbonyl group of a 2-bromoisobutyryl derivative

Living polymerisation does present disadvantages. Because of the dependency on the suppression of terminating reactions, purity is of the highest importance. Whereas uncontrolled methods are fairly impervious to impurities, controlled systems usually require stringent inert conditions and levels of reagent purity. The characteristic slow propagation of controlled radical polymerisation can also be seen as a disadvantage, as high molecular weight polymers can take a relatively long time to produce when compared to uncontrolled techniques.

However, the advantages far outweigh the disadvantages. The ability to control molecular weight and yield a narrow range of polydispersity due to this slow propagation is highly desirable. Having the capacity to stop and restart the polymerisation as the balance of equilibrium lies towards the dormant state is also advantageous for increasing molecular weight at a later time, self-repair, and controllable synthesis of block copolymers. Living polymerisation can be displayed by many types of chain-growth polymerisation, some of which are illustrated in Figure 9.

Figure 9: Classification of polymerisation types, and some examples of living/controlled polymerisation techniques (not an extensive list of examples)
1.3.4. Living anionic polymerisation

The earliest recorded example of living anionic polymerisation was published by Ziegler in the mid 1930's. He postulated that the polymerisation of styrene and butadiene by anionic initiation resulted in a mechanism whereby monomers were added in a consecutive fashion to the alkyl lithium initiator (n-butyllithium) used, and no chain transfer or terminating reactions were observed (Scheme 12). Ziegler, along with Natta, would later be awarded the Nobel Prize for Chemistry in 1963 “for their discoveries in the field of the chemistry and technology of high polymers” for this advance, as well as many others, in polymer chemistry.

Further advances in living anionic polymerisation were not made until the work of Szwarc some years later, producing polystyrene using sodium naphthalenide as the initiator. This was the first example of the term “living polymers” being used. Whilst Ziegler acknowledged the concept of living polymerisation, it was Szwarc who coined the term in his 1956 paper in *Nature* entitled “Living Polymers.” In this instance, the naphthyl anion acts as the initiating species. Rigorous purification of the reagents means that once again, no impurities are present to quench the reaction. When the sodium naphthalenide is dissolved in tetrahydrofuran, a green solution is observed. Addition of the highly-purified styrene immediately turns this reaction solution to a cherry-red colour. After complete reaction of the monomer, the cherry-red colour remains, suggesting that the initiator is still “alive”. Addition of further styrene then confirms the living nature of the polymerisation as the polymerisation solution increases in viscosity with further additions of styrene. This increased viscosity suggests an increase in molecular weight, and thus the lengthening of existing chains as opposed to the creation of new chains. Through these additions the solution remains noticeably red in colour, suggesting the ever-presence of

**Scheme 12:** Living anionic polymerisation of styrene-butadiene, demonstrated by Ziegler \(^{50,60}\)
the propagating species. This is illustrated below in Scheme 13. The polymeric dianion show in Scheme 13 is believed to allow propagation at either end of the chain. \(^{51}\)

To further demonstrate the benefit of living polymers, Szwarc then modified his initial experiment. Upon reaching 100% consumption of the styrene monomer, rather than adding further styrene, Szwarc demonstrated the advantage of living polymerisation when synthesising block co-polymers. By adding in a second monomer at this point (isoprene), a polymer was produced that could not be precipitated from isooctane. A 50:50 mixture of polystyrene and polyisoprene homopolymers could be separated by this method (with the polystyrene precipitating), an observation which proved that the styrene had all reacted with the isoprene to form the suspected block copolymer. \(^{51,52,63}\) If this had not occurred, the precipitation of polystyrene would have been observed.

These two experiments presented us with the widely accepted defining characteristics of a living polymer. If the stockpile of monomer is consumed, the polymerisation is not terminated; it does not die. Instead it remains living and will continue to grow when the monomer supply is replenished. If this monomer is different to the one previously used, then block copolymers can be synthesised with relative ease. This makes the synthesis of block copolymers by living polymerisation extremely versatile. \(^{64}\)
The absence of any intrinsic termination pathways does not mean that the polymerisation is never-ending. The reactive end groups may be destroyed by a suitable reagent, in a process known as “killing” a living polymer. Unlike spontaneous termination, which is determined by the law of probability and the conditions enforced during polymerisation, a killing reaction can be controlled by the scientist. A choice of reagent and pathway are available to the scientist, and can be implemented when the desired polymer properties have been attained. When discussing the example of styrene in Scheme 13, there are several termination routes that yield different end groups. Some of these are outlined in Scheme 14.

Scheme 14: Examples of “killing” reactions for the living anionic polymerisation of styrene

The versatility of having a range of terminating reactions available presents obvious desirability in being able to tailor the end group functionality of a polymer. This is particularly useful for surface attachment (i.e. grafting to), and polymers with two or more active end groups can become bifunctional (or multifunctional if there are more than two active groups).

In a perfect system, living polymers would retain their active centres with a degree of immortality; there would be no killing reaction. However, in practice, this is not possible. For example, some slow side reactions may cause annihilation of the growing ends. These may be unavoidable, even when the most stringent of purification has been undertaken and maximal inert conditions are used. If the relatively slow rate of such a reaction allows the desired polymerisation to be completed without these side reactions presenting themselves as a problem, then the polymerisation may still be considered living. Also considered is the inevitable exposure of the polymer to “real world” conditions when removed from an inert atmosphere. If not already subject to a killing reaction, the moisture in the air will likely be enough to kill the living polymer by the water termination route shown previously in Scheme 14.

Of all the living polymerisation techniques available, it is generally regarded that living anionic polymerisation exhibits the greatest degree of control over polymer architecture. When not
The group of Advincula have shown that polymer brushes can be grown by living anionic polymerisation from flat silicon and gold substrates. A precursor to the initiator, 1,1-diphenylethylene, is deposited on the surface from solution (using an alkysilane chain for silicon or an alkylthiol chain for gold substrates, which is attached to one of the phenyl rings as a tether). This is then activated using n-butyllithium to butylate the less-hindered end of the alkene via a nucleophilic addition, generating a carbanion at the tertiary carbon centre (the most favourable scenario for a carbanion). This is summarised below in Scheme 15.

Scheme 15: Deposition and initiation of 1,1-diphenylethylene species for living anionic polymerisation

The polymerisation is carried out under high vacuum conditions in a specialist reactor to maintain stringent anhydrous conditions, shown in Figure 10. Reaction components are added by breaking the appropriate ampule within the apparatus. By adding the required monomers in the correct order (from the base of the brush upwards), highly precise block copolymers of poly(styrene) and either poly(isoprene) or poly(butadiene) and were produced. It should be noted however that these brushes are significantly thinner than those attained by controlled radical techniques, and that the use of custom produced reactors make this method inaccessible to users with standard laboratory glassware. A similar reactor and procedure were also used to grow living poly(styrene) brushes from silica nanoparticles in another publication by the same group.
Examples of living brushes being grown by anionic polymerisation for use in organic electronic devices are scarce, but there are examples of free polymers grown by living anionic polymerisation for use in such devices. In the work of Higashihara,43 4-vinyltriphenylamine was polymerised by living anionic polymerisation, using sec-butyl lithium as initiator and performing the reaction under high vacuum conditions. Lithium naphthalenide can also be used as the initiator to generate a dianionic species akin to that discovered by Szwarc.51 Both routes are illustrated below in Scheme 16.
The noted molecular weight of the polymer increased with further addition of monomer (up to 30,000) as is characteristic with living chain growth polymerisation. Polydispersity also remained in a narrow region, between 1.04 and 1.10. Triblock copolymers of poly(styrene) and the poly(4-vinyltriphenylamine) were formed (PS-b-PVTPA-b-PS) to demonstrate the living nature of the poly(4-vinyltriphenylamine) produced. Finally, an opto-electrically active copolymer of regioregular poly(3-hexylthiophene) and poly(4-vinyltriphenylamine) was produced, by functionalising the ends of the P3HT with 1,1-diphenylethylene and allowing the living PVTPA to react with these functionalities, as shown in Scheme 17.

Scheme 17: Higashihara’s synthesis of PVTPA-b-P3HT-b-PVTPA

The PVTPA-b-P3HT-b-PVTPA system was then cast into thin films, and these were used as a novel p-type semiconductor in a photovoltaic cell. The PVTPA blocks are thought to give more effective charge transport than typically used P3HT based blocks containing polymers such as polystyrene and PMMA.\textsuperscript{83}
In another example, the group of Lee and Kang\textsuperscript{84} synthesise another polymer with triphenylamine as the hole-transporting moiety by living anionic polymerisation, for ultimate use in an OLED. This is again synthesised from a naphthenide type initiator. This ethynyl cross-linked polymer (ethynyl groups are revealed by a deprotection reaction using tetrabutylammonium fluoride (TBAF) to remove the trimethylsilyl groups), is referred to as PBAB, and is shown in Scheme 18. PBAB is shown to have significantly higher luminance (150\%) and luminous efficiency (400\%) over current PEDOT:PSS systems. It is thought that this may be due to the PBAB being able to "block" electrons, resulting in a reduction in exciton quenching (relative to PEDOT:PSS systems).

\textbf{Scheme 18:} Synthesis of PBAB by living anionic polymerisation and TBAF deprotection\textsuperscript{84}

In a final example of living anionic polymerisation that is presented, Chen, Frisbie and Bates\textsuperscript{85} use living anionic polymerisation to sequentially grow a triblock of poly(styrene-\textit{b}-ethylene oxide-\textit{b}-styrene) (given the acronym SOS), with molecular weights around 14,000 for the ethylene oxide block and 7,000 for each styrene block. After doping with lithium perchlorate, it was noted that when the SOS triblock co-polymer was spin-coated onto gold electrodes, the doped polymer exhibited very high specific capacitances (up to values of 4.5 $\mu$F cm$^{-2}$ at 10 Hz and 1.5 $\mu$F cm$^{-2}$ at 1 kHz with an amplitude of 0.1 V), depending upon the lithium concentration. Optimal oxygen to lithium concentration ratio for this study was around 24:1 [O:Li]. Figure 11 demonstrates that concentrations both above and below this point tend to yield lower specific capacitance values. It is also noted that a smooth surface was produced when spin coating SOS/LiClO$_4$ films when using optimised spinning conditions, which the authors felt would be an important property for potential application of this material, as a gate dielectric in organic thin film transistors.
1.3.5. Living cationic polymerisation

Cationic polymerisation itself is a long established technique, with the first known publication appearing in the late 1930s. The possibility of controlling cationic polymerisation was dismissed for a long time, even after the discovery of living anionic polymerisation. Carbocations generated at vinyl centres tend to be far less stable than their carbanion equivalents. So, much like radical polymerisation, the highly reactive and unstable charged centres reduce the ability to control disruptive side reactions, such as ionic combination and β-proton elimination (shown as termination routes in Scheme 19). Despite efforts to tune monomers to reduce such reactions, no real success was achieved, and for a long period of time cationic polymerisation was thought to be uncontrollable.

It was not until 1977 when a significant breakthrough was made towards the development of living cationic polymerisation. Higashimura and Kishiro observed typical living character (linear increase in molecular weight in relation to conversion) when polymerising p-methoxystyrene using iodine as the initiator. To further confirm the living nature of the poly(p-methoxystyrene) created, when further monomer was added the average molecular weight of the polymer increased. It was noted that the polarity of the solvent had a significant effect on the length of life of the polymerisation; carrying out the reaction in relatively non-polar
carbon tetrachloride was long-lived whereas carrying out the polymerisation in a more polar solvent such as dichloromethane yielded a relatively short-lived polymerisation. This would suggest that the dissociated iodo-triiodide\textsuperscript{89} “active” species is relatively short-lived, whereas the non-dissociated “dormant” diiodo equivalent shows a reasonably long lifetime. Using a solvent that limits this dissociation (i.e. a non-polar solvent) allows greater control over the position of that equilibrium towards the dormant state. This is illustrated in Scheme 20. A further publication which studied the polymerisation of isobutyl vinyl ether showed that the addition of a “common ion salt”, in this case tetra-\textit{n}-butylammonium triiodide could help to drive this equilibrium to the diiodo state, helping further control over molecular weight and polydispersity.\textsuperscript{90}

![Scheme 20: Living Cationic Polymerisation of \textit{p}-methoxystyrene](image)

Although long lived, these polymerisations were not technically fully living, as termination would eventually occur (hence the term “long-lived”). Higashimura suggested that this may be due to the slow initiation of the iodide initiator. To attempt to overcome this and create a truly living cationic polymerisation, Higashimura and co-workers added hydrogen iodide to the initiation system in equimolar proportion to molecular iodine, to attempt to speed up initiator formation, i.e. the generation of triiodide (shown in Scheme 21). This yielded near-monodisperse (\(\leq 1.1\)) polymers of isobutyl vinyl ether. The polymers showed living character, exhibiting a linear increase in average molecular weight with monomer conversion. Solvent polarity was again key, as living polymerisation was only seen in non-polar \textit{n}-hexane. Using more polar solvents such as dichloromethane and toluene did not yield living polymers.\textsuperscript{91} The principle was further illustrated in another publication producing living polymers of other vinyl ethers and \textit{p}-methoxystyrene, as well as block copolymers of these monomers.\textsuperscript{92}
A couple of years later, Faust and Kennedy developed another living system, for isobutene using an initiating system of boron trichloride and organic acetates.\textsuperscript{93,94} Their system held an advantage over Higashimura’s system because it could operate in a range of solvents – from non-polar n-hexane to more-polar solvents such as chloroform and dichloromethane. Slightly higher, but still acceptable polydispersities (1.2 - 1.3) were seen, but this method was also tolerant of small amounts of moisture, traditionally a problem for ionic polymerisation methods. This allows the polymerisation to be carried out under more conventional laboratory conditions, using anhydrous solvent without the need for further drying in a nitrogen atmosphere. Termination can be forced by the addition of nucleophilic reagents, or by thermal decomposition of the propagating complex by simply allowing the reaction to warm (polymerisation is carried out at sub-zero temperatures in both the work of Faust/Kennedy and Higashimura). Knowing that Lewis acids such as BCl\textsubscript{3} will complex exclusively with the carbonyl of the hindered esters used,\textsuperscript{95,96} the following mechanism (Scheme 22) was proposed.

**Scheme 21:** Triiodide formation using equimolar quantities of iodine and hydrogen iodide

\[
\text{H}^+ \quad \rightarrow \quad \text{H}^+ \quad \overset{i}{\rightarrow} \quad \text{i}^+ \quad \rightarrow \quad \text{i}^+ \quad \rightarrow \quad \text{H}^+ \quad \text{i}^+ 
\]

**Scheme 22:** Living cationic polymerisation of isobutene initiated by BCl\textsubscript{3}-OAc complexes

Complexes between organic acetates and boron trichloride form very quickly. As mentioned previously, complexation is exclusively with the acyl oxygen, and of the two conformers, the
least sterically strained will be favoured. Subsequent incorporation of the isobutene by a rearrangement-type mechanism creates a tertiary acetate-boron trichloride complex, very similar to the initiating system. Propagation can then proceed by a group transfer mechanism.\textsuperscript{93,94,97}

The nature of the propagating site is not immediately obvious as a cationic centre. The living nature of the polymerisation suggests that two propagation states will be in equilibrium – a dormant, non-dissociated state, and an active dissociated ionic state. Choice of solvent will impact the degree of dissociation, as was seen with the Higashimura\textsuperscript{88–92} systems. More polar solvents will accentuate the presence of the dissociated active species, shown in Scheme 23.\textsuperscript{93,94}

![Scheme 23: Dissociation of propagating species in Faust and Kennedy’s living cationic polymerisation technique](image)

As with living anionic polymerisation, cationic variants can be terminated by adding a suitable reagent such as an amine or an alcohol, or by simply elevating the temperature to cause thermolysis of the propagating ester-BCl\textsubscript{3} complex. Irrespective of the termination route chosen, isobutene polymers were always capped with a tertiary-chloro group,\textsuperscript{95} illustrated in Figure 12. This structure was confirmed using \textsuperscript{1}H NMR and IR spectroscopy.\textsuperscript{98}

![Figure 12: Functional end group of polyisobutene grown by the living cationic polymerisation method of Faust and Kennedy](image)

Whilst providing enough thermal energy may be enough to cause the reaction, the authors suggest that adding a nucleophile will make the boron trichloride suitably electron rich to allow the reaction to proceed without the aid of thermal energy. The mechanism of this termination route is shown in Scheme 24.\textsuperscript{93–96}
After the publication of these two key systems, plenty of publications on living cationic polymerisation followed, but like the works of Higashimura and Faust/ Kennedy, they all largely use a Lewis acid or Brønsted acid-base conjugate pair to initiate polymerisation. However, far fewer works utilising surface-initiated living cationic polymerisation exist. Those grafted from the surface operate on the principle of attaching an electrophile from the surface and utilising the nucleophilic reactivity of the monomers for surface initiated cationic polymerisation to occur.

The group of Tsubokawa presented examples of surface initiated living-like cationic polymerisation of isobutyl vinyl ether from carbon black surfaces using two different initiating systems: a combination of ethylaluminium dichloride and 1,4-dioxane, and a zinc chloride system. Both systems initiate the native carboxyl groups (which make up between 0.08% - 0.8% of the total mass depending on the supplier of the carbon black) on the surface of the carbon black. A linear correlation between conversion and molecular weight was observed when adding the Lewis acid systems, and the addition of a fresh feed of monomer once initial polymerisation was complete added molecular weight to the chains, at the same rate as previously observed. This is then compared to the carboxyl groups alone which gave slow polymerisation with broad polydispersity. This suggests that the Lewis acid initiators are critical to achieving living-like cationic polymerisation. The ethylaluminium dichloride system gave rapid polymerisation when the 1,4-dioxane was not included, but again polydispersity was broad without the dioxane additive. This is in agreement with the observations of Higashimura and Sawamoto whereby living cationic polymerisations can be achieved by stabilising the propagating carbocation using basic ethers, illustrated in Scheme 25.

Scheme 25: Stabilisation effect on propagating carbocation when adding 1,4-dioxane to living cationic polymerisation systems
Kim and Faust showed that surface-initiated cationic polymerisation of isobutylene from silica nanoparticles is possible. A range of homo- and block co-polymer silica particle materials were produced. Chlorosilyl electrophilic initiators (Figure 13) were attached to the surface of the silica. A single chlorine and two methyl groups was found to be the optimal configuration for surface attachment (over 2 Cl/ 1 Me and 3 Cl/ 0 Me).

Titanium(IV) chloride was used as the initiating Lewis acid. The polymerisation has been employed from the surface, as well as in solution and then attaching the end-functionalised polymer to the silicon. Predictably, the grafting from approach yielded brushes of greater uniformity and increased grafting density over the grafted to analogues. Film thickness was seen to increase linearly with molecular weight, suggesting living brushes. However, the grafted to polymer gave constant thickness irrespective of molecular weight. DTBP (2,6-Ditertbutylpyridine) was also added to the reaction, acting as a base and stabilising the carbocation in a similar role to 1,4-dioxane in the work of Tsubokawa discussed previously. This stabilisation effect is outlined in Scheme 26.

The group of Jordan et al. have reported surface-initiated living ring-opening cationic polymerisation of 2-oxazolines from gold substrates, as outlined in Scheme 27. SAMs of a triflate initiating group were deposited on the gold surface by condensing triflic anhydride with the terminal OH groups of the thiol tethers. Living cationic polymerisation was then initiated by reacting 2-ethyl-2-oxazoline with the triflate SAM to yield the cationic species. The nitrogen atom of the oxazoline provides resonance stabilisation for the carbocation. Terminating with a secondary amine with long substituent alkyl chains yielded dense polymer brushes with

---

**Figure 13:** Surface attachable cationic polymerisation initiator used by Kim and Faust

**Scheme 26:** Stabilisation of carbocation using 2,6-ditertbutylpyridine (DTBP) in surface initiated living cationic polymerisation of isobutylene
amphiphilic character; both hydrophobic and hydrophilic in nature. Such brushes could be useful for an application such as phase separation.\(^\text{107}\)

**Scheme 27:** Growth of amphiphilic polymer brushes from gold substrates by surface initiated living cationic polymerisation\(^\text{107,108}\)

Brittain and Zhao\(^\text{109}\) successfully grew polystyrene brushes from SAMs of initiator assembled on silicate substrates by living cationic polymerisation. Monolayers of 2-((4-(11-trithoxysilylundecyl))phenyl-2-methoxypropane and 2-(4-trichlorosilyl-phenyl)-2-methoxy-\(\text{d}_2\)-propane (Figure 14) were used as the cationic initiators, which were activated using titanium(IV) chloride.

**Figure 14:** Living cationic polymerisation initiating species deposited as SAMs for surface-initiated polymerisation of Brittain and Zhao

Control over brush thickness was influenced by solvent polarity, TiCl\(_4\) concentration (Figure 15), and the use of additives such as dimethylacetamide (DMA) and ditertbutylpyridine (DTBP).
DMA is an electron donor that coordinates to the Lewis acid (TiCl₄), and forms a complex in a similar fashion to the bases observed in previous examples.

**Figure 15:** Variation of polystyrene brush thickness when varying TiCl₄ concentration\textsuperscript{109}

Sequential polymerisations on the same substrate yielded a brush thickness increase, suggesting a living polymerisation. FTIR-ATR characterisation of samples coated with the deuterated initiator suggested that the second polymerisation utilises initiation from both pre-existing polymer chains, but also unreacted initiator within the SAM. However, AFM analysis suggested that the surface of the PS brushes was actually quite smooth, with a roughness value of 0.3 nm (root mean square) for a 30 nm thick PS brush (Figure 16).
Two further publications then utilise these brushes with terminal chlorides to initiate ATRP to grow a polyacrylate blocks on top of the poly(styrene) (Scheme 28), neatly combining two different living polymerisation methods.\textsuperscript{110,111}

Scheme 28: Synthesis of PS-\textit{b}-polyacrylate brushes using-surface initiated living cationic polymerisation and ATRP.\textsuperscript{110,111}

In a final example, in work by the group of Meerholz, living cationic polymerisation is initiated by a block of acidic polymer which is already attached to the surface, in a technique referred to as “LBLX” (layer-by-layer cross-linking).\textsuperscript{112} Ring opening cationic polymerisation of oxetanes activated by a protic acid is the basis of the mechanism (Scheme 29). This usually occurs by protonation of one oxetane molecule, and then this oxetane molecule is attacked by another oxetane monomer.
Ring opening occurs and leaves the second oxetane activated, and propagation occurs from this point. The LBLX idea originates from a similar concept called PIX. PIX is “PEDOT initiated cross linking”, whereby the source of the acidic proton for the cationic polymerisation of oxetane is from a previously deposited layer of PEDOT. LBLX takes this concept further by polymerising oxetane layers on top of each other, using the previous layer as the initiator for the next. Both are shown in Scheme 30.\cite{112}

The authors propose the technique as a simple method for producing useful multi-layered block copolymers for use in OLED devices by a grafting from approach. LBLX takes advantage of the fact that the cationic polymerisation used is “living”. A narrow molecular weight distribution was observed giving uniform film thicknesses. This gives a perfect replication of the initial PEDOT
surface structure that was used to craft the first poly(oxetane) layer. The devices show reduced delamination effects compared to spin-coated and other physisorbed equivalents. This also gives increased thermal stability, as all layers are chemically bonded to one another.\textsuperscript{112}

1.3.6. KCTP: Kumada Catalyst-Transfer Polymerisation

The Kumada (or Kumada-Corriu) coupling reaction was initially published in 1972 independently by Makoto Kumada\textsuperscript{113} and Robert Corriu,\textsuperscript{114} and is the cross coupling of a Grignard reagent, which may be alkyl or aryl, with an aryl halide (Scheme 31). The reaction also proceeds when using vinyl halides. The Kumada coupling is catalysed by either a nickel(0)\textsuperscript{113,114} or palladium(0) source.\textsuperscript{115} This traditional cross-coupling reaction has in recent years been utilised heavily as a polymerisation technique, dubbed Kumada Catalyst-Transfer Polymerisation (KCTP) in the synthesis of poly(thiophene)s, both in solution and on surfaces.\textsuperscript{6,20,116–122} KCTP monomers are bifunctional, incorporating both the required halide and Grignard functionalities required for Kumada coupling. The technique is also sometimes referred to as “Grignard Metathesis Polymerisation”, or “GRIM”.\textsuperscript{123}

\begin{equation}
R\text{–MgCl} \xrightarrow{\text{N}^0\text{ catalyst}} \text{R}^\prime –\text{Cl} \xrightarrow{\text{R}^\prime –\text{Cl}} \text{R} –\text{R}'
\end{equation}

\textbf{Scheme 31: The Kumada cross-coupling reaction}

The mechanism of the Kumada coupling is detailed in Scheme 32. It follows a similar narrative to most palladium/ nickel catalysed couplings. The catalytic cycle shows nickel in both the Ni(0) and Ni(II) oxidation states. Starting at the twelve o’clock positon, an electron-rich Ni(0) catalyst inserts into the R–X bond of the organic halide. An organo-Ni(II) complex forms as a result of this oxidative addition. Transmetallation between the Grignard reagent and the organo-Ni(II) complex forms a second organo-Ni(II) complex, this time consisting of the two groups to be coupled, the original catalyst ligands and the nickel itself. The halide is lost with the Grignard group as a magnesium halide. Trans-cis isomerisation then occurs to bring the coupling groups next to each other. Once this occurs, the final step is reductive elimination to form a carbon-carbon bond and yield the cross-coupled product, simultaneously regenerating the original Ni(0) catalyst. The rate-determining step is the oxidative addition step, and this occurs more readily with nickel catalyst systems compared to palladium-based systems.\textsuperscript{124}
Scheme 32: Catalytic cycle for the Kumada cross-coupling reaction using nickel(0).
Instances of Ni can be substituted here for Pd to show the equivalent palladium-based cycle.

Poly(thiophene)s are useful polymers as they are conjugated (i.e. they have overlapping π-orbitals) in their normal state. Poly(thiophene) conductivity can be increased by “doping” either by oxidation (p-doping, typically using iodine, Scheme 33) or reduction (n-doping, but this is uncommon).

Scheme 33: p-doping of poly(thiophene)

Owing to the large number of publications utilising KCTP to synthesise poly(thiophene)s, Luscombe and co-workers spent considerable time investigating the mechanism of Kumada catalyst-transfer polymerisation, as well as the effects of different external initiators and catalyst ligands. In their mechanistic investigations, Boyd, Jen and Luscombe queried the postulated mechanisms previously published individually by McCullogh and Yokozawa, for the formation of poly(3-hexylthiophene) (P3HT) via KCTP, shown in Scheme 34.
Whilst accepting the chain transfer mechanism as being correct, Luscombe et al. felt that the evidence proving that two monomer molecules combine to form the bithiophene bromide initiator was inconclusive. They also believed that the assumption that P3HT shows good head-to-tail (Figure 17) regio-regularity (as opposed to head-to-head) due to steric interactions between neighbouring \(n\)-hexyl chains required confirmation.

By generating the “reversed” monomer of the typical P3HT monomer (repositioning the \(n\)-hexyl group in the 4-position; nearer to the magnesyl chloride, as opposed to the conventional 3-position; nearer to the bromide), they successfully proved that the bithiophene bromide initiator species is required to initiate the polymerisation when an external initiator is not used. With the reversed monomer, the polymerisation did not occur. The authors cited that the steric hindrances of the two \(n\)-hexyl groups (caused by the two chains being in close proximity) prevented the formation of the necessary bithiophene bromide initiator, as illustrated in...
**Scheme 35.** These steric interactions also helped confirm the theory behind the supreme head-to-tail regio-regularity of P3HT formation by KCTP.

When studying the effects of an external polymerisation initiator, the Luscombe group used a series of substituted aryl halides as external KCTP initiators. They tested these initiators whilst again synthesising P3HT.\(^{128}\) They suggest that the initiators are a more facile way of initiating the polymerisation, as well as leading to higher yields, greater polymer molecular weights, lower polydispersity, and other beneficial properties in comparison to synthesising P3HT using the bithiophene halide, or “internal” initiator. At the time of writing, the reasons behind these favourable properties that are achieved when using external initiators remain unpublished.

However, what has been determined is how various substituents attached to the phenyl ring of these aryl halide initiators can affect the initiation of the polymerisation. The percentage of initiation values and subsequent reactivity series of the aryl halide initiators obtained suggests that the oxidative addition of the nickel(0) catalyst to the C-X bond is not the critical step in the initiation process. If this were true, then electron withdrawing substituents in the *ortho-* and *para-* positions would be highly beneficial. It transpires that electron withdrawing substituents in the *ortho-* position are beneficial, suggesting that they may stabilise the nickel catalyst by chelation\(^{127,129,133}\) (Figure 18).
Conversely, functionality of any description in the para-position is actually very disruptive to polymerisation initiation. This is thought to be due to the para-position being unable to stabilise the nickel(0) catalyst. It is more likely that the para-substituted initiators have the effect of lowering the energy of the highest filled orbital on the nickel(0) by bonding the \( \pi^* \) orbitals of the phenyl ring with one of the nickel(0) \( d \) orbitals, leaving the catalyst susceptible to disproportionation, which will ultimately result in undesired and uncontrolled side reactions.\(^\text{128}\)

As well as an external initiator, the other modifiable chemical parameter in KCTP is the nickel catalyst. \( \text{Bis}(1,5\text{-cyclooctadiene})\text{nickel}(0) \), written as \( \text{Ni(COD)}_2 \), is typically used, and one or both COD ligands are exchanged \textit{in situ} with phosphine ligands, for example triphenylphosphine (Scheme 36).\(^\text{116}\) The cyclooctadiene ligands are not covalently bonded to the nickel, but coordinated by metal-\( \pi \) interactions between the nickel and the electron density of the double bonds in the cyclooctadiene ring.

\[ \text{Scheme 36: Exchange of a COD ligand of bis}(1,5\text{-cyclooctadiene})\text{nickel}(0) \text{ for two triphenylphosphine ligands} \]

Luscombe’s group used triphenylphosphine (tpp) as a monodentate ligand, as well as three common bidentate phosphine ligands: 1,2-Bis(diphenylphosphino)ethane (dppe, or diphos), 1,3-Bis(diphenylphosphino)propane (dppp) and 1,1’-Bis(diphenylphosphino)ferrocene (dppf) (Table 1)\(^\text{129}\). It was observed that using tpp and dppf as ligands gave far superior results over the equivalent dppp and dppe complexes for polymerisation systems utilising the external initiator. However, the reverse was true for internally initiated polymerisation; dppp and dppe showed higher activity than the dppf and tpp equivalents. This can be attributed to the cone and bite angles (Figure 19 and Table 1) of the respective ligands.\(^\text{129}\)
Table 1: Structure and cone/bite angles of common phosphine ligands

<table>
<thead>
<tr>
<th>Phosphine</th>
<th>Cone or bite angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>tpp</td>
<td>θ = 145°</td>
</tr>
<tr>
<td>dppf</td>
<td>βn = 96°</td>
</tr>
<tr>
<td>dppp</td>
<td>βn = 91°</td>
</tr>
<tr>
<td>dppe</td>
<td>βn = 85°</td>
</tr>
</tbody>
</table>

Figure 19: Cone (left) and bite (right) angles of phosphine ligands

For the catalyst to be effective, the rate of the oxidative addition step in the catalytic cycle (Scheme 32) needs to be exponentially faster than the reductive elimination step.\textsuperscript{134,135} For the internally initiated system, oxidative addition is faster with a smaller cone or bite angle (Table 1), as the metal centre of the catalyst is less sterically hindered, making it easier for the nickel to insert itself across the Ar-X bond.

Logically these results would also appear to be analogous for the external initiator methodology, but the reverse is in fact seen, as noted previously. This can be explained using the relative lability of the respective ligands. Tpp, and dppf to a lesser extent, are more labile than dppp and dppe. Tpp is a particularly labile ligand, and as such can be lost easily, making oxidative addition of the Ar-X bond more feasible.\textsuperscript{129}

As a secondary observation, Ni(R\textsubscript{2}P-PR\textsubscript{2})X\textsubscript{2} [e.g. Ni(dppp)\textsubscript{2}Cl\textsubscript{2}] complexes are far more active as catalysts than the Ni(R\textsubscript{3}P-PR\textsubscript{2})\textsubscript{2} [e.g. Ni(dppp)\textsubscript{2}] and Ni(PR\textsubscript{3})\textsubscript{4} species,\textsuperscript{128} but the Ni(R\textsubscript{2}P-PR\textsubscript{2})X\textsubscript{2} species are also quite unstable and readily convert to the Ni(R\textsubscript{2}P-PR\textsubscript{2})\textsubscript{2} form, which exhibits superior stability but inferior catalytic ability; in reality Ni(R\textsubscript{2}P-PR\textsubscript{2})X\textsubscript{2} species are virtually inactive as catalysts. The inactivity is caused by the highly disfavoured conformation of the intermediate complex that would be formed by the oxidative addition across the Ar-X bond (Figure 20). Also, should such a complex arise, it would undoubtedly place an intolerable strain
on the bidentate bridge of the dppp or dppe, thus making its formation immensely disfavoured.

![Figure 20: Disfavoured Ni(dppp)₂ArX complex](image)

As previously mentioned, recent advances in KCTP have been developing quickly, but the field is still dwarfed by the significantly greater number of publications producing typical KCTP polymers, such as poly(thiophene)s, by more conventional step-growth polymerisation methods. Kiriy, Senkovskyy and Sommer suggest that the field does appear to be working towards the synthesis of all-conjugated block copolymers, with p-type and n-type blocks being produced in a controlled, one-pot synthesis.

The first published example of research utilising the KCTP method to produce polythiophenes can be traced to a paper on oligomeric 2,5-thienylenes by the Zimmer group using Kumada couplings. The authors acknowledged that a number of oligo(thiophene) compounds were already known, but comment that the synthesis of such compounds is cumbersome and low-yielding. The Kumada method yields compounds in a more convenient process leading to far more attractive yields.

Oligomers from dimeric up to hexameric in length were synthesised, both unsubstituted and methyl substituted in the 3 or 4 position. The optical and electrochemical properties of these oligomers were then studied to with the overall aim of creating “water-dopable poly(3-substituted-2,5-thienylenes)”.

![Scheme 37: Zimmer’s synthesis of thiophene oligomers](image)

The extent of the n-electron cloud of unsubstituted thiophene oligomers depends only on the number of repeat units. The λ_max values increase with increasing chain length, although the increment between adjacent compounds decreases, suggesting less overlap of n-electrons. The authors propose that this is “due to increasing thermal motion” of the oligomers. The
increased length of the conjugated system essentially increases the range of delocalisation for the induced positive charges when doping. Decreasing oxidation potential for longer chains suggests that this is the case. This data is summarised in Table 2.\textsuperscript{121}

**Table 2:** $\lambda_{\text{max}}$ and $E_{\text{ox}}$ values of thiophene oligomers synthesised by Zimmer et al.\textsuperscript{121}

<table>
<thead>
<tr>
<th>Oligomer</th>
<th>$\lambda_{\text{max}}$ (nm), CHCl$_3$</th>
<th>$E_{\text{ox}}$ (V)</th>
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<tbody>
<tr>
<td><img src="image1.png" alt="Oligomer 1" /></td>
<td>302</td>
<td>1.28</td>
</tr>
<tr>
<td><img src="image2.png" alt="Oligomer 2" /></td>
<td>355</td>
<td>1.05</td>
</tr>
<tr>
<td><img src="image3.png" alt="Oligomer 3" /></td>
<td>390</td>
<td>0.97</td>
</tr>
<tr>
<td><img src="image4.png" alt="Oligomer 4" /></td>
<td>432</td>
<td>0.46</td>
</tr>
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For substituted monomers increasing chain length leads to increased order (i.e. head to tail, head to head, tail to tail, as opposed to a random distribution). This ordering has a clear influence on the value of $\lambda_{\text{max}}$ and oxidation potential, as shown in Table 3. Whereas the extent of the $n$-electron cloud of unsubstituted thiophene oligomers depends only on the number of repeat units, the steric interactions between methyl groups in the 3- or 4-substituted equivalents influence planarity and therefore the overlap of the $n$-electrons. Greater steric interaction results in lower $\lambda_{\text{max}}$ wavelengths and greater oxidation potential.\textsuperscript{121}
Table 3: $\lambda_{\text{max}}$ and $E_{\text{ox}}$ values of 3- and 4-methyl substituted thiophene oligomers synthesised by Zimmer et al.\textsuperscript{121}

<table>
<thead>
<tr>
<th>Oligomer</th>
<th>$\lambda_{\text{max}}$ (nm), CHCl$_3$</th>
<th>$E_{\text{ox}}$ (V)</th>
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<tbody>
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<td>1.22</td>
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<td>270</td>
<td>1.58</td>
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<tr>
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<tr>
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<td>1.13</td>
</tr>
<tr>
<td><img src="image6.png" alt="Image" /></td>
<td>336</td>
<td>1.11</td>
</tr>
</tbody>
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As Table 3 shows, the relationship between the $\lambda_{\text{max}}$ and oxidation potential is less defined with the methyl substituted oligomers. The reasons for this are two-fold and conflicting. Firstly, the $n$-electron overlap decreases due to the steric hindrance imposed by the methyl groups would suggest a decrease in $\lambda_{\text{max}}$ and an increase in oxidation potential. However, this is counteracted to an extent because the methyl substituents are electron-donating groups when considering the inductive effect. This aids delocalisation and contributes to the stabilisation of the cationic species when the sample is doped. The two contrasting scenarios occur in proportions which are unequal and difficult to predict.\textsuperscript{121}

Progressing from oligomers to polymers, several groups have produced poly(thiophene)s for use in device applications by utilising KCTP. Russell and Emrick synthesised donor-acceptor diblock copolymers for use in a solar cell, using regio-regular poly(3-hexylthiophene) (P3HT) as
the electron-donor block and poly(perylene diimide acrylate) (PPDA) as the electron-acceptor block. Vinyl-terminated regio-regular P3HT was synthesised by KCTP and then converted to an alkoxyamine macroinitiator for subsequent nitroxide-mediated polymerisation of the perylene diimide acrylate (Scheme 38). The donor-acceptor diblock copolymers showed low-to-moderate polydispersity (1.2 - 1.4) and high molecular weight. Films of the diblock were then produced by spin coating. The block copolymers showed efficient photoluminescence quenching in the solid state, which is indicative of charge separation. The solar cell produced had a power conversion efficiency of 0.49%.

Scheme 38: Synthesis of poly(thiophene-b-perylene diimide) block copolymers

Seferos et al. have co-polymerised thiophenes with selenophenes. Acknowledging that although popular as a low cost electroactive polymer, controlling the morphological and optical properties of these polymers has historically been difficult. The ability to control the phase separation of such polymers proved an attractive option for producing a device that can facilitate charge transport and charge transfer. By synthesising block co-polymers, this can be
easily achieved by tailoring the functionalities present in each block. Although a common approach with non-conjugated polymers, the authors state that for conjugated polymers the approach presents “far fewer ways to design and synthesise distinct block structures and hence control phase separation”\textsuperscript{145}

The unique side-chain approach to control intermolecular interactions and phase separation is noted to at times be difficult to predict and can also influence optical properties. Instead, the authors used differing heterocycles (thiophenes and selenophenes) with identical side chains to control phase separation. Poly(selenophene) is a new conjugated polymer, with a narrower HOMO-LUMO energy gap than poly(thiophene). Using KCTP, distinct block copolymers were produced by the method shown in \textbf{Scheme 39}.\textsuperscript{145}

\begin{center}
\textbf{Scheme 39:} Synthesis of poly(3-hexylthiophene)-\textit{b}-poly(3-hexylselenophene) (P3HT-\textit{b}-P3HS)\textsuperscript{145}
\end{center}

The authors feel that poly(3-hexylthiophene)-\textit{b}-poly(3-hexylselenophene)s are an important new type of copolymer, due to their broad range of optical absorption (\textbf{Figure 21}), which is red-shifted by up to 80 nm relative to P3HT, providing easy access to higher absorption wavelengths for potential applications, such as infra-red sensors. This holds a critical advantage over the equivalent statistical copolymer, for which the absorbance curve lies between that of homopolymeric P3HT and P3HS.\textsuperscript{145}
Fluorescence spectra of the polymer solutions were also indicative of the structure. Whilst P3HT and P3HS emit at 578 and 623 nm, respectively (Figure 22), the block copolymer emission spectrum is dominated by emission at 578 nm from the thiophene block because thiophenes show far greater fluorescence intensity than selenophenes. However, the statistical copolymer shows a peak at 598 nm, a wavelength that is between the characteristic values for P3HT and P3HS emissions.\textsuperscript{145}

Films in the solid-state were prepared by spin-coating and annealing. The absorbance properties of these thin films were measured, and the absorption profile of the block copolymer possesses shoulders (indicated by the arrows in Figure 23). These are similar to those seen for homopolymeric P3HT and P3HS, and relate to the $\pi$-stacking of both polymers. These features in the diblock spectrum are indicative of association and organisation of blocks with
corresponding blocks in the adjacent chains. However, when analysing the statistical copolymer, the absorption profile does not contain such shoulders.\textsuperscript{145}

**Figure 23:** Fluorescence emission spectra of spin-coated P3HT and P3HS homo- and co- polymers. P3HT: \textbullet\textbullet\textbullet\textbullet\textbullet, P3HS: \textbullet\textbullet\textbullet\textbullet\textbullet, P3HT-b-P3HS 145

Using atomic force microscopy (AFM), the film morphology of the block copolymer was seen to contain clearly different regions within the film (Figure 24c), which are not seen in the statistical copolymer film (Figure 24b). The statistical copolymer shows a much smoother morphology. A blend of the two homopolymers appears unstructured when viewed by AFM (Figure 24a). Along with the absorption experiments, this AFM data suggest that the block copolymer is subject to a high degree of phase separation in the solid state.\textsuperscript{145}

**Figure 24:** AFM phase images of (a) 1:1 wt\% blend of P3HT and P3HS, (b) P3HT-s-P3HS, and (c) P3HT-b-P3HS\textsuperscript{145}

Prior to this work, the authors report that no previous phase separation has been seen using this method, all previous examples are a result of either using conjugated polymers with non-conjugated blocks or using differing pendant groups. Here, both phase separation and the optical properties are controlled by the heterocycle in the polymer chain. This approach offers a unique type of phase separation underpinned by elemental composition and at the same time yields a direct method for controlling optical properties. Therefore the authors feel that the poly(3-hexylthiophene)-b-(3-hexylselenophene)s should be a critical new material in future optoelectronic applications.\textsuperscript{145}
In a collaboration between Tajima and Hashimoto, highly regioregular poly(3-hexylthiophene)-b-(3-(2-ethylhexyl)thiophene)s were synthesised by KCTP (Scheme 40). Characterisation by NMR and GPC showed highly controlled block ratios (± 5 - 8%) and narrow polydispersity indices (1.10 - 1.17).\(^\text{146}\)

![Scheme 40: Synthesis of poly(3-hexylthiophene-b-3-(2-ethylhexyl)thiophene)\(^{146}\)](image)

The uniformity of well-controlled polymers enables the accurate study of other correlations between properties. In this case, analysis of the relationship between the overall structure and the nanostructures within P3HT-b-3EHT films was conducted. AFM studies revealed that the thin films are organised into clear “microphase separated nanopatterns” (Figure 25a) after annealing at 220 °C. The temperature at which nanopattern formation occurs was determined by DSC and was found to be very close to the melting point and recrystallisation temperatures of the polymers. The equivalent random copolymer (Figure 25b) and physical mixture (Figure 25c) of the equivalent polymers showed “featureless patterns”, suggesting that a well-defined diblock is essential for the formation of spontaneous nanopatterns.\(^\text{146}\)

![Figure 25: AFM phase images of (a) P3HT-b-P3EHT, (b) P3HT-co-P3EHT, and (c) 3:1 mol% blend of P3HT and P3EHT\(^{146}\)](image)

\(^{146}\)
UV-Vis absorption spectroscopy showed the P3HT blocks to be highly crystalline, with the \( \pi \)-planes and alkyl side chains in alignment. The presence of a shoulder between 570-610 nm after annealing at 220 °C is usually caused by excited state formed between excited chains. This suggests a highly ordered crystalline structure. This spectral pattern became more pronounced with increasing P3HT content. XRD patterns were close to those of P3HT homopolymer films and confirm the presence of an ordered lattice structure. Controlled orientation of the nanostructures within such polymers is critical in the construction of polymer electronics, for example polymer alignment will contribute strongly to effective hole mobility in devices such as OFETs.

\[ \text{Figure 26: UV-Vis spectra of thin films of P3HT-b-P3EHT with (a) 20\% P3HT, (b) 56\% P3HT and (c) 83\% P3HT\}^{146} \]

In another piece of work, Tajima and Hashimoto attached poly(thiophene)s grown by KCTP to fullerenes via “click” chemistry to create a single component photovoltaic cell. This is a reliable method for creating a donor-acceptor mixing morphology created by the design of the monomers that will self-arrange into well-ordered microstructures. The limited excitation diffusion length of organic materials (ca. 10 nm) means that organic solar cells require a close arrangement of electron donor and acceptor materials. Facilitating efficient charge separation in this way is key to effective charge transport. The way in which these donor and acceptor materials are mixed to form a mixed bulk heterojunction is critical in allowing organic photovoltaic devices to function.

Ordered morphologies achieved by processes such as thermally annealing or caused by differing solvent interactions between various component layers are usually arranged in a metastable state that is thermodynamically disfavoured. This limitation means that although the device is functional, it can be temperature sensitive; if taken above its glass transition temperature, the components will rearrange into the thermodynamically favoured lowest energy configuration, which may not be as efficient for charge separation and transportation. This has been overcome in more recent literature by attaching oligomers, or in this case
(and others\textsuperscript{158–164}) copolymers to acceptor systems such as fullerene and perylenediimide derivatives. These systems can then form thermodynamically stable nanostructures that can be fine-tuned by molecular design and thus unaffected by rearrangement above the glass transition temperature. These single component systems can suffer from low fill factors, which suggests poor connectivity of the charge transport path in the films.\textsuperscript{152,165}

Fullerene-attached diblocks were synthesised as shown in Scheme 41. Diblocks of 3-hexylthiophene and 3-(6-bromohexyl)thiophene were synthesised by KCTP, to a molecular weight of ca. 24,000 and with a polydispersity index below 1.1. Terminal side chain bromide groups were then converted to azide functionality by reaction with sodium azide. This creates a “clickable” functionality on the side chain for attachment to the alkyne derivatised fullerene.\textsuperscript{148}

![Scheme 41: Synthetic route for the fullerene-attached diblock copolymer\textsuperscript{148}](image)

AFM phase images again showed the fullerene-tethered block copolymer to be clearly nanopatterned, unlike the random copolymer equivalent (Figure 27). UV-Vis absorption spectra of solutions (Figure 28a) of the fullerene-attached diblock and random copolymers were identical to a similar w/w physical mixture of P3HT and [6,6]-phenyl-C\textsubscript{61}-butyric acid methyl ester (PCBM). However, films cast of the three homologous materials showed the physical mixture and random copolymer gave identical traces, whereas the diblock gave a distinctly different spectrum (Figure 28b) – the spectrum is redshifted and also shows a shoulder at 610 nm, which as before is indicative of a crystalline P3HT region; indicative of an environment similar to a bulk heterojunction. The random copolymer and the physical mixture both show no redshift and no absorption shoulder, suggesting a disordered structure.\textsuperscript{148}
Chapter 1: Introduction

Figure 27: AFM phase images of the fullerene-attached (a) diblock and (b) random copolymer films

Figure 28: UV-Vis absorption spectra of the fullerene-attached copolymers (a) in CHCl$_3$ solution and (b) as cast films

Photovoltaic devices using the diblock and the random copolymer were produced. Solar cell performance of the diblock was proven to be superior to that of the random copolymer. After annealing at 130 °C, the fullerene-attached diblock yielded significantly better numbers for key performance criteria: a power conversion efficiency (PCE) of 1.70% vs 0.48%, a short circuit current ($I_{SC}$) of 6.15 mA cm$^{-2}$ vs 1.80 mA cm$^{-2}$, an open circuit voltage ($V_{OC}$) of 0.54 V vs 0.76 V and a fill factor (FF) of 0.51 vs 0.35. The numbers for the diblock device are claimed to be the highest performing amongst single-component donor-acceptor copolymer systems published (at the time of publication), proving the device to be efficient. The diblock system also proved to be more thermally stable than its physical mixture counterpart. Although performance of the physical mixture was initially higher (PCE = 3.0%), this soon deteriorated with prolonged annealing at 130 °C (PCE falls to ca. 0.6 %, Figure 29), as the film began to degrade. Phase separation in the form of needle-like aggregations appeared, disrupting the previously-ordered structure (Figure 30). In contrast, the diblock system showed little degradation (PCE dropped
from 1.59% to 1.50% after annealing at 130 °C for 80 h), with no PCBM aggregation being observed.\textsuperscript{148}

![Figure 29](image1.png)

**Figure 29:** PCE change at 130 °C in solar cells containing the fullerene-attached polymers.$^{148}$

![Figure 30](image2.png)

**Figure 30:** Optical microscope image of disrupted P3HT:PCBM mixture after prolonged annealing at 130 °C for 80 h.$^{148}$

The groups of Kiriy and Senkovskyy co-authored a report on the use of surface-initiated KCTP to fashion “hairy” particles for use in a bulk heterojunction solar cell.$^{117}$ P3HT brushes were grown from substrates of organosilica nanospheres bearing immobilised efficient KCTP diphosphine nickel-based initiators,$^{166,167}$ as shown in Scheme 42.$^{117}$
Scheme 42: Immobilisation of nickel catalyst on modified silica nanoparticles and SI-KCTP of (5-bromo-4-hexylthiophen-2-yl)magnesium chloride to form “hairy” P3HT particles\textsuperscript{117}

The dense and well-ordered structure of particles with a low surface curvature can be seen in the SEM images in Figure 31, which also illustrate the change in a relatively smooth surface for the untreated particles to one that is much rougher. Particles with a higher surface curvature did not exhibit the high grafting densities seen with the particles with the lower curvature.\textsuperscript{117}

Figure 31: SEM images of organosilica particles (a) before and (b) after SI-KCTP with P3HT\textsuperscript{117}
These “hairy” nanoparticles showed significantly different optical properties to their untreated counterparts, red-shifting the UV-Vis absorption and fluorescence spectra by ca. 100 nm, and introducing features such as shoulders to the spectra that infer changes to the vibronic structure of the particles as a result of efficient formation of a planar and well-ordered structure (Figure 32).\textsuperscript{117}

![Figure 32: (a) UV-vis and (b) fluorescence spectra of free P3HT (black) and hairy P3HT nanoparticles (red) in tetrahydrofuran\textsuperscript{117}](image)

Thin films of the “hairy” nanoparticles cast with PCBM on ITO coated glass with a PEDOT:PSS layer produced photovoltaic devices with good performance indicators (Surface area of 1 cm\textsuperscript{2}, PCE = 1.8 - 2.3\%, \( I_{sc} = 5.5 - 6.8 \text{ mA cm}^{-2} \), \( V_{oc} = 0.60 - 0.62 \text{ V} \), FF = 55 - 58\%). Annealed devices (130 °C / 5 min) outperformed their non-annealed equivalents, suggesting that the annealing process gives rise to a more-ordered structure (Figure 33).\textsuperscript{117}

![Figure 33: IV curves of glass/ITO/PEDOT:PSS/P3HT particles:PCBM/Al device before (blue) and after (red) annealing at 130 °C for 5 min\textsuperscript{117}](image)

In a subsequent publication,\textsuperscript{20} Senkovskyy and Kiriy report a brominated P3HT nanoparticle produced by an identical method to that published previously. Use of a brominated monomer does not affect the course of the SI-KCTP, opening up a range of functionalised P3HTs. In this example, the brominated P3HT (“P3BrHT”) is modified in a two-step process using potassium phthalimide and hydrazine (Scheme 43). The introduction of ionisable amino groups results in
differing optical spectra in a range of chemical environments (Figure 34), suggesting sensory applications as another potential use of the “hairy” nanoparticles. This group also published work utilising a different monomer (9,9-dioctylfluorene, PFO), which again showed significant differences in the optical spectra, and proposed this as another type of “hairy” nanoparticle for optoelectronic applications. Clément recently published an article wherein P3HT was grown by SI-KCTP from TiO$_2$ nanoparticles and then cast from solution into a fabricated device. This did not yield the same results as the silica counterparts produced by Kiriy and Senkovskyy but did yield P3HT that absorbed a wider range of wavelengths and in fact suppressed fluorescent emission, which the author attributes to $\pi$-$\pi$ stacking interactions in the solid state.

Scheme 43: Post-modification of P3BrHT hairy nanoparticles for sensory applications

Figure 34: (a) UV-vis and (b) fluorescence emission spectra (excitation at 533 nm) of P3(NH$_2$)HT nanoparticles dispersed in THF, water, aqueous solution of $p$TSA (para-toluene sulfonic acid) and aqueous solution of MSA (methane sulfonic acid)

Locklin et al. have investigated the use of SI-KCTP for device applications in several publications. Their initial report detailed their technique for KCTP using aryl halide initiators, preparing poly(thiophene) and poly(phenylene) brushes. These were grown from a gold surface using a thiol linker and bromothiophene initiator, and a nickel based catalyst. These films had no particular application and served as the basis for further work by this group based on the
favourable results obtained from cyclic voltammetry experiments shown in Figure 35.\textsuperscript{116} A further publication\textsuperscript{169} saw the group adapt the nickel catalyst phosphine ligand exchange approach of Kiriy/Senkovskyy discussed previously\textsuperscript{117} and SI-KCTP of substituted poly(phenylene)s, again with no particular application.

![Figure 35: CV of poly(phenylene) and poly(thiophene) brushes grown from gold substrates by SI-KCTP. Inset shows anodic and cathodic peak currents vs scan rate\textsuperscript{116}](image)

The Locklin group had success using palladium catalysts instead of their nickel counterparts, creating films of poly(3-methylthiophene) (P3MT) with well controlled thicknesses up to 100 nm (Scheme 44).\textsuperscript{170,171} The breadth of palladium chemistry published within the literature makes information widely available, and the reduced oxygen sensitivity associated with palladium catalysis over nickel catalysis makes this approach highly desirable. This more robust chemistry leads to more active initiator groups per unit area leading to greater grafting densities\textsuperscript{170}

![Scheme 44: Synthesis of P3MT brushes by SI-KCTP using Pd catalysis\textsuperscript{170}](image)

The group has synthesised P3MT brushes as an efficient alternative hole transporting layer (HTL) in polymer solar cells to PEDOT:PSS. Although used as the go-to option for HTLs, PEDOT:PSS does have one major drawback: it has been shown to corrode ITO electrodes (due to its acidity)\textsuperscript{172,173}, which in turn can cause chemical instability at the p-n interface.\textsuperscript{174} To address this issue, the Locklin group are seeking to produce a PEDOT:PSS-free device
(and ultimately ITO-free). The P3MT device produced yielded a PCE value greater than 5% when thin layers of P3MT were doped electrochemically in dichloromethane with tetrabutylammonium hexafluorophosphate. With the added advantage of covalently bound polymer on the surface, substrates of ITO/P3MT can be reused and recycled without a significant drop in efficiency.

The group of Luscombe also worked on P3MT systems at the same time as Locklin, and published their findings concurrently.\textsuperscript{175} Using ITO and similar phosphate linked aromatic halide initiators; they too exhibited control over the film thickness of the brushes produced by KCTP. This level of control (solution monomer concentration having a direct effect on brush thickness) is the first report of its kind for KCTP.\textsuperscript{175} Again using electrochemical doping, the P3MT films showed good electrochemical properties when analysing the CV traces (Figure 36). This report also noted that the doped state remains even after removal from the electrochemical doping solution, which suggests great stability. Films grafted up to 265 nm in thickness are also reported as being the thickest grown by SI-KCTP to date, with previous examples being in the sub-100 nm range.\textsuperscript{116,117,169}

![Cyclic voltammogram of 80 nm P3MT film grown by Luscombe et al.](image)

**Figure 36**: Cyclic voltammogram of 80 nm P3MT film grown by Luscombe *et al.*\textsuperscript{175}

### 1.3.7. ROMP: Ring Opening Metathesis Polymerisation

The robustness, reliability and popular nature of metathesis chemistry culminated in the award of the Nobel Prize in Chemistry to Yves Chauvin, Robert H. Grubbs and Richard R. Schrock in 2005 for their efforts in “the development of the metathesis method in organic synthesis”.\textsuperscript{176} There are many different guises of olefin metathesis chemistry (Scheme 45) and Ring Opening Metathesis Polymerisation (ROMP) is a commonly exploited pathway. The first example of ROMP was reported by Truett in 1960, when he reported successful polymerisation of high molecular weight poly(norbornene) using a titanium catalyst.\textsuperscript{177} Over fifty years later, ROMP is still being used to open strained ring systems that incorporate a double bond to generate polymer chains\textsuperscript{178–182} via the example mechanism summarised in Scheme 46.
The success of any olefin metathesis reaction is crucially dependant on the formation of several metallocyclobutane complexes between the alkene and the transition metal centre of the catalyst via a [2+2] cycloaddition. The metallocyclobutane intermediate then undergoes a retro [2+2] reaction to give an alkene product and another catalytic intermediate. The first [2+2]/ retro [2+2] combination yields an activated alkylidene. Another olefin, or in the case of ROMP another molecule of the monomer, comes in to then react with the alkylidene in a second [2+2]/ retro [2+2] sequence to furnish the metathesis product. Finally the catalyst is regenerated. This sequence of events is summarised in Scheme 47.\(^\text{183,184}\)
In order for the alkene to be able to complex to the transition metal, it is critical that the transition metal be in the 16-electron state. Grubbs’ catalysts, as well as other alkylidene-based catalysts, fulfill this requirement by dissociation of a readily-labile ligand. Grubbs’ catalyst therefore loses a phosphine ligand to invoke the necessary 16-electron configuration. The development of Grubbs’ 2nd generation catalyst was based around the fact that the newly incorporated imidazol-2-ylidene ligand is an N-heterocyclic carbene. This is significantly more electron donating than the original phosphine ligand used in Grubbs’ 1st generation catalyst (NHC’s are basic ligands, as opposed to being a neutral ligand like tricyclohexylphosphine). This therefore makes it easier to push the remaining phosphine ligand out from the complex when required, making it far easier to attain the desired 16-electron arrangement needed for catalysis (Scheme 48). Also, the increased steric bulk provided by the imidazol-2-ylidene compared to the phosphine predecessor further encourages the alkene to approach from the opposite, catalytically active, face.
Grubbs showed examples of conjugated polymers synthesised by ROMP when he published reports of poly(acetylene)s produced from cyclooctatetraenes (Scheme 49).\textsuperscript{181,182} No addition of solvent was needed, just the addition of a small amount of tungsten metathesis catalyst to initiate bulk polymerisation of the cyclooctatetraene monomer. Polymerisation is rapid, occurring in a matter of seconds at ambient temperature and pressure.\textsuperscript{181} Similar polynes were produced in a later publication using the more familiar Grubbs' first and second generation ruthenium catalysts. In this reports, the polynes created were soluble and telechelic, successfully creating diblocks with other olefin-terminated polymers (PMMA, PEG acrylate, polystyrene) to form block copolymers.\textsuperscript{187}

The unsubstituted “poly(cyclooctatetraene)” is identical to poly(acetylene) when characterised by NMR. The conductance exhibited is good when doped with iodine, and is equivalent to that shown by poly(acetylene) produced from direct polymerisation of acetylene monomers.\textsuperscript{181} Polymers of acetylene derivatives were produced by adorning the cyclooctatetraene with various substituent alkyl groups, to aid solubility and allow for conjugation to remain intact. This also allows for less random (or more ordered) versions of copolymers produced from acetylene and the equivalent substituted-acetylene monomers.\textsuperscript{182}
Grubbs also successfully used ROMP to grow diblock copolymers of derivatised norbornenes.\textsuperscript{188} Using variants of his first generation catalyst, he successfully carried out living polymerisation of unsubstituted norbornene in a dichloromethane and dichloroethane co-solvent at room temperature. The polymer was shown to have a polydispersity of 1.2 for an average molecular weight of 58,000. Polymerisation was successfully restarted when adding a functionalised norbornene to the poly(norbornene) solution and heating to 50 °C. Average molecular weight increased to 129,000, whilst polydispersity still remained narrow (1.25).\textsuperscript{188} This diblock synthesis is summarised in Scheme 50.

\textbf{Scheme 50: Synthesis of norbornyl diblock copolymers by living ROMP}\textsuperscript{188}

Surface-initiated ROMP was also first published by Grubbs, when he used a norbornyl-thiol linker on a gold surface before initiating with a first-generation ruthenium catalyst and polymerising TBDMS-norbornene and isoindoledione-oxanorbornene derivatives from this initiated surface (Scheme 51).\textsuperscript{189} This work was followed up with another publication in which norbornene was polymerised from a silicon surface using a pendant allyl group on the surface initiated with Grubbs’ I (Scheme 52).\textsuperscript{190} Both publications showed little else than proof of the concept that ROMP could be used to grow brushes, but they did state that norbornene-based brushes had potential applications as Schottky barriers in diodes, as well as other metal-insulator type semiconducting devices.

Girolami and Nuzzo published the successful polymerisation of similar norbornene brushes on silicon surfaces, but the tethered alkene was applied to the surface selectively using microcontact printing.\textsuperscript{17,191,192} Selectivity was achieved by protecting some areas of the hydroxylated silicon surface with octadecyltrichlorosilane.

The Jennings group have also successfully performed SI-ROMP of functional norbornenes. They have polymerised alkyl-substituted norbornenes for use as aqueous barriers, but have also shown norbornene brushes to be a good electrical insulation material.\textsuperscript{193} Subsequent sulfonation of the double bonds along the backbone of these hydrophobic films (Scheme 53) reduced the water barrier character and facilitated ion transport through the films.\textsuperscript{22} They have also produced coatings that are simultaneously hydrophobic and lipophobic by polymerising
monomers that have fluorinated alkyl side chains. Zhou and co-workers also made fluorinated brushes with similar barrier properties, but instead attached to titanium nanowires by a bio-mimicking catechol linker.

Scheme 51: Surface-initiated ROMP of norbornene from gold substrates
Polymer brushes grown by SI-ROMP have been applied to a wide range of areas. Buchmeiser et al. have produced poly(norbornene-b-oxanorbornene) type brushes from silica surfaces for use as chromatographic stationary phases. These materials show outstanding ion selectivity and extraordinary pH stability, which also makes them excellent candidates as transition metal sequestration agents (useful for applications such as the treatment of groundwater and radioactive waste disposal).

Applying ROMP to organic electronic applications, Weck has undertaken synthesis of functionalised poly(cyclooctene) polymers for use in organic light-emitting diodes. Facial iridium tris(2-phenylpyridine) (fac-Ir(ppy)₃) and its derivatives has received significant literature interest for their high quantum efficiencies due to the readily-accessible intersystem crossing from the singlet to the triplet excited state. This allows complexes to use both singlet and triplet excitons. Commonly devices containing such moieties suffer from poor processability. Usual production techniques for such devices include high vacuum deposition or being used as a doping agent in polymer matrices. This often results in phase separation and poor device
performance. Weck’s approach to avoid this problem was to incorporate $\text{fac-Ir(ppy}_3\text{)}$ as side chains to a ROMP produced polymer, allowing for simple solution-based production (Scheme 54).\textsuperscript{199–201} Carbazole co-monomers were also incorporated to improve solubility and provide a group that could harvest more light energy before transferring it to the iridium complex.

The copolymers showed good optical properties, the fluorescence spectra (Figure 37) show little difference to untethered $\text{fac-Ir(ppy}_3\text{)}$, and the maximal emission wavelengths do not differ, suggesting that none of the benefits of untethered $\text{fac-Ir(ppy}_3\text{)}$ are lost when tethering to a polymer backbone. Quantum yields (87 - 95% dependent on Ir concentration) and lifetimes (1.2 - 1.4 $\mu$s) are also measured, and are again similar to the $\text{fac-Ir(ppy}_3\text{)}$ reference. This suggests the polymer to be a viable candidate for OLED applications.

Scheme 54: Synthesis of iridium functionalised cyclooctene polymers by ROMP
Figure 37: Fluorescence spectra of iridium copolymers produced by ROMP, containing 20% (5a), 10% (5b) and 5% (5c) iridium

Saunders and Turner synthesised poly(dioctylthiophene-2,5-diyl) (PDOTV) by ROMP (Scheme 55). Molecular weight was well-controlled (average molecular weight 18,500, polydispersity index 1.8) and was used in combination with PCBM to fabricate photovoltaic devices with PCE values of up to 0.18% for films of 100 nm thickness and a PDOTV:PCBM ratio of 1:2. Measurement of the quantum efficiency from the absorption spectra suggested that the efficiency value of the device was limited. Upon inspection of the film morphology by AFM, it was determined that hole-mobility may be limited by an unexpected phase separation within the blend (Figure 38). The results still show the ROMP produced material to be a viable option as a bulk heterojunction in organic photovoltaics.

Scheme 55: Synthesis of PDOTV by ROMP

Figure 38: AFM phase image showing unexpected phase separation of PDOTV:PCBM blend
Examples of SI-ROMP for producing electronic devices are scarce. Grubbs utilised SI-ROMP of norbornene to manufacture the dielectric layer of an organic thin film transistor.\textsuperscript{5} By polymerising poly(norbornene) from a gold electrode, he created a dielectric layer on top of which he then vapour deposited pentacene before adding more gold electrodes as the drain and source. This device is illustrated in Figure 39. The thickness of the dielectric layer was found to be easily controllable, simply by varying the concentration of the norbornene solution up to a maximal concentration of 3 M to achieve a film thickness of 2 μm. Current-voltage characteristics (Figure 40) of the device show good flow of current with increasing voltage between the drain and the source (up to a gate bias of 100 V, where a potential difference of -100 V between the drain and the source yielded a current change of 20 μA), good field-effect mobility (0.1 - 0.3 cm\(^2\) V\(^{-1}\) s\(^{-1}\)) as well as little to no hysteresis, which would indicate minimal charge build-up between the dielectric and semiconductor layers.\textsuperscript{5}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure39.png}
\caption{Construction of FET using SI-ROMP norbornene dielectric layer\textsuperscript{5}}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure40.png}
\caption{Current-voltage characteristics of FET containing SI-ROMP norbornene dielectric. Drain bias swept from 0 to -100V and back at gate biases between 40 and -100V in -20V steps. Inset shows drain current as gate voltage was swept from 40 to -100V and back.\textsuperscript{5}}
\end{figure}
1.3.8. ATRP: Atom Transfer Radical Polymerisation

Atom transfer radical polymerisation, also referred to as metal-catalysed living radical polymerisation,\textsuperscript{45} was independently invented around 1995 by Krzysztof Matyjaszewski\textsuperscript{202} and Mitsuo Sawamoto.\textsuperscript{203} It is a form of controlled radical polymerisation, and is interchangeably referred to as being “pseudo-living”. Control over conventional free-radical polymerisation is notoriously hard to achieve, due its proneness to biradical combination and disproportionation, as previously discussed in Section 1.3.3. Due to the high degree of control available, ATRP is a versatile polymerisation method and is very useful for producing different polymer compositions on surfaces: for example block co-polymers, gradient systems and alternating systems.\textsuperscript{45,58,204}

As is hinted by the name, the atom-transfer step is the most critical in the mechanism of ATRP. Typically, an organic halide is used as the masking group to the polymerisation initiating radical. Polyhalides, e.g. chloroform and carbon tetrachloride, can also be used, as well as weak heteroatom-halide bond containing substrates (i.e. N-X, S-X, O-X). A reversible redox process then generates the polymerisation initiator, and this is catalysed by a transition metal. Matyjaszewski chose copper,\textsuperscript{202} whilst Sawamoto opted for ruthenium.\textsuperscript{203} These transition metals are both suitable; the main requirement is that the metal needs to be able to readily access two oxidation states separated by one electron. The metal also needs to have a good affinity for halogens. Finally, an expandable co-ordination sphere is required to accommodate a pseudo-halogen. A wide range of transition metals fit this billing- molybdenum,\textsuperscript{205} rhenium,\textsuperscript{206} ruthenium,\textsuperscript{207,208} iron\textsuperscript{210,211} and rhodium\textsuperscript{212} have all been used to carry out ATRP. However, Matyjaszewski describes copper\textsuperscript{202,213-216} as the superior metal for catalysts in ATRP, as it is highly versatile and very cost-effective.\textsuperscript{204} The polymerisation initiator forms by electron transfer to the transition metal with simultaneous halogen abstraction, shown in Scheme 56.\textsuperscript{204}

![Scheme 56: Mechanism of ATRP\textsuperscript{204}]

Uses of polymer brushes grown by ATRP for device applications are plentiful. For example, Brittain presented the synthesis of poly(t-butylacrylate brushes) by ATRP which were then deprotected by simply heating to 200 °C to leave poly(acrylic acid) (PAA) brushes. These PAA brushes respond to stimuli such as changes in pH or electrolyte salt concentration (Figure 41). With changes in pH (Figure 42a) and salt (ion) concentration (Figure 42b, c), it can be seen that the thickness of the brushes changes with increases and decreases in these properties.\textsuperscript{217}
In another publication, Locklin and co-workers produced a colorimetric sensor for ions using a spiropyran (SP) functionality to produce photochromic brushes. These ATRP-grown copolymer brushes (Scheme 57) showed selectivity for reversible binding with particular metal ions inferred by intense colour changes and vastly differing UV spectra (Figure 43). They also showed drastic changes in surface wettability when interacting with different metal ions.  

Scheme 57: SI-ATRP of spiropyran methacrylate (SPMA)-co-PMMA brushes

Figure 41: Formation and behaviour of PAA brushes as pH/electrolyte sensors

Figure 42: Plots of PAA brush thickness vs (a) pH of solution, (b) concentration of sodium in solution (NaCl) and (c) concentration of calcium in solution (CaCl₂)
Figure 43: Colour change and UV-Vis spectra of various metals binding with SPMA-co-PMMA brushes\textsuperscript{218}

Spiropyran shows a distinctive change from a colourless closed form to a strongly coloured merocyanine (MC) open form when bound to metallic ions (Scheme 58). This change in geometry also induces a large shift in dipole moment, which for brush films will affect the surface energy and thus the surface wettability. When complexed with Fe\textsuperscript{2+}, these brushes showed a drastic change in contact angle, moving from 104° to 34° when exposed to 365 nm UV radiation. This was then reversed back to 104° by exposing to visible light of a wavelength greater than 560 nm.\textsuperscript{218}

\begin{center}
\begin{tikzpicture}
  \node (1) at (0,0) {\textbf{Scheme 58:} Isomeric structures of spiropyran and two tautomers of the merocyanine.}
  \node (2) at (2,0) {Dimeric metal complex with metal(II) ions is also shown\textsuperscript{218}};
\end{tikzpicture}
\end{center}

Huck and Friend have published a method for producing effective charge-transporting character in polymer brushes produced by ATRP, with a view to application in heterojunction photovoltaic devices.\textsuperscript{219,34} Polyacrylate brushes with triphenylamine (TPA) side groups as hole-transporting components were synthesised (Scheme 59), and show characteristics of high mobility for hole-transport.\textsuperscript{34}
Scheme 59: Synthesis of poly(triphenylamine acrylate) brushes by ATRP

The self-aligning nature of the polymer brushes (caused by the highly sterically hindered environment) creates an ordered structure that allows for effective charge transportation. In this case, hole-transport occurs by hopping between stacked TPA units. This high degree of ordering over spin-coated equivalents shows polymer brushes to be superior performers as charge-transporting layers. A simple sandwich device was fabricated from poly(triphenylamine acrylate) (PTPAA) on ITO (brush form and spin coated), with a PEDOT:PSS n-type layer above, topped with a gold electrode. Current density was measured at various bias voltages, with positive bias corresponding to hole injection from the PEDOT:PSS and negative bias corresponding to hole injection from the ITO. This showed the current density of the brush device to be superior to that of the spin coated device. This data is shown in Figure 44.

Solution processing of a second component, such as a diblock, would be able to provide the electron-transport that would make a good heterojunction device. In this case, the brush network was infiltrated with cadmium selenide nanocrystals (as a n-type semiconductor, applied by spin coating from a pyridine:chloroform solution and annealing at 150 °C for 30 min) to produce a composite with photovoltaic quantum efficiencies up to 50%.
The group of Ye and Zhou have grown brushes of poly(methacrylic acid cadmium) from a graphene surface treated with a macroinitiator by ATRP, before treating with hydrogen sulfide and sodium selenosulfate to yield quantum dot loaded brushes by ion exchange. This is illustrated in Scheme 60. The macroinitiator contains pyrene groups for bonding to the graphene surface and tertiary bromo groups for ATRP initiation. Addition of the quantum dots to the composite showed a significant enhancement in the current density observed in the visible region of the electromagnetic spectrum (between 400 and 600 nm, Figure 45). These brushes provide a good basis for a photovoltaic device.220

Scheme 60: Fabrication of CdS/CdSe brushes grown by ATRP from graphene substrates220

Sirringhaus and Huck produced a thin-film transistor with the polymer dielectric grown from a gold gate electrode by SI-ATRP of methyl methacrylate (MMA) cross-linked with ethylene glycol dimethacrylate (EGDMA). The uniform nature of polymer brushes lead to low surface roughness compared to spun-cast equivalents and showed high electrical capacitance. Fabrication of two low voltage OFETs was possible, using evaporated pentacene and solution deposited P3HT as the semiconducting materials. Key differences that have already been highlighted (in other reviewed works) between spun-cast and surface-initiated brush films were also observed and noted here, with some slight surface roughening noted.

Figure 45: Photocurrent dependence on the wavelength of illuminating monochromatic light of graphene (black), CdS graphene (blue) and CdS/CdSe graphene (red)220
This roughness is caused by the rigidity offered from the inclusion of a cross linker (EGDMA).\textsuperscript{221} At low gate voltages (below 5 V), the device controls the flow of current between the source and the drain well, as can be seen by the plateaus in the voltage-current curves (\textbf{Figure 46}). At higher voltages, this plateau is less prominent, suggesting less control over current resistance. To this effect, the PMMA-pentacene combination (\textbf{Figure 46a}) works more effectively than the PMMA-P3HT pairing (\textbf{Figure 46b}).

\textbf{Figure 46:} Current-voltage characteristics of OFET containing SI-ATRP PMMA dielectric and \textbf{(a)} pentacene or \textbf{(b)} P3HT semiconductor layers. Drain bias swept from 0 to -6V and back at gate biases between 0 and -6V in -1V steps.

With a lot of attention on green chemistry, and efforts to make reactions more environmentally friendly, it was identified that ATRP uses high loadings of copper (or alternative transition metals) and thus risked becoming an unattractive option to many chemists. To counteract this potential problem, ARGET-ATRP was evolved from traditional ATRP.\textsuperscript{222–225} Instead of using a high loading of copper(I) salts an excess of cheaper and more environmentally friendly reducing agents, such as ascorbic acid, were added to reaction mixtures to reduce the oxidised salt [i.e. Cu(II) or Ru(III)] to the active (reduced) form [i.e. Cu(I) or Ru(II)]. This is outlined in \textbf{Scheme 61}, with a more detailed mechanism shown in \textbf{Scheme 62}. This reduced copper(I) levels vastly, down to the parts per million (ppm) scale.\textsuperscript{223,224}

\textbf{Scheme 61:} Basic concept of ARGET-ATRP using copper as an example
As an added advantage, ATRP previously required the chemist to be very cautious of oxygen. Small quantities of oxygen were capable of terminating the polymerisation early by trapping propagating radicals. Thus, stringent deoxygenation and inert atmospheres were previously required. With ARGET-ATRP, the reducing agent is able to buffer the reaction mixture against small ingresses of oxygen. As a result, polymerisation by ARGET-ATRP is far more robust than traditional ATRP. Although thorough deoxygenation is less important with ARGET-ATRP, it is still advisable to deoxygenate as good practice, because this will increase the lifetime of the polymerisation solution. This excess of reducing agent has been shown to accelerate polymer growth slightly, but does not interfere with the good control over molecular weight and polydispersity exhibited by ATRP.

The Matyjaszewski group published the first example of ARGET-ATRP when they synthesised poly(n-butyl acrylate) brushes and poly(n-butylacrylate)-block-poly(styrene) copolymer brushes. Research into brushes grown by surface initiated ARGET-ATRP is less popular than traditional ATRP and solution ARGET based research, but the area is growing. In addition, simple PMMA brushes have been grown using ARGET-ATRP on a variety of substrates to demonstrate the versatility of the technique. These range through silicon wafers, high surface area porous silica, and imogolite nanotubes (an aluminosilicate clay). Since then, polymers with reactive functional groups (which are prime candidates for post-modification) such as amines (PDMAEMA), epoxides (PGMA) and hydroxyl groups (PHEMA) have also been prepared by ARGET-ATRP. Compared to traditional ATRP, it can be seen that far fewer people are using ARGET-ATRP. Reported post-functionalisation of ARGET synthesised brushes are discussed by Zong et al., when they graft poly(acrylonitrile) and cross-link it with N-chlorosulfonamidated polystyrene, using the resulting resin in mercury removal. Other examples of post modified ARGET synthesised brushes are scarce.
1.3.9. RAFT: Reversible Addition-Fragmentation Chain Transfer Polymerisation

Reversible addition-fragmentation chain transfer polymerisation was first reported and acronymised as RAFT polymerisation in 1998 by Moad, Rizzardo and Thang. Using a range of acrylates and methacrylates with dithioester chain transfer agents, they produced a range of polymers with a low polydispersity index (1.04-1.29).\textsuperscript{238}

RAFT is advantageous over other techniques as it can be carried out in a wide range of solvents (including water), it can be carried out at a wide range of temperatures, it is tolerant of many functional groups, and unlike ATRP there are no metals involved in the polymerisation. However, disadvantages include RAFT agents being specifically tuned to particular monomers and are therefore not universal, and the requirement for consuming and labour-intensive multi-step synthesis of RAFT agents. RAFT agents are also particularly unstable over long periods and are prone to decomposition into smaller, more pungent thio compounds. They are also highly coloured so even small traces remaining in polymers can have a marked effect on the overall colour of the product.\textsuperscript{15,239}

Mechanistically, RAFT is initiated by conventional free radical initiators such as AIBN (azobisisobutyronitrile), and then controlled by dithioester chain transfer agents. This means that in theory, established free-radical polymerisations can be converted into controlled polymerisations simply by adding the appropriate RAFT agent. The “reversible addition-fragmentation” chain transfer implied by the name is a series of equilibria involving the addition and fragmentation of various adducts with the sulfur-based RAFT reagent. This is outlined in Scheme 63.\textsuperscript{240}
In more detail, the mechanism will start with initiation. This is the generation of a radical species, usually by traditional decomposition methods (e.g. heating) of azo or peroxide compounds such as AIBN, benzoyl peroxide etc. These decomposition radicals will then combine with a monomer to form a single repeat unit propagating species, i.e. $P_n$, $n=1$. Propagation can proceed as “normal” here, with monomers adding to the propagating species to create a new propagating species that is $n+1$ units in length. This polymeric propagating species can then react with the RAFT agent to form a RAFT adduct (chain transfer step). This unstable species may then fragment in either the reverse direction to return the polymeric propagation species and the RAFT agent, or it may fragment in the forward direction to yield a polymeric RAFT species and a new radical species. This new radical species can act in the same way as an initiator, initiating a new polymer chain. This is intuitively named the re-initiation phase.

At this point, the chain equilibration equilibrium is introduced. Similar to the chain transfer step, it involves a polymeric propagating species. However this time, the propagating species adducts with the polymeric RAFT agent formed previously. This again may fragment in either the reverse direction to return the polymeric propagation species and the polymeric RAFT agent, or it may fragment in the forward direction to yield a new polymeric RAFT species and the polymeric radical species. This process of radical interchange is fast, and allows all radical propagation species that have not been terminated to share an equal rate of propagation. In
order to remain living (or pseudo-living), termination reactions such as biradical combination are suppressed by creating a sufficiently hindered RAFT adduct.\textsuperscript{240}

Choice of the RAFT agent is critical. It is important that it is paired correctly with the monomer to be polymerised, as RAFT agents are generally not universal. The chain transfer activity of the RAFT agent is largely controlled by the activating group (Z) and the relative lability and radical stabilising abilities of the R group (Figure 47). The Z group must be activating of the double bond for radical addition, but not be so stabilising of the intermediate radical that it ends up hindering the propagation of the polymerisation. The R group should be a good leaving group relative to the propagating radical, and be able to reinitiate polymerisation of the monomer when radicalised.\textsuperscript{238,240}

![Free radical leaving group, R* (must be able to re-initiate polymerisation)](image)

![Reactive C-S double bond](image)

![Weak C-S bond](image)

![Z-group control the reactivity of the C=S bond, influences the rate of radical addition and fragmentation](image)

**Figure 47:** Requirements when designing RAFT agents\textsuperscript{57}

Thermal initiator selection is also an important consideration when carrying out RAFT polymerisations. In order to maintain a high degree of control over the polymerisation, a high ratio of the RAFT agent to initiator should be utilised. This will maintain a constantly low level of radical species. The less initiating radicals present, the greater the element of control, as propagation will be slowed (as before, fast initiation and slow propagation result in control). An initiator with a longer half-life at the required reaction temperature is favourable as this feed stock of radicals will keep the polymerisation alive for longer.\textsuperscript{57}

Polymers produced by RAFT and used for optoelectronic application have been widely reported, as shown by a comprehensive review article of over 200 examples compiled by Moad, Rizzardo and Thang in 2011.\textsuperscript{241} Grafted from examples primarily follow two basic approaches. The first approach is the same as the other surface-bound techniques covered thus far; it involves attaching the radical-generating species to the surface, and the RAFT agent being free in solution with the monomer(s). The second approach is the reverse of this, having a RAFT agent tethered to the surface and having free initiator in solution. This second approach also has two further options within – whether the RAFT agent is tethered to the surface by the "R" substituent or the "Z" substituent. These two tethered RAFT agent approaches are shown in Scheme 64.\textsuperscript{241}
Having “R” bound to the surface is known as the “away from” process. The “away from” technique is advantageous because the propagating radicals are never directly attached to the surface. Any termination that occurs due to biradical combination will result in a by-product that is not confined to the surface and can be simply washed away, making it difficult to terminate the surface directly. The dithioate functionality remains attached to the surface throughout. As conversion increases, steric hindrance of the propagating radical by the surface-bound RAFT agent can become an issue, especially at high conversion. This effectively limits the thickness of film accessible by this method. Another disadvantage here is that any reaction that breaks down the dithioate functionality (such as thermolysis or hydrolysis) will thus cleave the brushes from the surface. “Z” attachment, known as “attached to”, allows propagation species to remain attached to surface and the unstable dithioate species to be at the chain end, limiting any damage should any decomposition occur.\textsuperscript{241}

\subsection{1.3.10. NMP: Nitrooxide Mediated Polymerisation}

Nitroxide Mediated Polymerisation was first reported by Solomon, Rizzardo and Cacioli in a patent filed in the United States in 1984 (published 1986).\textsuperscript{242} They reported the polymerisation of a range of acrylates and methacrylates using various nitroxides as a reversible radical-masking group at the active end of polymer chains. The predominant basis of NMP is similar to that of ATRP, in that it relies upon the reversible activation and deactivation of the chain ends, in this case masked by a nitrooxide radical.\textsuperscript{243–248}
Although initially NMP was limited to a narrow class of monomers, the development of new nitroxides (and alkoxyamines) has allowed NMP to be a more-widely applicable method (although still with limitations). With NMP, the nitroxide or alkoxyamine is the only component of the catalysis system. This makes it favourable over multi-component systems such as ATRP (copper source, ligand, alkyl halide initiator) and RAFT (thermal initiator, RAFT agent) as its simplicity presents far fewer variables that require adjustment. To this end, the application does not require any specialist knowledge for optimisation. NMP is widely considered the least technically challenging of the CRP methods. The system is also more “green” than ATRP as it is metal-free. Simple nitroxides are readily available on an industrial scale which makes NMP mediators an attractive option over laboratory scale RAFT agents. The main drawback of NMP is the limitations on monomers that can be used – less activated monomers such as vinyl acetate, vinyl chloride and N-vinylpyrrolidone all present significant synthetic challenges when attempting to polymerise by NMP.

The mechanism of NMP was not fully explained until Fischer\textsuperscript{250} and Fukada\textsuperscript{251} explained how the termination reactions (as with all CRP techniques) were suppressed. This was explained by the persistent radical effect (PRE). The PRE is illustrated by Scheme 65 and Figure 48.

\begin{equation}
\begin{align*}
R - Y & \xrightarrow{k_d} R^\cdot + Y^\cdot \\
R^\cdot + Y^\cdot & \xrightarrow{k_c} R - Y \\
R^\cdot + R^\cdot & \xrightarrow{k_l} R - R
\end{align*}
\end{equation}

\textbf{Scheme 65: Formation of persistent radicals}\textsuperscript{249}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{persistent_radicals.png}
\caption{Percentage of original concentration of RY, R\textsuperscript{\cdot} and Y\textsuperscript{\cdot} over time during persistent radical formation\textsuperscript{249}}
\end{figure}

\textbf{Scheme 65} depicts a compound (RY) decomposing into radicals. It decomposes into a transient (R\textsuperscript{\cdot}) radical and a persistent (Y\textsuperscript{\cdot}) radical. \textbf{Figure 48} illustrates that from a concentration of zero, as these radicals form concentration increases linearly controlled by the decomposition coefficient \(k_d\). This continues until the concentration of radicals becomes sufficiently large enough that the possibility of biradical combination becomes greater than the predominant factor. Biradical combination of two transient (R\textsuperscript{\cdot}) radicals results in the
accumulation of the persistent (Y) radicals. The persistent radicals cannot self-combine and terminate, leading to either biradical combination of transient radicals (R-R), or return of the starting material when a transient and persistent radical combine (R-Y). This eventually leads to the concentration of transient radicals dropping to zero, leaving only non-combinable persistent radicals. The persistent radical then acts as the initiator and propagates the monomer. Polymerisation then proceeds similarly to ATRP (i.e. deactivation favoured over activation), shown in Scheme 66. Typically, the activation equilibrium is reached by raising the temperature, and the polymerisation is deactivated by cooling.249

Surface-initiated NMP has typically been studied on silicon wafers and silica particles, so various nitroxides have been linked to the surface through a typical trialkoxysilane or trichlorosilane tether. Many reports of various alkene brushes have been made, but the most common examples are styrene brushes.249 Devices for opto-electric applications such as OLEDs252-257 and photovoltaic cells258-260 have been reported using polymers produced by NMP. However, upon searching the literature, no examples of SI-NMP brushes being used for opto-electric devices could be found.

1.4. Project standing and rationale

In the grand scheme, as can be seen from the literature review undertaken here, there are still plenty of niche areas of the polymer brush research field that are relatively unexploited. In the field of electronic devices, it can clearly be seen that most of the work in KCTP has been carried out with alkyl substituted thiophene monomers, so more heavily substituted monomers would be unique here. With regard to ROMP, work with monomers other than cyclooctadiene and norbornene is scarce, presenting opportunities for unique monomers to be used in brushes for device application. Little work has been carried out using the newer ARGET-ATRP to produce electroactive brushes, so this area could also be targeted.

![Scheme 66: The mechanism of nitroxide mediated polymerisation (NMP)](image_url)
Chapter 2: Isocyanide (isonitrile) monomers for the synthesis of poly(isocyanide)s and poly(quinoxaline-2,3-diyl)s

The aim of this research project was to produce a polymer brush system with a view to an application in an electronic semiconducting device. As such, a conjugated system would be a major advantage, as conjugation provides conductance, as electrons (or positive charges) can move up and down the molecular backbone. Such products could then be used in applications such as those aforementioned in Chapter 1. Also, growing brushes (as opposed to deposition of a pre-grown polymer) will provide a direct conduction pathway from the surface to the polymer. The poly(isocyanide) and poly(quinoxaline) suggested in Scheme 67 would make good polymer brushes due to their inherently conjugated backbone.\textsuperscript{261,262} Due to the steric crowding of the phenyl groups,\textsuperscript{263} and restricted rotation about the carbon-carbon bonds in the backbone (known as atropisomerism),\textsuperscript{264} poly(isocyanide)s and poly(quinoxaline)s will grow in a helical manner, therefore standing upright and allowing for good grafting density and brush lengths on substrates. This helical structure is exceptionally robust, and will remain intact even in harsh conditions (such as being at elevated temperatures for several days\textsuperscript{265}). Any side-chain functionality that is introduced will be spatially-fixed and well-ordered due to the inherent stiffness and rigidity of the helix.\textsuperscript{262}
Chapter 2: Isocyanide (isonitrile) monomers for the synthesis of poly(isocyanide)s and poly(quinoxaline-2,3-diyl)s

Scheme 67: Common synthetic approach to poly(quinoxaline)s (top) and poly(isocyanide) s (bottom)

A simple three step synthesis from commercially available o-phenylenediamine was proposed. The bis(amine) would be formylated using formic acid, with EDCI as a coupling agent. EDCI is a carbodiimide that is commonly used in peptide chemistry for the activation of carboxyl groups before coupling with amines to form amide linkages. The amide would be dehydrated using trichloromethyl chloroformate to yield the isocyanide monomer, before being polymerised by nickel (or palladium) catalysis. This chapter describes the efforts made to try and synthesise the isocyanide monomers for the intended polymerisation.

2.1. Formylation of amines

Previous work within the Christie group had determined an optimised procedure for the formylation of o-phenylenediamine (Scheme 68). Formic acid (6 eq.) was used as the formylating agent, N-methylmorpholine (3 eq.) was used as a base and EDCI (3 eq.) was used as a coupling agent. EDCI was preferred as a coupling agent to reagents such as DCC, as the aminopropyl group of EDCI is easily quaternised during an acidic workup, and the resulting salt becomes water soluble and is therefore simple to wash away in aqueous media. DCC and analogues do not have such functionality and cannot afford such a luxury, and are notoriously difficult to remove from a reaction mixture. Due to the absence of such an amino group, they cannot be simply washed away in water.

Scheme 68: Formylation of o-phenylenediamine
The reaction proceeds with the formic acid being activated by the EDCI, then the lone pair of the nitrogen on the substrate amine will attack the carbonyl of the formic acid, and EDCI is eliminated as a urea (Scheme 69).

Scheme 69: Mechanism of EDCI formylation coupling

The procedure gave the product once in 30% yield, however reproducibility issues and the cost of using three equivalents of EDCI (1 g = £24.80\textsuperscript{271}, 1 mmol = £5.10) made the procedure less appealing. The three equivalents are required to drive the reaction to completion; the EDCI is not used catalytically, it is consumed and not recycled by the reaction. The low yield and irreproducibility problems indicate that there may be an issue with the ortho-substituted nature of the o-phenylenediamine. It is postulated that perhaps an intramolecular attack of the first amide formed by the remaining amine could be occurring, and is being favoured over the intermolecular conversion of the second amine to an amide (Scheme 70). There is no literature precedent for such a ring closing reaction, but it would be favoured in accordance with Baldwin's rules.\textsuperscript{272} 1H NMR data of the crude reaction product showed sharp singlets at 8.21 ppm (N-H) and 3.69 ppm (NH-CH-NH), and a broad singlet at 3.40 ppm (OH). This is suggestive that the ring closed product forms to some degree. The procedure also failed when trying to use aniline as the substrate.

Scheme 70: Proposed ortho-substitution problem with o-phenylenediamine

An alternative procedure was attempted using the work of Shekhar et al.,\textsuperscript{273} in which a Lewis acid was used as a catalyst for the coupling of the amine and formic acid (Scheme 71). It was hoped that this would improve both the yield and reproducibility of the synthesis. The paper cites good to excellent yields for aromatic compounds, including aniline (96%). However, it does not mention any attempt at reacting bis(amines) under these conditions. The work was reproduced for aniline with comparable results to the publication (90% yield), but no product
was formed when attempting the work with ω-phenylenediamine, furthering the belief that the lack of reactivity is caused by the 1,2- substitution pattern and enforced close proximity of the two amine groups, as previously suggested.

Scheme 71: Formylation of amines using zinc(II) chloride as a Lewis acid catalyst

2.2. Dehydration of formamides

Dehydration of the previously synthesised formamide \( N,N'-(1,2\text{-phenylene})\text{diformamide} \) (the latter obtained only once as production was not reproducible, as discussed previously) and commercially available \( N\text{-phenylformamide} \) were initially attempted using trichloromethyl chloroformate (diphosgene). Although a powerful dehydrating agent, diphosgene breaks down into two molecules of phosgene, which is a highly toxic gas (renowned for its use in chemical warfare), so a safer reagent was also sought. Phosphorus(V) oxychloride was also used on \( N\text{-phenylformamide} \) with success. The dehydration of \( N\text{-phenylformamide} \) and \( N,N'-(1,2\text{-phenylene})\text{diformamide} \) using both reagents (diphosgene and \( \text{POCl}_3 \) ) were somewhat successful, as the aryl isocyanide FTIR peak (2150-2110 cm\(^{-1}\)) and the distinctively foul smell of the isocyanide functionality were both present in the crude products, but the \(^1\text{H} \text{NMR} \) spectra showed a complex mixture of inseparable products. As the mixture was unable to be purified, no quantitative yield can be given.

Purification of these products proved problematic, as a 2D-TLC on both silica and alumina gels indicated that they are not stable to chromatographic manipulation. A 2D-TLC (Figure 49) is firstly run as a normal TLC (\( a, b \)). Once complete, the plate is removed and dried. The plate is then rotated through 90° (\( c \)) so that the previous separation now acts as the base spotting for a new TLC. Using the same solvent ratio, this second TLC is run under the same conditions as the first (\( d \)). At the conclusion, if the R\(_f\) values of the spotted compounds do not match for the two tests, then it is inferred that the TLC process imparts some form of chemical change on the
compound (if not, the \( R_f \) values should match, as the compounds are identical). This can be visualised easily by drawing a line from the origin of the two baselines to the intercept of the solvent fronts (e). Any spot with matching \( R_f \) values should then fall on this line. For the compounds in question, the spots formed a curve below this line, suggesting that they were binding with the silica.

**Figure 49:** Procedure for running a 2D-TLC to determine compound stability on silica

Distillation also caused problems, as isocyanides are highly sensitive to thermal energy; small amounts of heat lead to the formation of trimers and tetramers (Figure 50).

**Figure 50:** Trimer (left) and tetramer (right) of isocyanobenzene

In addition, the presence of water can also drive the reverse of the dehydration reaction, causing the isocyanide to revert back to the formamide from which it was formed, shown in Scheme 72. In a 2009 publication, Fernández-Bolaños claimed that isocyanides are “non-isolated intermediates”. By definition, an intermediate can be isolated (but a
transition state cannot be isolated), so in this instance we infer that the isocyanides produced are either a high-energy, disfavoured transition state involved in the formation of the compounds shown Figure 50, or they are simply too reactive and even small amounts of water are ample enough to quench them (Scheme 72). However, some isocyanides have been isolated in the literature.281

\[
\begin{align*}
\text{R-N=C} & \quad \text{R-N=C} : \\
\xrightarrow{\text{H}_2\text{O}} & \quad \text{R-N=O} \\
\end{align*}
\]

Scheme 72: Water quenching of isocyanides

Before dismissing isocyanides as a viable route to conjugated polymers, one final avenue was also exhausted. It was felt that a cleaner synthesis without the need for purification was necessary as purification was not a plausible option. A microwave-assisted synthesis using cyanuric chloride published by Porcheddu and co-workers282 was attempted (Scheme 73). A short microwave reaction time (3 min) was hoped to reduce side reactions by accelerating the main reaction, allowing the desired product to form before the accumulation of any unwanted by-products. Also, it was hoped that the intense thermal energy provided by the microwaves would drive the reaction to completion before the formation of the undesirable side products. The paper states that the order of addition of the reagents is important (firstly triethylamine, then dichloromethane, and finally cyanuric chloride), so this was adhered to. However neither product could be formed and the reaction simply returned starting materials in both cases. The paper also suggests the unwanted products can be easily washed away with saturated potassium hydrogen sulfate, but this also proved unsuccessful.

\[
\text{R-N=C} \xrightarrow{\text{NEt}_3} \quad \text{N-N=Cl} \xrightarrow{\text{HN}} \quad \text{N-N=Cl} \xrightarrow{\text{NEt}_3} \\
\]

Scheme 73: Microwave assisted dehydration of formamides using cyanuric chloride
Chapter 2: Isocyanide (isonitrile) monomers for the synthesis of poly(isocyanide)s and poly(quinoxaline-2,3-diyl)s

2.3. Phase transfer Hofmann carbamylamine reactions

To attempt to eliminate the unreliable EDCI coupling method for producing formamides, and the low yielding dehydration methods attempted, a phase transfer Hofmann carbamylamine reaction was proposed. If successful, this preparation would be advantageous as not only does it eliminate a step, but all of the reagents are relatively cheap and readily available compared to the EDCI coupling method. Following Gokel, Widera and Weber’s method for aniline (Scheme 74), the isocyanide had again been made, but purification and isolation was once more a problem. The paper suggests using a spinning band column for purification, but this was not possible (the spinning-band equipment was not readily available). Instead, attempts were made to try and increase the conversion and yield of the reaction, summarised in Table 4.

Scheme 74: Hofmann carbamylamine reaction of aniline

Table 4: Attempts to optimise Hofmann carbamylamine reaction of aniline

<table>
<thead>
<tr>
<th>Entry</th>
<th>Eq. aniline</th>
<th>Eq. \text{CHCl}_3</th>
<th>Eq. NaOH</th>
<th>Mol% cat.</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.5</td>
<td>1</td>
<td>7.5</td>
<td>0.5</td>
<td>Impure (complex mixture of products unresolved by $^1$H NMR analysis), decomposed on attempted purification</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>6</td>
<td>8</td>
<td>0.5</td>
<td>Still unresolved by $^1$H NMR.</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>17.5*</td>
<td>8</td>
<td>0.5</td>
<td>Still unresolved by $^1$H NMR.</td>
</tr>
</tbody>
</table>

*Entry 3 shows the effect of removing dichloromethane from the reaction, as it was thought that it may compete with the chloroform in the carbene formation step.

All three entries yielded a viscous black oily product, which would suggest some form of oligomerisation (i.e. trimers and tetramers; as previously discussed). The TLC plate showed a continuous streak of spots, with several spots overlapping. 2D TLC suggested that the product
formed would be unstable on silica, so column chromatography was not a viable purification option. $^1$H and $^{13}$C NMR of the crude mixture showed two distinct aromatic compounds, but attempts to purify returned spectra that suggested loss of the isonitrile functional group (peak at 164.2 ppm in the $^{13}$C NMR spectra no longer present, paired with the loss of the distinct isonitrile odour). Infra-red spectra of the crude material gave a peak at 2128 cm$^{-1}$, characteristic of the isonitrile functionality.

Attempts at this reaction were also made using o-phenylenediamine, summarised in Table 5. However, once again all efforts yielded the product, but within a complex and inseparable mixture of other products. Identical characterisation and observations to the results discussed in the previous paragraph apply here. As stated before, these are presumably oligomers and degradation products.

| Table 5: Attempts to optimise Hofmann carbamylamine reaction of o-phenylenediamine |
|---|---|---|---|---|---|
| Entry | Eq. o-phe. | Eq. CHCl$_3$ | Eq. NaOH | Mol% cat. | Result |
| 1 | 1 | 1 | 7.5 | 1.5 | Complex mixture of products, unresolved by $^1$H NMR, decomposed on purification |
| 2 | 1 | 3.5 | 1.6 | 1.5 | Still unresolved by $^1$H NMR. |
| 3 | 1 | 3.5 | 3.5 | 1.5 | Still unresolved by $^1$H NMR. |

It was also noted that using potassium hydrogen sulfate during workup was a good way of washing away any leftover aniline, however this did not seem to work for the o-phenylenediamine. Attempts to react the o-phenylenediamine under the conditions in entry 3 twice with a KHSO$_4$ wash in between reactions did not yield any significant results. The reaction was also tried under the conditions of entry 3 using p-phenylenediamine, but this also leads to an unresolved complex mixture of products when analysed by $^1$H NMR. It could merely be said that some conversion was achieved, as this could be proved qualitatively by IR spectroscopy and the nauseating smell of isocyanides, but quantification of the conversion was not possible. This still leaves the previous problems with the ortho-substitution pattern as a possible failing of this reaction.

2.4. Future work towards the poly(isocyanide) system

On the whole, work on the poly(quinoxaline-2,3-diyl) and poly(isocyanide) systems has been reduced significantly in priority, due to the unlikelihood of being able to solve the described
oligomerisation problems. However, one possible avenue for the synthesis of the formamide precursors would be via the use of a mixed formic anhydride as the formylating agent. This would be a viable solution, given the cost of EDCI and limited success of the current methods. The theory is to have an anhydride with a formate group and a bulky, sterically hindered group (e.g. tert-butyl, Scheme 75), which would promote attack of the formate carbonyl. The use of a tert-butyl group also helps aid attack of the formate group in the mixed anhydride as it is inductively a weak electron-donating group, negating the $\delta^+$ charge of the neighbouring carbonyl group.

Scheme 75: Proposed mechanism for mixed anhydride approach

A paper by Fife and Zhang suggests synthesis of such reagents using poly(vinyl 4-pyridine N-oxide) as a catalyst (Scheme 76). According to the publication, 4-methoxybenzoyl chloride and cinnamoyl chloride are good starting reagents. Both yield a solid anhydride product and are therefore considered more stable, and both are claimed to be good formylating agents as both functionalities are quite sterically bulky.

Scheme 76: Proposed synthesis of mixed formic anhydrides

2.5. Conclusions

Five synthetic routes towards the preparation of the required monomers for the creation of poly(phenyl isocyanide) and poly(quinoxaline-2,3-diyl) were exhausted. EDCI-assisted formylation couplings of amines to form amides were unreliable and irreproducible. Lewis acid catalysed synthesis of the amide was not compatible with 1,2-phenylamines, but was very successful with unsubstituted aniline. Dehydration reactions of the resulting amides were qualitatively successful but purification was not possible due to the inherent instability of the monomer. Phase-transfer Hofmann carbamidine reactions were attempted with some success, but again with no ability to isolate the required product. It was concluded that although the
desired monomers were quite clearly forming in all the reactions utilised, their isolation and purification proved an insurmountable obstacle.
Chapter 3: Poly(thiophene) substrates by Surface-Initiated Kumada Catalyst-Transfer Polymerisation (SI-KCTP)

A recent area of considerable activity in polymer research, both in solution and confined to surfaces, is Kumada Catalyst-Transfer Polymerisation (KCTP).\textsuperscript{116–118,120,121,122} In light of the oligomerisation problems associated with the isocyanides discussed previously, attempts were undertaken to synthesise conjugated polymers via KCTP. Grignard reagents are used as monomers in KCTP, so several approaches towards the synthesis of useful 2,5-substituted halothiophene-Grignard monomers were undertaken. These would be used to create poly(thiophene)s, which are useful polymers as they are conjugated (they have overlapping π orbitals) in their normal state. Poly(thiophene) conductivity can be increased by doping either by oxidation (p-doping, typically using iodine, \textbf{Scheme 77}) or reduction (n-doping, although this is uncommon).\textsuperscript{125}

\textbf{Scheme 77:} p-doping of poly(thiophene)

3.1. Synthesis of Grignard type monomers

Four methods towards the synthesis of the desired thiophene monomer have been attempted (\textbf{Scheme 78}). \textbf{Method 1} is derived from the paper by Locklin and coworkers,\textsuperscript{116} whereby the MgCl group on the isopropyl Grignard reagent will exchange with one of the iodine atoms on
the 2,5-diiodothiophene. **Methods 2, 3 and 4** all use elemental magnesium to try and form the related magnesium iodide. **Method 2** uses only magnesium tunings with no additives to serve as a control reaction. **Method 3** uses 1,2-dibromoethane as an activator for the magnesium. **Method 4** utilises elemental iodine as the activating agent. **Methods 2, 3 and 4** try to form the Grignard by inserting into one of the C-I bonds of the diiodothiophene. An aldehyde was then used to attempt to trap the Grignard species, by forming a secondary alcohol. 4-Methoxybenzaldehyde for **Methods 1-3** and isobutyraldehyde for **Method 4** were used as the first aldehydes to come to hand at the time, and both are easily identifiable by \(^1\)H NMR. The results of these attempts are summarised in **Table 6**. 2,5-Diiodothiophene was retained as the reagent for two reasons. Firstly, the work of Locklin used 2,5-diiodothiophene so it had been shown to work. Secondly, although more expensive than its bromo- and chloro- analogues, the iodide's large ionic radius makes it a much more labile halogen than bromide and chloride. This in theory should make thiophene more reactive and the Grignard reagents easier to attain.

![Scheme 78: Synthetic routes towards thiophene-Grignard reagents](image)

**Table 6**: Synthetic routes to (5-iodothien-2-yl)magnesium iodide

<table>
<thead>
<tr>
<th>Entry</th>
<th>Method</th>
<th>Temp</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>50 °C</td>
<td>No conversion; starting materials recovered</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>Reflux</td>
<td>Complex mixture; Aldehyde remaining in (^1)H NMR spectrum</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>50 °C</td>
<td>No conversion; starting materials recovered</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>Reflux</td>
<td>Complex mixture; Aldehyde remaining in (^1)H NMR spectrum</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>Reflux</td>
<td>Complex mixture; Aldehyde remaining in (^1)H NMR spectrum</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>Reflux</td>
<td><strong>Aldehyde consumed</strong>; no peak observed in (^1)H NMR spectrum</td>
</tr>
</tbody>
</table>

The proposed Grignard-halogen exchange reaction (**Method 1**)\(^{116}\) seemed very stubborn, reflected by the results of experimental entries 1 and 2. Even at reflux (Entry 2) there was still aldehyde remaining and no obvious conversion to alcohol after 16 h (inferred from a lack of...
indicative peaks in $^1$H NMR and IR spectra, the absence of a unique spot on TLC). Experiment entries 3 and 4 serve as control experiments, showing that un-activated magnesium turnings alone did not yield the Grignard reagent, i.e. some form of activating agent was required when adopting this approach. The use of 1,2-dibromoethane leads to low conversions, suggesting that Method 3 proved unsuccessful. It is suspected that the presence of two halogens on the 2,5-diodothiophene made it very hard to drive the Grignard formation reaction to completion. However, this has been achieved in the literature. Ideally, for a mono-substituted thiophene, an excess of the magnesium source would be used, but in this case it risked attacking both iodine atoms of the 2,5-diodothiophene.

The change of aldehyde in Method 4 was not deemed relevant, as the purpose of these experiments was to obtain a qualitative result, testing for the presence of the Grignard reagent, as opposed to a quantitative yield. Yield was a secondary consideration here as only a small amount of monomer (the Grignard reagent) is required to facilitate polymerisation of brushes, as the concentrations involved are miniscule. The success of experimental entry 6 shows that elemental iodine acted as the best activator in this reaction set, and suggests that this method would successfully produce the (5-iodothiophen-2-yl)magnesium iodide KCTP monomer.

### 3.2. Pre-polymerisation functionalisation of substrate surface

Substrates were prepared based on the work of Locklin and co-workers. Silicon wafers were subsequently prepared for surface modification as outlined in Scheme 79.
Chapter 3: Poly(thiophene) substrates by Surface-Initiated Kumada Catalyst-Transfer Polymerisation (SI-KCTP)

Before any chemistry could proceed on the silicon surface, it needed to be first cleaned of grease and contaminants and rendered hydrophilic. An RCA-SC-1 clean was utilised. RCA cleaning is commonplace in this field of work, and was developed in 1965 by Werner Kern whilst working for the Radio Corporation of America (RCA). RCA-SC-1 cleaning uses an aqueous solution of concentrated (35% wt.) ammonia and hydrogen peroxide (30% w/w), diluted with distilled water (1:1:5 v/v/v respectively) at 75 °C for 15 min. This removes any contaminants from the surface and also removes the thin native oxide layer on the silicon, to create a layer of hydroxyl groups, making the surface active. Although this is a common technique, it is not the only cleaning technique available. Other solution-based cleans include “Piranha” and aqueous hydrofluoric acid “etch” cleans or dry techniques such as UV-Ozone cleaning (exposing the wafer to an atmosphere of ozone generated by UV light inside a UV-Ozone photoreactor).

A self-assembled monolayer (SAM) of the desired functionality was next deposited to tailor the surface to the specific chemical needs of the experiment. In this case a primary amine group was required for the subsequent condensation reaction with the acyl chloride group on the initiator molecule. The most common deposition technique (for silicon wafers) is to use the equivalent trialkoxysilane or trichlorosilane of the desired functionality and deposit either by forming a vapour under vacuum and then annealing, or by immersion in a solution of organic solvent with a small concentration of the silane. Different types of substrate have different surface chemistries, and therefore use different types of molecule for assembling monolayers. For example, gold substrates do not use silanes, but are instead prepared with
Chapter 3: Poly(thiophene) substrates by Surface-Initiated Kumada Catalyst-Transfer Polymerisation (SI-KCTP)

thiol-based monolayers.\textsuperscript{5,118,301,302} The silane undergoes a condensation reaction with the silanol groups at the surface, eliminating the equivalent alcohol of the alkoxy groups (or hydrochloric acid when using trichlorosilanes) and creates Si-O-Si linkages, tethering the required functionality to the substrate. For this experiment, vapour deposition of (3-aminopropyl)triethoxysilane was opted for, using either a vacuum desiccator (min. 6-7 mbar) or a purpose built vacuum oven (min. 1-2 mbar).

Next, a condensation reaction with the terminal amine introduced the phenyl bromide initiator, and the substrate was ready for surface-initiated polymerisation. The hydrophobicity of samples increased as more organic matter is added, and washing the wafer with water and observing the contact angle (Figure 51) was used as a simple and rapid indication as to whether this series of reactions had been successful or not. Measured contact angles for each stage are shown in Table 7, and as can be seen there is a change between each step, suggesting that some form of surface modification has occurred.

![Hydrophilic and Hydrophobic Contact Angles](image)

**Figure 51:** Using contact angle measurements to indicate the hydrophobicity of a sample

**Table 7:** Static contact angle measurements of silicon wafers functionalised for SI-KCTP

<table>
<thead>
<tr>
<th>Entry</th>
<th>Stage</th>
<th>Static contact angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Native Si</td>
<td>45°</td>
</tr>
<tr>
<td>2</td>
<td>UV/ O\textsubscript{3} cleaned</td>
<td>7°</td>
</tr>
<tr>
<td>3</td>
<td>APTES</td>
<td>58°</td>
</tr>
<tr>
<td>4</td>
<td>Bromobenzyl initiator</td>
<td>76°</td>
</tr>
</tbody>
</table>

### 3.3. Attempts at KCTP from functionalised surfaces

Samples functionalised with the bromobenzyl monolayer were initiated with bis(1,5-cyclooctadiene)nickel(0) and triphenylphosphine, before being introduced to the monomer solution (Scheme 80).
Scheme 80: KCTP of (5-iodothiophen-2-yl)magnesium halides
Attempts to grow these polymer brushes using the nickel(0) catalyst and the Grignard monomer shown in Scheme 80 proved unsuccessful. Whilst producing a brush thickness of 156 nm, coverage was very heterogeneous, and when modelled as a rough surface layer (comprising of a mixture of polymer and air), the ellipsometry data suggested that the coverage of polymer only amounted to between 8 and 9% of the total surface area of the silicon wafer, the rest comprising of either air or surface contamination. Articles published within this research area generally conduct experiments within an argon glovebox, and due to the known high air sensitivity of most nickel(0) compounds, this is the only practical method to make these brushes grow. The Schlenk techniques employed under nitrogen in our laboratory may have been inadequate. Any continued work in this area should be completed in a glovebox where possible (not readily available, needs to be sourced). In summary, the success or failure of this type of polymerisation relied heavily upon maintaining an inert and dry atmosphere between the initiation and subsequent polymerisation of samples.

It should also be noted that brush thicknesses were expected to be thin for this type of polymerisation, ca. 30-40 nm according to the Locklin publication (this is still an acceptable thickness for polymer brushes).\textsuperscript{116} This is because of the chain-transfer polycondensation type mechanism via which the polymerisation proceeds (see Section 1.3.6).\textsuperscript{130,131}

### 3.4. Future work

For completeness, to accompany the current work towards synthesising the Grignard monomers, studies towards the effect of using mono-halothiophenes instead of dihalothiophenes would help to show whether a using a dihalothiophene makes it more difficult (as postulated) to synthesise the desired monomers or not.

Attempting to use excessive amounts (>2 eq.) of a magnesium source to investigate if this will yield undesirable monomers (\textit{i.e.} di-Grignards or oligomers, as predicted) from the dihalothiophenes should also be considered.

Future work involving the nickel catalyst for this area of research will need to be conducted within a glovebox, as previously discussed. Alternatively, more air-stable palladium(0) sources\textsuperscript{170} could be used as an alternative catalyst, owing to the similar chemistries of nickel and palladium. More stringent oxygen exclusion is also required for the synthesis and subsequent use of the required Grignard reagents.
3.5. Conclusions

The synthesis of a suitable KCTP monomer was attempted via numerous methods with limited success. It was found that the monomer was best produced from a system of magnesium turnings at reflux in THF with elemental iodine as an activator for the magnesium turnings. Upon attempting the polymerisation, the results were encouraging, but not satisfactory. Some film growth had evidently occurred but it was very inhomogeneous. The suspected problem lies with the air and moisture sensitivities associated with both the Grignard monomers and the nickel(0) catalyst. There are several improvements that can be made to this work, including the use of more stringent anhydrous/oxygen-free conditions (e.g. glovebox), combined with the use of reagents that are more tolerant to atmospheric conditions (e.g. palladium(0) catalysts).
Chapter 4: Substrates prepared by Surface-Initiated Ring Opening Metathesis Polymerisation (SI-ROMP)

ROMP is used to open strained ring systems and generate polymer chains via the mechanism discussed earlier in Section 1.3.7. Given the encouraging but limited results achieved with the work on KCTP, ROMP appeared to be another viable avenue to increase the chances of this project succeeding. Commonly, ROMP is applied to functionalised norbornenes, however cyclopropenes are also strained rings, due to the fact that they are three-membered rings with tight bond angles. They also contain a double bond which further increases the ring strain. The synthesis and application of cyclopropenes and cyclopropanes has been a long-term interest of the Christie group. This wealthy knowledge base made them a useful, and logical, choice as monomers for these attempts to synthesise polymer brushes using ROMP. Norbornene was also used as a monomer due to the vast literature precedent documenting its use in ROMP.

4.1. Cyclopropene synthesis

Cyclopropenes are a group of molecules that are viable ROMP monomers - they are small three-membered rings, and like norbornene, also contain a strained double bond. Ring opening is highly favoured to relieve this strain. The Schrock group have published work on the ROMP of cyclopropenes, using their novel molybdenum-based catalysts (Scheme 81). They report good stereo-selectivity due to the absence of chain transfer in ROMP based polymerisations. This combination makes them obvious candidates as ROMP monomers.
Cyclopropenes were synthesised using a three-step synthesis, outlined in Scheme 82 with results listed in Table 8. This method is well established within the Christie group, and has been used by several past and present Ph.D. candidates and undergraduate project students with plenty of success. Mesyl azide was synthesised from mesyl chloride and sodium azide. This was then reacted with dimethyl malonate under basic conditions to give dimethyl 2-diazomalonate. The diazomalonate was then added slowly to an alkyne to yield the desired cyclopropene. A diphenyl monomer was synthesised by utilising an additional step from the monophenyl equivalent and iodobenzene via a Heck coupling reaction, as published by Chuprakov et al.\textsuperscript{305} This monomer is considered to be useful due to the conjugation between the two phenyl groups when polymerised (Figure 52), which could allow for side-chain conductance.
Table 8: Summary of yields for cyclopropene monomer syntheses

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reagent</th>
<th>Cyclopropene</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="entry1.png" alt="Image" /></td>
<td><img src="entry1.png" alt="Image" /></td>
<td>55%</td>
</tr>
<tr>
<td>2</td>
<td><img src="entry2.png" alt="Image" /></td>
<td><img src="entry2.png" alt="Image" /></td>
<td>47%</td>
</tr>
<tr>
<td>3</td>
<td><img src="entry3.png" alt="Image" /></td>
<td><img src="entry3.png" alt="Image" /></td>
<td>31%</td>
</tr>
<tr>
<td>4</td>
<td><img src="entry4.png" alt="Image" /></td>
<td><img src="entry4.png" alt="Image" /></td>
<td>48% (26% over 2 steps)</td>
</tr>
</tbody>
</table>

Figure 52: Conjugation between phenyl groups in polymerised cyclopropene

The decrease in yield of entries 2 and 3 compared to entry 1 can be attributed to the electron withdrawing nature of the trifluoromethyl and nitro groups, which pull electron density away from the alkyne triple bond due to their inductive (CF₃) and mesomeric (NO₂) conjugation with the benzene ring (Scheme 83). This suggests that an electron rich alkyne is preferable in the diazodimethylmalonate addition step, as it is an electron deficient carbene that is attacked by the alkyne (Scheme 84). It should also be noted that the rate of addition of the diazomalonate to the alkyne is intentionally very slow, otherwise the reaction products will dimerise. Although the yield of the Heck coupled product (entry 4) was reasonably low (26% across two steps), it should be noted that such a small yield is not necessarily a problem for growing polymer
brushes, as only small quantities of monomer are required to grow brushes of substantial length (tens to hundreds of nanometres).

Scheme 83: Inductive and mesomeric resonance structures of 4-nitrophenylacetylene and 4-(trifluoromethyl)phenylacetylene, respectively

Scheme 84: Mechanism for carbene formation and attack by an alkyne to form a cyclopropene

4.2. Attempted solution ROMP of cyclopropenes

When ROMP of 2-phenyl-cycloprop-2-ene-1,1-dicarboxylic acid dimethyl ester was attempted in solution, polymerisation was unsuccessful: only starting material was recovered. The various conditions tried for this reaction are summarised in Table 9.
Table 9: Conditions tried for ROMP of 2-phenyl-cycloprop-2-ene-1,1-dicarboxylic acid dimethyl ester

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Temp</th>
<th>Time</th>
<th>Catalyst loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH₂Cl₂</td>
<td>rt</td>
<td>48 h</td>
<td>1 mol%</td>
</tr>
<tr>
<td>2</td>
<td>CH₂Cl₂</td>
<td>rt</td>
<td>24 h</td>
<td>2 mol%</td>
</tr>
<tr>
<td>3</td>
<td>CH₂Cl₂</td>
<td>40 °C</td>
<td>24 h</td>
<td>2 mol%</td>
</tr>
<tr>
<td>4</td>
<td>PhMe</td>
<td>110 °C</td>
<td>24 h</td>
<td>2 mol%</td>
</tr>
</tbody>
</table>

With the help of some computational structure modelling of the ring-opened transition state (Figure 53), it was established that the possible cause of the failure was due to the ester groups of the cyclopropene sitting on the same face as the Grubbs’ catalyst, and therefore interfering with the Grubbs’ catalyst by coordination to the ruthenium centre (Scheme 85), preventing the formation of the required metallocyclobutane to drive the polymerisation forwards.

Figure 53: 3D representation of catalyst-cyclopropene intermediate, modelled using Spartan computational modelling software (Wavefunction, Inc., Irvine, California USA). The carbonyl oxygen atoms (red) of the two methyl esters are situated on the same face as ruthenium catalyst (maroon, ligands not shown for simplicity)
In order to try and prevent this from happening, several solutions were proposed to try and conformationally lock the ester groups together to keep them away from the ruthenium catalyst. It was thought that this could be achieved by one of three methods: using a Lewis acid or transition metal to form a complex, reducing the esters to alcohols and performing an acetal protection, or synthesising a new monomer from a dihalocarbene rather than the diazodimethylmalonate (Scheme 86).

A common ligand for transition metal complexes is acetylacetone. As it has two carbonyl groups spaced by a single carbon, it was thought that perhaps this would be comparable to the pair of esters on the cyclopropenones synthesised. Owing to this similarity, it was hoped that the ester carbonyls would readily bind to a transition metal. This however was not the case, as starting material was returned when synthesis of such a complex with copper was attempted (Scheme 87).
Acetylacetone readily exhibits keto-enol tautomerism, and the enol form (abbreviated Hacac) readily loses a proton to form “acac”, which makes it such an effective bidentate chelating ligand to a wide range of metals, usually transition metals such as copper, as well as p-block metals such as aluminium (Scheme 88). As the cyclopropene has a quaternary carbon in the α-position between the two carbonyls, it cannot form the enol tautomer required to be a successful ligand like acetylacetone; it does not have the required proton to lose.

Attempts to reduce the ester groups to alcohols (for a subsequent acetal protection) proved unsuccessful. Using both lithium aluminium hydride and diisobutyl aluminium hydride (DIBAL) reduced the esters but characteristic peaks in the $^1$H NMR spectrum (absence of H-C=C singlet at ~7.0 ppm) also indicates that both reagents have also either ring-opened or hydrogenated the double bond in the cyclopropene ring in the same reaction, making the monomers redundant for ROMP reactions. As a result of these problems, surface-initiated ROMP of these monomers is yet to be attempted.

### 4.3. Norbornenes

Poly(norbornene)s are a very common group of metathesis polymerisation products, and are readily made by ROMP from norbornene monomers. Due to its bridged nature and the incorporation of a double bond, norbornene is a very strained molecule and is therefore highly reactive. It is prone to ring opening reactions, such as ROMP to relieve this strain. Norbornenes are typically synthesised via a Diels-Alder reaction from cyclopentadiene and ethylene derivatives (Scheme 89).
Although poly(norbornene)s are not conjugated, there is some evidence to suggest that they can display conductive properties.\textsuperscript{308} Given that there are three insulating carbon atoms between double bonds, unsubstituted poly(norbornene) still shows a small degree of electrical conductance (0.1 S/cm) when doped with iodine on a glass surface, however this is four orders of magnitude lower than a fully conjugated polymer \textit{e.g.}\ poly(acetylene) (\textbf{Table 10}). There is also plenty of literature precedent for the incorporation of poly(norbornene)s into thin films on surfaces.\textsuperscript{18,194,193,309}

\textbf{Table 10:} Conductivities ($\sigma$) of non-conjugated conducting polymers after iodine doping\textsuperscript{308}

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Polymer</th>
<th>DBNF*</th>
<th>$\sigma$ (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta$-Pinene</td>
<td>poly($\beta$-pinene)</td>
<td>1/6</td>
<td>0.008</td>
</tr>
<tr>
<td>Norbornene</td>
<td>poly(norbornene)</td>
<td>1/5</td>
<td>0.01</td>
</tr>
<tr>
<td>cis-Isoprene</td>
<td>poly(cis-isoprene)</td>
<td>1/4</td>
<td>0.1</td>
</tr>
<tr>
<td>Alloocimene</td>
<td>poly(alloocimene)</td>
<td>1/3</td>
<td>1.0</td>
</tr>
<tr>
<td>Acetylene</td>
<td>poly(acetylene)</td>
<td>1/2</td>
<td>$\approx$100</td>
</tr>
</tbody>
</table>

\textsuperscript{*} DBNF: Double bond number fraction = Number of double bonds/Total number of bonds; only counting bonds along the backbone (\textit{i.e.} disregard side chains)
4.4. Solution grown poly(norbornene) by ROMP

Solution and SI-ROMP of unsubstituted norbornene proved much more successful than the ROMP of cyclopropene counterparts. Solution polymerisation of norbornene and the triethoxysilyl norbornene (used as it was a readily-available substituted norbornene in the laboratory) was observed, and has been noted as being very rapid, with a dramatic increase in viscosity of the solution being observed within 5-10 min typically (a stereotypical observation when solution polymerisation occurs, indicative of an increase in molecular weight).

$^1$H NMR analysis of solution polymerised poly(norbornene) can be hard to interpret, often appearing “messy” due to varying tacticity along the polymer backbone. This made the interpretation of the poly(norbornene) $^1$H NMR very challenging, but it was still possible. The polymeric form of the norbornyl silane that was synthesised was insoluble in all the organic solvents tried (chloroform, DMSO, DMF, THF, toluene, petroleum ether, diethyl ether and methanol) and is yet to be analysed by $^1$H NMR. It is suspected that the polymer is heavily cross-linked by the pendant silyl groups.

The backbone of saturated polymers (“polysaturates”) will exhibit tacticity if the two side chains on the backbone differ. This is comparable to stereoisomerism in small molecules. In polymer chemistry, the relative stereo-configuration of a saturated backbone is known as tacticity. Tactic saturated polymers can be either isotactic (all side chains on the same face of the backbone) or syndiotactic (side chains alternate between the faces of the backbone). An atactic saturated polymer is one where the stereochemistry is randomised along the backbone (Figure 54). The degree of tacticity of a saturated polymer can be determined by the ratio between the integral of the NMR peaks for the individual stereo-chemistries.

\[
\begin{align*}
\text{Isotactic} & \quad \begin{array}{c}
R \quad R \quad R \quad R \quad R \quad R \\
\end{array} \\
\text{Syndiotactic} & \quad \begin{array}{c}
R \quad R \quad R \quad R \quad R \\
\end{array} \\
\text{Atactic} & \quad \begin{array}{c}
R \quad R \quad R \quad R \quad R \\
\end{array}
\end{align*}
\]

Figure 54: Tacticity of aliphatic polymers

Although poly(norbornene) is an unsaturated polymer, the cis-trans geometric isomerism displayed by poly(norbornene) can be quantified in a similar way to tacticity in polysaturates. By analysis of the $^1$H NMR and the relative integration of the cis- and trans-alkene peaks, it was determined that the poly(norbornene) synthesised was approximately 6:4 cis:trans.
4.5. Pre-polymerisation functionalisation of substrate surface

Silicon wafers were prepared for SI-ROMP of commercially-purchased unsubstituted norbornene, using several types of system, shown in Scheme 90.

Firstly, the wafers were cleaned using a UV-Ozone clean. Silane monolayers were deposited from the corresponding triethoxysilane [left to right, vinyl triethoxysilane, allyl triethoxysilane, norbornyl triethoxysilane and (3-aminopropyl)triethoxysilane] either by vacuum deposition or by toluene solution deposition. There were no significant differences between the two deposition techniques; contact angle observations (Table 11) showed increased hydrophobicity in all cases. The norbornyl amide system was created by first depositing a monolayer of (3-aminopropyl)triethoxysilane onto the surface and then condensing a norbornyl acyl chloride onto the amine. An attempt to make the amide in-solution first and then deposit onto the surface was successful, but deposition was heterogeneous compared to performing the condensation with the amine already on the surface (suggesting a poorer grafting density, as expected when trying to pack larger molecules compared to smaller molecules, c.f. grafting to vs. grafting from). This was to be expected as smaller molecules will always be able to pack more closely on the surface to give a much greater grafting density.
Table 11: Static contact angle measurements of silicon wafers functionalised for SI-ROMP

<table>
<thead>
<tr>
<th>Entry</th>
<th>Silane</th>
<th>Solution deposition</th>
<th>Vapour deposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>UV/O$_3$ cleaned</td>
<td></td>
<td>7°</td>
</tr>
<tr>
<td>2</td>
<td>Vinyl</td>
<td>43°</td>
<td>47°</td>
</tr>
<tr>
<td>3</td>
<td>Allyl</td>
<td>63°</td>
<td>64°</td>
</tr>
<tr>
<td>4</td>
<td>Norbornyl</td>
<td>43°</td>
<td>47°</td>
</tr>
<tr>
<td>5</td>
<td>APTES-Norbornyl</td>
<td>57°</td>
<td>56°</td>
</tr>
</tbody>
</table>

When depositing the triethoxysilyl amine in basic solution, a thick multilayer (~90 nm) was observed. This may have been due to the fact that the batch of triethylamine that was being used for this deposition was not anhydrous. Whilst small amounts of water will aid deposition, a “wet” base tends to hinder SAM deposition for trialkoxysilanes, potentially giving the cross-linked multilayer that seems to have been observed in this instance (Scheme 91).

Scheme 91: Cross-linking effect of water on alkoxy silanes

Despite this, these mono and multilayer systems were then initiated with Grubbs’ 2nd Generation catalyst by soaking in a dichloromethane solution of the catalyst for 1 h. Longer soakings showed signs of catalyst degradation (solution changing colour from pale pink to dark green). Excess catalyst solution was removed by cannula and followed by a series of dichloromethane washes to try and minimise exposure to air and moisture. It is also suggested, like the Kumada-type work, that this work should ideally be carried out in a
Chapter 4: Substrates prepared by Surface-Initiated Ring Opening Metathesis Polymerisation (SI-ROMP)

glovebox if possible, although the Grubbs’ catalyst for ROMP is far more air stable than the nickel(0) species used for KCTP, as has been shown by the slightly better results attained.

4.6. Surface-initiated ROMP of norbornene using solvated (“wet”) systems

SI-ROMP from the vinyl and allyl surfaces proved unsuccessful. The failings are thought to be down to the surface “backbiting”, and reacting with itself to make an inert surface (Scheme 92), by undergoing cross metathesis with neighbouring chains and forming closed rings, comparable to a ring closing metathesis (RCM) reaction.

\[
\text{Scheme 92: “Backbiting” on an allylsilyl functionalised surface}
\]

SI-ROMP using the norbornyl SAM systems was more successful. A small growth (5 nm) was observed with the norbornyl silane system, and a very encouraging film of 131 nm was achieved with the norbornyl amide system. This included the ~90 nm silyl multilayer (Scheme 91), but a substantial increase in ellipsometric thickness (41 nm) between the samples from the multilayer formation to the polymer growth can be confidently asserted as being poly(norbornene). This would also suggest that despite the cross-linking of the multilayer, there are still free pendant amine groups for the norbornyl chloride to attach to. On another occasion, attempted growth of poly(norbornene) was unsuccessful on the silicon surface in solution, but growth of polymer was observed on the silicon wafer above the fill level of the polymerisation solution. This suggested that the polymer can grow in the vapour phase, and further investigations into this theory were conducted (discussed in Section 4.9).
4.7. **Effect of concentration on ruthenium deposition**

After some failures with the solvated system, it was debated as to how best to prove that the ruthenium had actually attached to the functionalised surface, in order to eliminate the possibility of the catalyst not attaching to the surface as an explanation. After a screening of the literature, it was noted that the concentration of catalyst used ranges from micromolar quantities, through millimoles and up to 0.35 moles. In general, the concentrations of catalyst used in such solutions were typically between 5 and 25 mmol. It was decided that an experiment should be carried out to try and determine an optimal concentration of catalyst for the initiation phase.

Norbornyl-amide functionalised wafers were treated with 5, 10, 15, 20 and 25 mmol of Grubbs’ first and second generation catalysts in 2 mL of dichloromethane. After 30 min at room temperature, this solution was removed using a cannula, the tubes and wafers within were washed with dichloromethane (10 x 5 mL), and then immersed in 2 mL of a 3 M solution of norbornene (6 mmol). Polymerisation was left for 1 h, capped with ethyl vinyl ether and the ellipsometric thicknesses of the subsequent films were measured.

The films produced using Grubbs’ first generation catalyst were undetectable by ellipsometry, suggesting a very thin film (below the minimum detectable thickness of the ellipsometer used, 1 nm). Films grafted from Grubbs’ second generation catalyst were also thin, but were measurable. The results are summarised in Table 12 and Figure 55.

**Table 12:** Thicknesses of films of poly(norbornene) grown from substrates initiated with different concentrations of Grubbs’ 2nd generation catalyst

<table>
<thead>
<tr>
<th>Entry</th>
<th>Concentration of catalyst used</th>
<th>Average polynorbornene film thickness after 1 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5 mmol</td>
<td>1.6 ±0.8 nm</td>
</tr>
<tr>
<td>2</td>
<td>10 mmol</td>
<td>4.8 ±0.7 nm</td>
</tr>
<tr>
<td>3</td>
<td>15 mmol</td>
<td>6.2 ±1.3 nm</td>
</tr>
<tr>
<td>4</td>
<td>20 mmol</td>
<td>32.1 ±6.3 nm</td>
</tr>
<tr>
<td>5</td>
<td>25 mmol</td>
<td>46.9 ±1.3 nm</td>
</tr>
</tbody>
</table>
Chapter 4: Substrates prepared by Surface-Initiated Ring Opening Metathesis Polymerisation (SI-ROMP)

4.8. XPS of ruthenium-initiated substrates

As can be seen from the data, at catalyst loading concentrations below 20 mmol, brush growth was minimal. This suggests that the catalyst did not load well with a less concentrated solution. The significant upturn in brush thickness between the samples loaded with 15 mmol and 20 mmol catalyst solution shows that a solution with a minimum concentration of 20 mmol was critical when activating surfaces for SI-ROMP. This may be because the catalyst solution is not agitated during initiation, simply relying on diffusion at the wafer surface for successful activation between the tethered olefin groups and free catalyst. An increased concentration of catalyst in solution when the concentration of activatable groups on the surface remains constant will increase the chances of a collision between a moving catalyst molecule and a static tethered olefin. At 20 mmol, the concentration of catalyst reaches a threshold excess over the surface-bound initiator. Film thickness greatly increased, suggesting better catalyst loading on the surface. Catalyst age and storage history could be an issue, but this was the only batch available. The high cost of the catalyst made repeating this experiment with a different batch of catalyst prohibitive.

Figure 55: Graphical representation of thicknesses of films of poly(norbornene) grown from substrates initiated with different concentrations of Grubbs’ 2nd generation catalyst

After reading the work of Bowden and Perring, it was decided that it should be possible to use XPS with a selection of samples coated with ruthenium-initiated SAMs. It was hoped that this would provide the necessary data to eliminate the possibility of the catalyst not attaching to the surface as a reason for the failures experienced with some solution-based samples. The
instrument is able to detect ruthenium to 0.5 atom%. Ruthenium has a relative atomic sensitivity of 3.6 for its $3d$ electrons which should be seen at approximately 280 eV, and a relative sensitivity of 1.3 for $3p^3$ electrons which should hold a binding energy of around 284 eV. To compare, the $1s$ binding energy of carbon is regularly observed by XPS, and has a relative sensitivity value of 0.25.\textsuperscript{313,314} Decomposition by oxidation of the catalyst should be irrelevant as the ruthenium should be detectable regardless of its oxidation state,\textsuperscript{315} so exposure to air was not considered a major problem.

Four substrates were submitted for analysis: two of the norbornyl-silane functionalised and two of the norbornyl-amide functionalised samples. The silanes (norbornyl silane and APTES) were each deposited by vapour-phase deposition for one sample and solution-phase deposition for the other. The APTES samples were then functionalised with the norbornyl group using a condensation reaction with the acyl chloride in THF for 1 h. The findings of the XPS data are summarised in Table 13.
Table 13: Summary of elemental composition of samples as determined by XPS

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sample technique used</th>
<th>Composition (atom%, excluding H)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>1</td>
<td>Solution</td>
<td>83.1</td>
</tr>
<tr>
<td>2</td>
<td>Solution</td>
<td>56.2</td>
</tr>
<tr>
<td>3</td>
<td>Vapour</td>
<td>14.3</td>
</tr>
<tr>
<td>4</td>
<td>Vapour</td>
<td>22.1</td>
</tr>
</tbody>
</table>

A sample spectrum for sample 2 is shown in Figure 56.
Firstly, it can be noted that the monolayers have definitely been deposited. Denser monolayers have been deposited in the solution phase than in the vapour phase. However, these samples appeared inhomogeneous (or “rough”) by visual inspection. This “roughness” leads to the deduction that the sample has multilayer (instead of monolayer) coverage. Essentially, the layer covers the surface everywhere, but is thicker in some places than others. The XPS data reflects this. The apparent “lower” degree of coverage for the vapour-phase depositions does not mean a monolayer is not present - this actually helps confirm that the solution deposited samples are more than monolayered.

The detection of chlorine in the amide substrates could be due to the condensation reaction undertaken to formulate these substrates. The chloride anion lost from the norbornoyl chloride may become loosely associated with the monolayer by weak dipole interactions between the monolayer and the anion. We can also determine from the relative percentages of carbon and
nitrogen in samples 2 and 4 that the coupling of the norbornoyl chloride with the amine group has amidified around 75% of the amino groups.

The key issue is that there appeared to be no ruthenium present. The binding energies of ruthenium 3d and carbon 1s are similar (280 eV), so high-resolution experiments between 276 eV and 296 eV were undertaken to try and resolve any overlap in such peaks (Figure 57).

As can be seen in the high-resolution spectrum in Figure 57, there was no sign of any ruthenium. The integrals of the yellow, blue and green peaks are 8:2:1 respectively. This ties up with the carbon count in the uninitiated norbornyl amide species. The eight carbons under the yellow peak represent those marked in yellow on the structure in Figure 57. This peak presents most of the carbon atoms bonded to other carbon atoms. The two carbon atoms that the blue peak represents are categorised as the sp³ carbon atoms bonded to heteroatoms, as well as the α-carbon to the carbonyl group. The green peak is indicative of the carbonyl carbon atom.
Overall, this peak pattern suggests that the norbornene species exists in its ring-closed double bond form.

Despite initially considering oxidation of the ruthenium by unavoidably exposing the substrates to air as irrelevant, it may have led to these results. Although ruthenium is detectable regardless of its oxidation state, if the ruthenium is oxidised and does not have the ability to convert to the required 16 electron state for forming complexes with the alkene (Section 1.3.7), then it would be washed away when the wafers were washed with dichloromethane before the XPS analysis was carried out (to remove anything not attached to the surface). It is also plausible that the ruthenium species will also be oxygen-sensitive in the catalytically active state (willing to revert back to a stable 18 electron configuration), and could therefore be cleaved in the presence of atmospheric oxygen, when in storage before running the XPS experiment. The “backbiting” discussed in Section 4.6 could also be a possible explanation for why no ruthenium was seen in the XPS results. If this has occurred then the catalyst would have been freed from the surface and again would be removed when the wafers were washed with dichloromethane before the XPS analysis was undertaken.

4.9. Surface polymers of norbornene grown in the vapour-phase

As mentioned in Section 4.6, on one attempt to grow poly(norbornene) brushes in solution, growth of polymer was observed above the fill level of the monomer solution. This experiment was deliberately repeated with success. This suggested that the polymer can grow in the vapour phase. The sample in question from the repeat experiment is pictured in Figure 58, in situ approximately one minute after the addition of the monomer solution.
Chapter 4: Substrates prepared by Surface-Initiated Ring Opening Metathesis Polymerisation (SI-ROMP)

Figure 58: Substrate coated with surface-initiated vapour-phase ROMP polymerised norbornene after ca. 1 min

As an approximate guide, comparison to the thin film colour chart (Figure 59) shows a gradient of rapid growth within the minute, from ca. 10-20 nm at the top of the substrate, where the vapour concentration is lower, to ca. 275-280 nm just above the surface (centre, purple spot). These colours and hence values will be a slight exaggeration, as the polymer film will be swollen by the solvent vapour, but importantly it can be noted that very respectable growth is achieved in a relatively short period of time. Matching the purple spot to the colour chart between 275 nm and 280 nm when swollen in DCM, and then measuring film thickness at this point by ellipsometry once the sample had dried showed that the dry film thickness of this area of brushes to be 187 nm. This means the brushes are swollen by approximately 47-50% of their length in the dry state in Figure 58.
**Figure 59:** Thin-film colour chart: Intended as a guide, these colours can be observed on substrates to give an approximate indication of film thickness.
It was decided that a specialist piece of apparatus for polymerisation in the vapour phase may be advantageous. The method stated previously had some of the wafer immersed in solution, where film does not grow, which made this part of the substrate of little use. With a specialist setup it was also hoped that controlled gradients of different brush lengths could be achieved, as this may be useful for some applications.

The apparatus constructed can be seen in Figure 60. A pre-washed ruthenium-initiated silicon substrate was sealed in flask A. Flask B contained the monomer. Flask B was heated to vaporise the monomer. Polymerisation was then attempted by pulling a vacuum and opening taps 1, 2 and 3 to reduce the pressure in flask A. Once flask A had been sufficiently evacuated, taps 5 and 6 were opened to attempt to draw the monomer vapour across from flask B into flask A. Unfortunately, when this was attempted with norbornene, the norbornene solidified on the cooler glass at the top of flask B and was just pulled across into flask A in the solid state. No polymerisation was seen. Suggested improvements to the equipment and procedure are outlined in Section 4.10.

Figure 60: Specialist reactor setup for vapour-phase surface-initiated polymerisation
4.10. Future work

As discussed, refinements need to be made to the cyclopropene monomers to attempt to prevent the suspected interference of the ester groups with the ruthenium catalyst, either by reduction of the ester groups or by using alternative syntheses, for example via a dihalocarbene precursor. Attempts to reduce the esters with LiAlH₄ and DIBAL were successful but also hydrogenated the cyclopropene functionality. Other reducing agents that could be tried include (but are not restricted to) cerium trichloride and borane.

The formation of a cyclopropenyl silane (Figure 61) would also be of interest, in order to create a SAM for the polymerisation of cyclopropenes that is comparable to the norbornyl silane SAM’s used for the SI-ROMP of norbornene.

![Figure 61: General structure of a cyclopropenyl silane](image)

Also, given the encouraging results of the norbornene polymerisations, synthesis of some functionalised norbornene monomers would be a logical progression. Synthesis via a Diels-Alder reaction would be a simple route, ideally with the introduction of conjugation to these monomers, to be either incorporated in the polymer back bone or as side chains. If benzyne intermediates were used as the dienophile then aromatic functionality could be easily incorporated (Scheme 93).

![Scheme 93: Diels-Alder reaction with benzyne for the formation of functionalised norbornenes](image)

Experiments conducted using the vapour-phase setup have also shown initial signs of success, and should be pursued further. The reservoir of monomer could be dissolved in solvent (dichloromethane or toluene) and bubbled with nitrogen gas to try and generate a better vapour, using the solvent vapour as a carrier for the monomer. Additionally, the rest of the apparatus may need heating and/or insulating to try and prevent the condensation of the monomer on the sides of the glassware.
Finally, combining the favourable electronic properties of the thiophenes used in the KCTP work, and the easier handling techniques associated with metathesis chemistry, the use of a 2,5-divinylthiophene to generate a conjugated poly(thiophene) via acyclic diene metathesis (ADMET) is also an appealing idea (Scheme 94).\textsuperscript{316} The possible problem with this however is that it would be a step-growth polymerisation, and would be slower and less reliable than the current chain growth polymerisation methods being tried.\textsuperscript{317}

![Scheme 94: ADMET of 2,5-divinylthiophene](image)

### 4.11. Conclusions

The synthesis of several cyclopropenes for use as ROMP-able monomers was undertaken with success. Unfortunately, the ROMP of these monomers was not successful and this was believed to be due to the ester functionality incorporated into these monomers. It was suggested that the ester groups are ligating with the ruthenium and hindering the progress of the catalysis.

Norbornene was polymerised by ROMP with varying success. It was determined that 20 mmol of Grubbs' second generation catalyst in 2 mL of dichloromethane was the optimal concentration for initiating substrates functionalised for ROMP. XPS data suggested that the vapour phase deposition of the monolayer was more likely to give monolayers than the solution phase method, which appears prone to depositing inhomogeneous multilayers.

Polymerisation in the vapour phase was very efficient - brushes of up to 187 nm grown in 1 min. Growth was not homogenous due to the evaporation of norbornene from solution being more concentrated closer to the solution surface, but for some applications a gradient of brush thicknesses is useful. Specialist apparatus for this polymerisation method has been developed and optimisation of this setup and further investigation of its capabilities are suggested as a future project.

Although the cyclopropenes and norbornenes do not form polymers with conjugated backbones, there is scope to introduce conjugation via side chains with groups that can stack and will allow charge transport by “hopping” between neighbouring side chains. Alternatively, this low conductance also makes any potential polymer a viable candidate as a polymer dielectric for field-effect transistors.\textsuperscript{5}
Chapter 5: Substrates prepared by Surface-Initiated Atom Transfer Radical Polymerisation (SI-ATRP)

ATRP is a common and long-established technique for the growth of polymer brushes. Under the circumstances, although the results achieved with ROMP looked to be progressively improving, the Edmondson group holds a wealth of knowledge, experience and expertise in the field of SI-ATRP. The majority of SI-ATRP experiments utilise methacrylate-based monomers. One desirable monomer is 2-hydroxyethyl methacrylate (HEMA), as the terminal hydroxyl group can be used to post-modify a polymer. This post-modified polymer can then be re-initiated (as ATRP is a pseudo-living method) to grow more poly(2-hydroxyethyl methacrylate) or another polymethacrylate such as PDMAEMA, which can then also be post-functionalised. This is an effective and efficient way of synthesising functionalised diblocks.

5.1. Solution polymerisation of 2-hydroxyethyl methacrylate: ATRP vs. ARGET-ATRP

When working with surface-confined polymers, the equivalent free polymer can be a useful tool. With the free polymer, products can be characterised more easily, most are soluble (if not cross linked or otherwise rendered insoluble), and can be processed by solution NMR for example. As a general principle, if polymerisation proceeds in solution to produce the free polymer, then it can be sensibly assumed that there is no obvious reason as to why, if the conditions are controlled appropriately, the same polymerisation should not be compatible with the corresponding surface-tethered initiator. This is obviously not always the case, but is a perfectly reasonable argument to justify attempting to grow brushes by a comparable method.

As previously mentioned, PHEMA [poly(2-hydroxyethyl methacrylate)] appeared to be a useful polymer to this project. Therefore, PHEMA was synthesised in solution by both traditional ATRP and the newer ARGET-ATRP methods (Scheme 95).
Chapter 5: Substrates prepared by Surface-Initiated Atom Transfer Radical Polymerisation (SI-ATRP)

Scheme 95: ATRP and ARGET-ATRP of 2-hydroxyethyl methacrylate

Copper(I) initiates the polymerisation by generating a radical in place of the bromine on the ethyl α-bromoisobutyrate. In traditional ATRP, the copper(I) bromide is the obvious source of copper(I). For ARGET-ATRP, the ascorbic acid (sodium ascorbate can also be used) reduces the copper from copper(II) to copper(I). As an example of a living radical polymerisation, the growth is controlled by the equilibrium between the dormant and active states (Scheme 96). Fast and simultaneous initiation is required, partnered with slow propagation to give low polydispersity.

Scheme 96: Controlling the polymerisation of 2-hydroxyethyl methacrylate

An excess of ascorbate as the reducing agent ensures there is sufficient copper(I) to catalyse the polymerisation, even if the reaction mixture is exposed to atmospheric oxygen. The ARGET-ATRP method is advantageous over traditional ATRP because, as the unabridged name suggests, the “activators” (copper(I) source) are re-generated by electron transfer (from the reducing agent). The primary justification for choosing ARGET over traditional ATRP is that it uses distinctly less copper-based salts, and thus it is considered to be a far more “green” method. Obviously ARGET is not totally green as copper is still used, but it is incorporated in much smaller quantities.

The typical reducing agent is ascorbic acid, which is more commonly known as Vitamin C, and as a waste product is far less toxic than the large quantity of copper salts associated with traditional ATRP. This decreased use of copper combined with the addition...
of a reducing agent also affords a second rationale for the use of ARGET over traditional ATRP, as it is far more tolerant of mildly challenging conditions; the reaction does not have to be rigorously dried or deoxygenated (although this is still good practice to give longevity to the reaction mixture). Should there be any contact with oxygen, or termination as a result of biradical combination, the copper(I) species that have been generated are recoverable, as the reducing agent simply re-reduces the copper(II) to copper(I).

5.2. Pre-polymerisation functionalisation of substrate surface for SI-ATRP

Silicon wafers were prepared for surface modification as outlined in Scheme 97. The cleaning and deposition steps are identical to those discussed earlier in Section 3.2 and will therefore not be discussed any further. Vapour deposition of (3-aminopropyl)triethoxysilane was again carried out twice using both a vacuum desiccator (min. 6-7 mbar) and a vacuum oven (min. 1-2 mbar) to investigate the effect of vapour deposition pressure on grafting density (discussed in Section 5.3). As before, a condensation reaction with the terminal amine introduced the polymerisation initiator: an isobutyryl bromide group (of which the bromine atom is the masking group for the initiating radical). The substrate was ready for surface-initiated polymerisation at this stage. These samples were also washed with distilled water and contact angle observed as a qualitative indicator of success, details of which are shown in Table 14. The changes in contact angle reflect the change in surface hydrophilicity detailed in Scheme 97.

Scheme 97: Preparation of silicon wafers for SI-ATRP and SI-ARGET ATRP of methacrylates
Table 14: Static contact angle measurements of silicon wafers functionalised for SI-ATRP using a vacuum oven (min. 1-2 mbar) to carry out APTES deposition

<table>
<thead>
<tr>
<th>Entry</th>
<th>Stage</th>
<th>Static contact angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Native Si</td>
<td>45°</td>
</tr>
<tr>
<td>2</td>
<td>UV/ O&lt;sub&gt;3&lt;/sub&gt; cleaned</td>
<td>7°</td>
</tr>
<tr>
<td>3</td>
<td>APTES</td>
<td>58°</td>
</tr>
<tr>
<td>4</td>
<td>Bromoisobutryl bromide Initiator</td>
<td>88°</td>
</tr>
</tbody>
</table>

5.3. The effects of efficient vapour-phase deposition of SAMs

In order to understand how different vapour-phase SAM deposition conditions affect the grafting density and therefore length of polymer brushes grown, a comparison of deposition apparatus was undertaken, to establish which was best to use. Substrates previously functionalised for polymerisation with 2-bromoisobutryl bromide (BIBB) from APTES monolayers deposited using the vacuum desiccator (min. 6-7 mbar) and the vacuum oven (min. 1-2 mbar) were immersed in a 1:1 v/v solution of 2-hydroxyethyl methacrylate and methanol, along with copper (II) bromide, 2,2'-bipyridyl and sodium ascorbate (the ARGET-ATRP method was chosen for its robustness in the presence of oxygen<sup>227</sup>). The polymerisation is summarised in Scheme 98. Conditions and molar ratios (1:2 Cu(II):bpy, 1:10 Cu(II):ascorbate) of the components already established by Edmondson and Zhu were used.<sup>230</sup>
Samples were removed after 1 h, 4 h, 7 h and 24 h and the film thickness was measured by ellipsometry. The results are summarised in Table 15 and Figure 62.

**Table 15:** Thickness of poly(2-hydroxyethyl methacrylate) brushes at varying time intervals, grown on silicon wafers using different vapour-phase deposition techniques for (3-aminopropyl)triethoxysilane.

<table>
<thead>
<tr>
<th>Growth time (h)</th>
<th>Desiccator-functionalised substrates</th>
<th>Vacuum oven-functionalised substrates</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>17.6 ±1.9</td>
<td>24.2 ±1.6</td>
</tr>
<tr>
<td>4</td>
<td>49.2 ±2.1</td>
<td>63.1 ±2.2</td>
</tr>
<tr>
<td>7</td>
<td>52.3 ±1.3</td>
<td>70.2 ±5.2</td>
</tr>
<tr>
<td>24</td>
<td>105.8 ±5.1</td>
<td>134.1 ±6.3</td>
</tr>
</tbody>
</table>

* Although chain transfer is shown, polymerisation can also terminate via biradical combination.

**Scheme 98:** SI-ATRP of 2-hydroxyethyl methacrylate
When studying brush thickness systematically over time under these two different initiator deposition conditions, two conclusions can be drawn. Firstly, it is observed that the longer a wafer sample was left in the polymerisation solution the thicker the polymer brush grew. The rate of growth observed at the start of polymerisation was faster than that seen in the later stages of polymerisation. This is illustrated by the high gradient of the plot line at the earlier time points in Figure 62, followed by flattening into a lower gradient in the latter stages of the experiment. This is typical behaviour in ATRP experiments.

The second conclusion that can be formed is that samples that were functionalised with the amine using the vacuum oven (min. pressure 1-2 mbar) gave thicker brushes than those functionalised in the vacuum desiccator (min. pressure 6-7 mbar), suggesting that a lower pressure during the vapour-phase functionalisation stage of the process gave a more densely grafted SAM. This is can be validated using the equation for grafting density (Equation 3), which shows that brush thickness ($h$) is directly proportional to the grafting density ($\sigma$) achieved. As the polymerisation conditions were identical between samples treated using either vacuum vessel, it can be assumed that molecular weight ($M_n$) and bulk density ($\rho$) do not differ between the samples, so the observed difference in brush thickness must be due to the differences in grafting density.
\[
\sigma = \frac{h \rho N_A}{M_n}
\]

**Equation 3:** Calculation of grafting density – \(h\) is polymer brush thickness, \(\rho\) is the bulk density of the brush composition, \(N_A\) is Avogadro’s constant (6.022 \times 10^{23} \text{ mol}^{-1}), \(M_n\) is the average molecular weight of the polymer chains.

The data obtained when using the vacuum oven for SAM deposition, as per the protocol used by Zhu,\(^{324}\) yields identical results to those seen in the referred article. No examples of quoted higher pressures, such as that found in the desiccator, could be found to use for comparison.

### 5.4. PHEMA and PDMAEMA homopolymer brush growth

PHEMA and PDMAEMA brushes were grown from BIBB-functionalised substrates by the ATRP and ARGET-ATRP methods. For the ATRP of PHEMA, a mixed solvent system of water and methanol in 1:1 v/v ratio was used, along with 0.3 mol% of copper(I) bromide, 0.03 mol% copper(II) bromide and 0.6 mol% 2,2’-bipyridine (bpy) as ligand for the copper catalyst. For the ARGET-ATRP of PHEMA, 0.5 mol% of reducing agent (ascorbic acid) was combined with 0.03 mol% copper(II) bromide catalyst and 0.06 mol% 2,2’-bipyridine (bpy). These conditions were taken from the previous work within the group,\(^{324}\) and were not optimised further as they produce brushes of sufficient thickness (i.e. detectable by ellipsometry) for this study.

ATRP and ARGET-ATRP of PDMAEMA require modifications to the conditions of the PHEMA polymerisation. Firstly, the ligand must be changed from bpy to something with a higher affinity than the tertiary amine monomer for the copper species. The copper to monomer ratio is critical for controlling growth to a specific molecular weight (and therefore brush thickness) over a fixed period of time with low polydispersity, as discussed by Matyjaszewski et al.\(^{224}\) HMTETA was selected as ligand, as it is known to be excellent for copper-mediated ATRP polymerisations. In some cases the use of HMTETA leads to an increased rate of polymerisation.\(^{325}\) HMTETA has a stronger affinity for copper than both bpy and the DMAEMA, and therefore shifts the equilibrium towards the copper being ligated by the ligand rather than the monomer. Secondly, the methanol and water solvent system can be incompatible with PDMAEMA polymerisation by ATRP. It has previously been shown by Bories-Azeau and Armes\(^{326}\) that using methanol as solvent with tertiary amine methacrylates, such as PDMAEMA, for ATRP at ambient temperatures can result in transesterification of the acrylate with the methanol. This can be overcome by changing the co-solvent from methanol to isopropanol. Although some transesterification may be seen with isopropanol, it is minimal (virtually unobserved) compared to the same effect with methanol. A mixture of isopropanol and water in a 4:1 v/v ratio was used for these polymerisations. The relative amount of alcohol had to be increased, despite slowing
the rate of polymerisation, in order to dissolve the HMTETA and DMAEMA monomer adequately. For ATRP, a ratio of 10:1 [Cu(I)]:[Cu(II)] in relatively low concentration (0.4 mol%: 0.04 mol%) with 1 mol% of HMTETA ligand was previously established within our research group and was used for this work without optimisation. For ARGET-ATRP, conditions of 10:1 [ascorbic acid]: [Cu(II)], in even lower concentration (100 times less) were employed, with a concentration ratio of 2:1 HMTETA: ascorbic acid. Once again, these conditions were previously optimised within our group and proved sufficient for this work.

Kinetic studies of these polymerisations were undertaken to determine the degree of control in these polymerisation when comparing ATRP and ARGET-ATRP. These results are summarised in Figure 63. A perfectly living polymerisation would show a linear behaviour on the plot; molecular weight (and hence film thickness) should increase linearly with time, with narrow polydispersity. As can be seen, the PHEMA ATRP and ARGET-ATRP exhibit excellent control up to 10 h of growth time, and then growth slows through to 24 h, presumably due to termination of the polymerisation caused by biradical combination (the most likely termination path for SIP), catalyst oxidation or catalyst disproportionation. The timeframe for good control with the PDMAEMA polymerisation by both ATRP and ARGET-ATRP is a lot shorter, approximately 4 h.
With a view to producing a diblock system, it is critical to have brushes in the first block that are well-controlled and still alive (i.e. capped with the tertiary bromide “masked” initiator) to enable a high degree of re-initiation. The first layer also needs to be thick enough that it can be easily characterised. Finding a balance between a fast growth and a high degree of control over film thickness is important. The polymerisation times used (24 h) were deemed acceptable for the production of a brush diblock system based on these criteria. In order to grow the thickest brushes possible, the most efficient polymerisation technique (ATRP or ARGET-ATRP) was selected. Using the traces in Figure 63, PHEMA was grown by ARGET-ATRP, and PDMAEMA
was grown by ATRP as these yielded the thickest brushes at each time point for the respective monomers.

### 5.5. PHEMA-PDMAEMA diblock growth

The re-initiation of PHEMA brushes to form diblock copolymer brushes was attempted. Using the 24 h PHEMA ARGET-ATRP substrates (thickness 241 nm), polymerisation was restarted to grow the PDMAEMA block on top of the PHEMA using the standard ATRP conditions described previously for a further 24 h. Ellipsometry measurements showed a film thickness increase of 70 nm to a total of 321 nm. The IR spectrum in Figure 64 shows features of both homopolymers. The PDMAEMA peaks present at 2808 cm\(^{-1}\) and 2746 cm\(^{-1}\) are also observed in the diblock. These can only come from successful growth of PDMAEMA on top of the PHEMA block, as the reference spectrum of PHEMA does not show these peaks, so they must be contributed by the PDMAEMA. The carbonyl peak at 1735 cm\(^{-1}\) has also developed a shoulder, suggesting two different carbonyl environments (one for each methacrylate monomer). This data combined with the thickness increase observed by ellipsometry suggests successful diblock growth has been achieved.

![Figure 64: Transmission FTIR spectra of PHEMA, PDMAEMA and PHEMA-block-PDMAEMA brushes on silicon wafers](image)

Figure 64: Transmission FTIR spectra of PHEMA, PDMAEMA and PHEMA-block-PDMAEMA brushes on silicon wafers
5.6. Polyaromatic groups, for \( \pi \)-stacking

Polyaromatic species, such as those in Figure 65 have the ability to \( \pi \)-stack when brought into close proximity to one another.\(^{327-329}\) Due to their large size, and the \( \pi-\pi \) orbital interactions between two neighbouring ring systems, the polyaromatics will arrange in a stacked system, approximately parallel to one another in order to reduce the steric interactions between these bulky groups.\(^9\) Similar systems using carbazole\(^3\) and triphenylamine\(^34\) side chains have been reported, but there are no literature examples of an anthracene system linked to a PHEMA or PDMAEMA unit to our knowledge, so this would be a novel system. Such a system would be useful for applications requiring an electron carrier, typically used for bulk heterojunction photovoltaic devices.\(^{330}\) Ideally, the PHEMA-anthracene layer would be the electron transporting layer, and the PDMAEMA layer could be quaternised to create the hole-transporting layer.

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**Figure 65:** Some examples of polyaromatic groups

5.6.1. Post-modification of PHEMA brushes with anthracene

Whilst the synthesis of pre-functionalised monomers is useful, post-functionalisation of ready grown polymers on the surface of a substrate is an invaluable strategy in the synthesis of polymer brushes.\(^{15,58,331,332}\) With this in mind, 9-anthracoyl chloride was synthesised from the corresponding acid using thionyl chloride and was attached to pre-grown surface-confined PHEMA brushes (Scheme 99). This strategy was chosen as it is straightforward, and reagents are both cheap and readily available. A wealth of expensive and less readily available peptide coupling agents have been used in other examples.\(^{15}\) Anthracene was selected as the electronic and fluorescent properties it holds are well known.\(^{333,334}\)
Chapter 5: Substrates prepared by Surface-Initiated Atom Transfer Radical Polymerisation (SI-ATRP)

Scheme 99: Post-modification of PHEMA brushes with aromatic groups

Acyl chlorides provide an easy-to-attach functionality when coupling with PHEMA. The acyl chlorides were afforded by refluxing the carboxylic acid with thionyl chloride in chloroform. This method was preferred to warming in neat thionyl chloride, as it was found to give cleaner products with less signs of degradation. Attempts to couple the acid directly using esterification coupling agents such as DCC and PyBOP proved unsuccessful, perhaps due to the steric confinement caused by the brush regime. The anthracenoyl chloride was attached to pre-grown PHEMA brushes (thickness of 44.8 ±1.3 nm) in tetrahydrofuran with triethylamine as a secondary base. The resulting film thickness on the substrate was measured by ellipsometry and the data obtained is outlined in Table 16.

Table 16: Percentage increase in thickness of PHEMA films post-functionalised with anthracene groups

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ar</th>
<th>Total film thickness (nm)</th>
<th>Increase in thickness (%)</th>
<th>Increase in molecular wt. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None (PHEMA)</td>
<td>44.8 ±1.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td><img src="image" alt="Anthracene" /></td>
<td>133.0 ±2.2</td>
<td>196.9 ±5.0</td>
<td>156.9</td>
</tr>
</tbody>
</table>

The data obtained suggests that there was attachment of the anthracene groups to the polymer. The percentage change in thickness and molecular weight were similar after
post modification. This increase in thickness can be attributed to the increased volume of the repeat unit. This is suggestive of a relatively high yield from the reaction, assuming there was no degrafting of the PHEMA chains. The perceived thickness to percentage yield ratio will drop as refractive index increases, as the ellipsometric model used assumed a refractive index of 1.5. As brushes become more aromatic in nature, the refractive index will increase, and therefore the interaction with visible light will increase, resulting in a film that appears thinner than it truly is when characterised. Fixing the refractive index at 1.5 for the ellipsometry model was chosen as a median point between the refractive indexes of PHEMA (1.4) and polystyrene (an aromatic polymer, RI = 1.6). In summary, a change in thickness suggests that something was successfully attached to the polymer brushes.

The functionalised anthracene samples were of particular interest because, as mentioned previously, the electronic and fluorescent properties are well documented. When placed under a UV light (of wavelength 365 nm), the sample was observed to fluoresce blue light. This suggested that these brushes exhibit fluorescent behaviour, and absorption and emission spectra would give a good indication of successful anthracene attachment. It should be noted that some of the samples were produced on glass slides, in parallel with the silicon wafers. All types of substrate were exposed to the same initiator deposition conditions (using the vacuum oven at 1-2 mbar) and immersed in the same polymerisation solutions for all the work undertaken. We consider the results to be parallel; whereby data for one type of substrate may be difficult to obtain (e.g. ellipsometry of glass substrates, UV transmission of silicon) it is assumed that the data attained from a glass substrate is the same as the data that would be obtained from a silicon wafer exposed to identical conditions, and vice versa. It was felt that this is justified because all have the same hydroxyl-terminated surface chemistry and in turn functional silanes attach in a similar way to both types of substrate.

UV-Vis (Figure 66) and fluorescence (Figure 67) spectra of the PHEMA-anthracene (PAnt-HEMA) samples showed characteristic anthracene traces, and the addition of anthracene was confirmed by FTIR with the appearance of aromatic C-C peaks in the fingerprint region (below 1000 cm⁻¹) and a new carbonyl peak at 1797 cm⁻¹, as well as the disappearance of the broad OH peak around 3500 cm⁻¹, illustrated in Figure 68.
**Figure 66**: UV-Vis spectrum of PAnt-HEMA post modified brushes on glass slides. Blue line shows spectra of PHEMA on glass and green line shows free anthracene for reference.

The red trace seen in the UV-Vis spectra in Figure 66 suggests two things: firstly, the change between the PHEMA brushes (blue trace) and the anthracene-modified brushes (red trace) is evident, as the PHEMA brushes showed virtually no absorbance trace. This attached group was clearly anthracene as the peaks resemble those in the free anthracene trace (green trace). Secondly, the redshift of the modified brush trace compared to the free anthracene trace by 10 nm suggests an extension of conjugation. This would infer that the anthracene groups of the modified polymer fell in to some degree of alignment (i.e. π-stacking).
Figure 67: Fluorescence emission spectrum of PAnt-HEMA post-modified brushes on glass slides, excited at a wavelength of 300 nm. Blue line shows spectra of PHEMA on glass and green line shows free anthracene for reference.

The fluorescence emission spectrum in Figure 67 confirms some further details about the intrinsic properties of the modified PHEMA brushes. As with the UV-Vis spectra, the change between the PHEMA brushes (blue trace) and the anthracene-modified brushes (red trace) was evident, as the PHEMA brushes show no fluorescent emission. The attached group was clearly anthracene as the peaks resemble those in the free anthracene trace (green trace), despite being slightly masked by the low resolution of the instrument used (operated at a high bandwidth to create detectable levels of fluorescence). The maximal intensity at 470 nm ($\lambda_{max}$) explains why the sample appeared blue when irradiated with UV light, as blue light has an emission wavelength of between 450 and 490 nm. The substantial redshift of the modified brush trace compared to the free anthracene trace (approximately 100 nm) suggests a very extensive network of conjugation. This significant shift indicates that the anthracene groups of the modified polymer aligned to a high degree (i.e. high level of $\pi$-stacking, low disorder). Finally, the saturated peaks at 600 nm in the PAnt-HEMA and PHEMA traces can be ignored: these are the second order harmonic peaks of the excitation light at 300 nm. These are intrinsic peaks that cannot be removed when using instruments with a diffraction grating based monochromator (rather than a prism based monochromator).
Figure 68: IR spectrum of PHEMA brushes and PHEMA brushes modified with anthracene groups (PAnt-HEMA). Free anthracene trace included for reference

The FTIR spectra in Figure 68 confirmed the successful attachment of the anthracene groups, with the appearance of aromatic C-C peaks in the fingerprint region of the PAnt-HEMA (red) trace at 848 cm\(^{-1}\) and 671 cm\(^{-1}\) that correspond to the peaks at 871 cm\(^{-1}\) and 717 cm\(^{-1}\) in the free anthracene spectrum (green trace). Some shifting to lower wavenumbers in the PAnt-HEMA is not unexpected, as this is akin to the redshifts (to higher wavelength, i.e. lower wavenumbers) seen in the UV-Vis and fluorescence spectra discussed previously. The formation of a new ester linkage at the terminal hydroxyl site of the PHEMA was confirmed by a new carbonyl peak at 1797 cm\(^{-1}\), as well as the disappearance of the broad OH peak seen in the PHEMA (blue) trace at around 3500 cm\(^{-1}\).

The possibility that the anthracene acyl chloride (or derivative) may only have been physisorbed within the brushes and not physically attached was also explored. After vigorous Soxhlet extraction of the substrates for 48 h in toluene, the UV, fluorescence and FTIR data showed no significant change, suggesting covalent attachment of the anthracene group to the polymer.

5.6.2. Post-modified PHEMA-PDMAEMA diblocks

With a diblock bulk heterojunction photovoltaic device application in mind, the feasibility of whether the polymerisation could still be restarted from these post-functionalised PAnt-HEMA brushes was investigated. Using the ATRP conditions for PDMAEMA growth mentioned
previously, we attempted to create a diblock by leaving the PAnt-HEMA wafer immersed in the PDMAEMA ATRP solution for 24 hours. Ellipsometry suggested a film thickness increase of 177 nm (±8 nm, averaged over five samples). FTIR (Figure 69) also suggested successful growth of a PDMAEMA layer, with an obvious change in the peak profiles of the fingerprint region (670 cm⁻¹) and the carbonyl environments (1750 cm⁻¹). If fabricated into a device, the intention is for the quaternisable nitrogen groups to act as hole carriers in this system, and the anthracene polymer to act as an electron carrier.

![Figure 69: IR spectrum of PHEMA brushes modified with anthracene groups (PAnt-HEMA), PDMAEMA brushes and attempted diblock growth (PAnt-HEMA-block-PDMAEMA)](image)

The FTIR spectra in Figure 69 confirmed the successful growth of a diblock. Firstly, there was a change in the anthracene peak profile in the fingerprint region (671 cm⁻¹), suggesting a relative decrease in the overall percentage of the polymer that is made up of anthracene-modified PHEMA. This would be expected when adding non-anthracene groups (i.e. PDMAEMA) to the existing polymer. There was also a change in the carbonyl environments. The ratio between the peaks at 1728 cm⁻¹ and 1813 cm⁻¹ increased in favour of the 1728 cm⁻¹ peak. This peak is clearly seen in the PDMAEMA (green) trace. The 1813 cm⁻¹ peak is clearly seen in the PAnt-HEMA (blue) spectrum, and decreased for the same reasons as the peak at 671 cm⁻¹. Finally, the PDMAEMA peaks present at 2808 cm⁻¹ and 2746 cm⁻¹ were also observed in the diblock. These can only come from successful growth of DMAEMA on top of the PAnt-HEMA block, as the reference spectrum of PAnt-HEMA did not show these peaks, so they must be contributed by the PDMAEMA block.
Subsequently, attempts to quaternise the PDMAEMA brushes with anthracene using an anthracyl chloride were unsuccessful (no increase in brush thickness was observed, no obvious changes in the FTIR spectra) when using the procedure of Armes et al.\textsuperscript{340} This could be due to two things. Firstly, the sterically bulky size (rigid and planar) of the anthracene group will be preventing the quaternising group from being within close enough proximity to the tertiary nitrogen of the PDMAEMA to react. Secondly, the electron rich anthracene system is reducing the required electron withdrawing effect of the chloride on the electrophilic CH\textsubscript{2} that is necessary to facilitate such a substitution, illustrated by the mechanism in Figure 70.

![Figure 70: Attempted quaternisation of PDMAEMA with anthracene methyl chloride](image)

5.6.3. Post-modification with other polyaromatic species

With the success seen with anthracene attachment to PHEMA brushes, other polyaromatic species were used to post-modify PHEMA brushes. With this in mind, various acyl chlorides were synthesised from the corresponding acid using thionyl chloride and were attached to pre-grown surface confined PHEMA brushes. This strategy was retained as it is straightforward, and reagents are both cheap and readily available. The resulting film thickness on the substrate was measured by ellipsometry and the data obtained is outlined in Table 17 and Figure 71.
Table 17: Percentage increases in thickness of PHEMA films post-functionalised with polyaromatic groups

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ar</th>
<th>Total film thickness (nm)</th>
<th>Increase in thickness (%)</th>
<th>Increase in molecular wt. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None (PHEMA)</td>
<td>44.8 ±1.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td><img src="image1" alt="Chemical Structure" /></td>
<td>133.0 ±2.2</td>
<td>196.9 ±5.0</td>
<td>156.9</td>
</tr>
<tr>
<td>3</td>
<td><img src="image2" alt="Chemical Structure" /></td>
<td>102.8 ±22.2</td>
<td>129.4 ± 28.8</td>
<td>118.5</td>
</tr>
<tr>
<td>4</td>
<td><img src="image3" alt="Chemical Structure" /></td>
<td>104.6 ±17.5</td>
<td>133.5 ±23.4</td>
<td>99.2</td>
</tr>
<tr>
<td>5</td>
<td><img src="image4" alt="Chemical Structure" /></td>
<td>80.5 ±5.3</td>
<td>79.7 ±4.4</td>
<td>81.5</td>
</tr>
<tr>
<td>6</td>
<td><img src="image5" alt="Chemical Structure" /></td>
<td>76.4 ±9.9</td>
<td>70.5 ±7.0</td>
<td>87.7</td>
</tr>
</tbody>
</table>
Figure 71: Percentage increase in ellipsometric thickness against percentage increase in molecular weight when post-functionalising PHEMA with polyaromatic groups on silicon wafers.

The data obtained suggests that attachment of functional groups to the polymer was successful. None of these post-polymerisation modified polyaromatic brush examples have been previously seen in the literature; they are novel to this work. The percentage change in thickness and molecular weight were similar after post modification. This increase in thickness can be attributed to the increased volume of the repeat unit. This is suggestive of a relatively high yield from these reactions, assuming there was no degraffing of the PHEMA chains. The perceived thickness to percentage yield ratio will drop as refractive index increases, as the ellipsometric model used assumed a refractive index of 1.5. As brushes become more aromatic in nature, the refractive index will increase, and therefore the interaction with visible light will increase, resulting in a film that appears thinner than it truly is when characterised. Fixing the refractive index at 1.5 for the ellipsometry model was chosen as a median point, as the refractive indexes of PHEMA (1.4) and polystyrene (an aromatic polymer, RI = 1.6). In summary, a change in thickness suggests that something has been successfully attached to the polymer brushes. The larger errors associated with the naphthoyl and cyanobenzoyl films are due to the interaction of the red light of the ellipsometer laser with the blue interference of the polymer thin films. This is an intrinsic error of the characterisation technique. Ellipsometry using a laser of any given wavelength will have issues in certain regions of delta/psi model, as there are multiple solutions to the model. This model can be seen in Figure 72.
Figure 72: Silicon-PHEMA Psi/ Delta to Film Thickness Model for Ellipsometry at 633 nm

5.6.4. Functionalised monomers

With the desire to manufacture a π-stacked polymer, the synthesis of monomers to create such polymers was also undertaken. These were methacrylates by design, with a polyaromatic group attached using simple esterification chemistry. We decided to focus primarily on anthracyl monomers again, as the fluorescent and electronic behaviour of anthracene is well documented. Upon searching the literature, we could not find any previous examples of polymer brushes with anthracene side chain functionality, so these brushes would also be novel.
Chapter 5: Substrates prepared by Surface-Initiated Atom Transfer Radical Polymerisation (SI-ATRP)

Scheme 100: Synthesis of anthracen-9-yl methacrylate

The first target was anthracen-9-yl methacrylate (Scheme 100). The monomer is a known compound in the literature, but thus far it has only been polymerised in one example: in solution and using a molar ratio of 50:1 AIBN initiator to monomer. ATRP is yet to be attempted with this monomer. Using anthrone, attempts were made to deprotonate and form the enolate and to then quench this intermediate with methacryloyl chloride. Firstly, pyridine was used and the reaction only returned starting materials. Although reported as successful in the literature, no yield was reported. It was inferred that the pKₐ of the aliphatic protons was higher than 5 (as the pKₐ of pyridinium salt ca. 5) so a stronger base was needed, and when trying sodium hydride (pKₐ ca. 35) instead the product was afforded in 85% yield. However, this product was not polymerisable by ATRP when using a ratio of 10:1 [Cu(I)]:[Cu(II)] in relatively high concentration (1.0 mol%: 0.1 mol%) with 10 mol% of bpy ligand, in a 1:1 v/v co-solvent of methanol and water. Its use may be limited due to the lack of carbon units between the potential polymer backbone and the anthracyl group; there may not be sufficient sp³ centres to allow sufficient rotation when the anthracyl groups attempt to stack up.

Scheme 101: Preliminary synthesis of anthracen-9-ylmethyl methacrylate

To allow more degrees of freedom by introducing another sp³ hybridised carbon, the synthesis of anthracen-9-yl methyl methacrylate was also undertaken. A similar methodology to the previous synthesis was undertaken, using anthracen-9-yl methanol and methacryloyl chloride, with a base to mop up the hydrochloric acid liberated (Scheme 101). Several sets of conditions were utilised, and are summarised in Table 18.
Table 18: Conditions used to synthesise anthracen-9-ylmethyl methacrylate

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base used</th>
<th>Additives</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Et₃N</td>
<td>None</td>
<td>17%</td>
</tr>
<tr>
<td>2</td>
<td>pyridine</td>
<td>None</td>
<td>25%</td>
</tr>
<tr>
<td>3</td>
<td>Et₃N</td>
<td>DMAP</td>
<td>37%</td>
</tr>
<tr>
<td>4</td>
<td>pyridine</td>
<td>DMAP</td>
<td>49%</td>
</tr>
</tbody>
</table>

As can be seen in Table 18, two conclusions can be made. Firstly, the use of pyridine as a base was much better than the use of triethylamine as a base for this reaction. Although the pKₐ of pyridine (~5) is lower than that of triethylamine (~11), the pyridine yielded better results. As these are mopping up bases (quenching the hydrochloric acid yielded by the esterification reaction), it would suggest that the pKₐ of the anthryl protons may be low enough to be deprotonated by triethylamine but not pyridine, and therefore lies somewhere between 5 and 11. Comparing to similar compounds and proton environments in pKₐ tables suggests this could be possible. Secondly, the use of 4-dimethylaminopyridine (DMAP) as an additive to activate the methacryloyl chloride by making the carbonyl more nucleophilic appeared to increase yield significantly. The mechanism for catalytic DMAP activation of methacryloyl chloride is outlined in Scheme 102.

![Scheme 102: Catalytic activation of methacryloyl chloride using DMAP](image)

Although the yield of this procedure (49%) was deemed acceptable, the synthesis itself was not particularly clean, the crude TLC (several, streaking spots, hard to resolve) and ¹H NMR (suggested a complex mixture of several aromatic and polyaromatic products) spectrum showed multiple products that were very difficult to separate by recrystallisation in several polar and non-polar solvents, and by column chromatography. An alternative strategy was to try coupling sodium methacrylate with 9-(chloromethyl)anthracene (Scheme 103). 9-(chloromethyl)anthracene was synthesised with relative simplicity from the alcohol by
refluxing in thionyl chloride,\textsuperscript{347} to give >99% purified yield, so it was not felt necessary to try and develop a procedure to improve this.

Scheme 103: \(\text{S}^{-}\text{N}^{-}\text{1}\)-promoted and \(\text{S}^{-}\text{N}^{-}\text{2}\)-promoted synthesis of anthracen-9-ylmethyloxyl methacrylate

9-(chloromethyl)anthracene was then put into two solutions: one with methanol as the solvent (a polar protic solvent, which should favour the \(\text{S}^{-}\text{N}^{-}\text{1}\) pathway) and \(N,N\)-dimethylformamide (an aprotic solvent, which should favour the \(\text{S}^{-}\text{N}^{-}\text{2}\) pathway). The product was both much cleaner (crude product) and attained in higher yield (pure product) for the reaction conducted in DMF, suggesting that the reaction prefers to react via a \(\text{S}^{-}\text{N}^{-}\text{2}\) pathway (Scheme 104). Both the \(\text{S}^{-}\text{N}^{-}\text{1}\) and \(\text{S}^{-}\text{N}^{-}\text{2}\) pathways to synthesise this monomer are unpublished in the literature and are thus a novel short and simple synthesis to the target compound.

Scheme 104: Coupling sodium methacrylate and (9-chloromethyl)anthracene via the favoured \(\text{S}^{-}\text{N}^{-}\text{2}\) pathway

Attempts thus far to polymerise this monomer in solution have proved unsuccessful (monomers are returned) by both classical free-radical polymerisation initiated with 2 mol% AIBN in toluene at 60 °C for 24 h, and by ARGET-ATRP using a ratio of 10:1 sodium ascorbate to copper(II) bromide in relatively high concentration (10 mol%:1.0 mol%) with 10 mol% of bpy ligand, in a 1:1 v/v co-solvent of methanol and water, at room temperature for 24 h (Scheme
Chapter 5: Substrates prepared by Surface-Initiated Atom Transfer Radical Polymerisation (SI-ATRP)

105). It is thought that the anthracene group could be acting as a radical trap\textsuperscript{348,349}, resulting in termination of the polymerisation before it has begun, or at very low molecular weight. Anthracene is known to be stable in anionic\textsuperscript{40} and cationic\textsuperscript{348,349} radical forms. The inability to form a homopolymer with this monomer also leads to suggestion that the anthracen-9-yl methacrylate (with less degrees of freedom) would also not favour polymerisation for the same reason. Post-modification of poly(sodium methacrylate), both brushes and free polymer using the same conditions as the monomer synthesis (substituting sodium methacrylate for the polymeric equivalent) was also unsuccessful.

![Scheme 105: Attempted homopolymer polymerisations of anthracen-9-yl methacrylate](image)

Synthesis of a complimentary acridine group to attach to sodium methacrylate in a similar fashion to (9-chloromethyl)anthracene proved unsuccessful. Acridine functionality would be desirable, as nitrogen is relatively stable when positively charged, allowing the generation of electron holes in an acridine functionalised polymer layer.\textsuperscript{350} Firstly, 9-methylacridine was successfully synthesised, via the Bernthsen synthesis (Scheme 106).\textsuperscript{351} Attempts to synthesise (9-chloromethyl)acridine (with a view to attaching this to sodium methacrylate via similar chemistry to that illustrated with anthracene) by this method from chloroacetic acid and diphenylamine were unsuccessful; no reaction occurred and starting materials were returned. It is thought that the chlorine on the chloroacetic acid is too electron withdrawing and negates the activating effect of the zinc(II) chloride. Radical chlorination of 9-methylacridine using N-chlorosuccinimide and AIBN in cyclohexane was also unsuccessful, suggesting preferential formation of chlorinated cyclohexyl derivatives over the desired product.\textsuperscript{352} (Scheme 107). After attempting to dissolve in toluene, xylene, cyclohexane, n-hexane and pentane without success, a solvent that would dissolve the acridine but would not be chlorinated could not be found.
Chapter 5: Substrates prepared by Surface-Initiated Atom Transfer Radical Polymerisation (SI-ATRP)

5.7. Investigation of covalent surface attachment

One uncertainty in the process is that there is no definitive evidence to suggest whether or not the surface attachment is truly covalent, despite a plethora of literature discussing APTES deposition. Raman studies were undertaken to attempt to prove, or disprove, the covalent attachment of APTES to silicon surfaces.
Using silicon nanoparticles, the RCA-SC-1, APTES deposition, BIBB attachment procedure was followed (Scheme 108).

**Scheme 108:** Progressive treatment of Si surfaces for polymer brush growth

Samples were then analysed by Raman spectroscopy.

### 5.7.1. Raman spectroscopy

The Raman results were expected to show an enhanced spectrum due to the surface attachment of the APTES. The obtained spectra are shown in Figure 73.

**Figure 73:** Raman spectra of progressive treatment of Si surfaces for polymer brush growth. Black – SiOH standard, Blue – RCA-cleaned Si, Green – APTES treated, Red – BIBB treated
It can be seen in Figure 73 that the RCA cleaned (blue line) Si powder showed a distinct shift in the Si-O peak at 521.43 cm\(^{-1}\) for the Si 111 standard down to 519.05 cm\(^{-1}\) – a significant shift in Raman spectroscopy away from the Si-OH standard at 521 cm\(^{-1}\), suggesting a new silicon environment was formed - concurrent with covalent APTES attachment. Attachment of APTES then suggested further success as the peak again shifts to 517.86 cm\(^{-1}\). Attachment of BIBB to APTES has no profound effect on the silicon environments, and there was no further shift. An increasing broadness of the shoulder at ca. 505 cm\(^{-1}\) also suggested multiple silicon environments on the surface. These results were encouraging to suggest attachment of APTES to a RCA-SC-1 cleaned silicon surface.

### 5.8. Future work

Some initial success was found with ferrocene ligands, this work could be taken further with enough time to optimise conditions, monomer synthesis etc. The redox chemistry of ferrocene is well understood. Ferrocene and its derived compounds readily undergo reversible oxidation.\(^{358}\) This would make it a good candidate for transporting charge, which in turn could be useful for electron excitement in applications such as OLEDs.\(^{359}\)

Following a similar strategy to the anthracene post modifications, work was undertaken to produce a ferrocenyl monomer, as well as a ferrocene acid chloride for the post modification of PHEMA brushes. A preparatory method from Organic Syntheses\(^{360}\) was undertaken, outlined in Scheme 109.

**Scheme 109:** Attempted synthesis of ferrocene carboxylic acid

The initial formation of the (2-chlorobenzyl)ferrocene was successful, but the hydrolysis step was not possible. Reeves notes that the molar ratio of potassium tert-butoxide to water is critical, and the amounts specified in the original paper represent optimum quantities for cleavage of 100 mmol of ketone\(^{360}\). These were scaled down accordingly but with no success after several attempts. However, as an alternative, a direct carboxylation attempt proved successful, using deprotonation with a strong base (\(n\)-butyllithium) and direct addition of carbon dioxide.

Chlorination of the acid was performed in thionyl chloride as previously described. Attachment to the PHEMA brushes proved unsuccessful during these initial studies. If the post-modification...
can be successful, this is another brush system (ferrocenyl groups coupled with PHEMA) that is unseen in the literature by the post-modification approach. As mentioned, the ability of ferrocene compounds to readily undergo reversible oxidation\textsuperscript{158} make it a good candidate for transporting charge. FTIR showed characteristic ferrocene signals at 1487 and 1448 cm\textsuperscript{-1}. Brush thickness increased was rapid initially but then decayed over time (Figure 74). This suggests that the brushes may be degrading over the course of the experiment, or experiencing some degrafting. XPS analysis showed that the small amount of iron found in the samples was removed after 24 h Soxhlet extraction in dichloromethane. The small quantities observed before extraction (~4\%) were determined to have been dispersed in the polymer matrix, but not chemically bonded.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{plot.png}
\caption{Change in thickness of ferrocenyl modified PHEMA brushes over 24 h}
\end{figure}

\section*{5.9. Conclusions}

ARGET-ATRP was established as the optimal method over traditional ATRP for this work, due to the fact that it uses distinctly less copper-based salts. It is also more tolerant of mildly challenging conditions; the reaction does not have to be rigorously dried or deoxygenated. Should there be any contact with oxygen, the copper(I) species are easily regenerated by the reducing agent. The decrease in copper usage also makes it a much more “green” method than traditional ATRP.
Monolayers of (3-aminopropyl)triethoxysilane deposited in the vapour phase attain a better grafting density at lower pressures. This in turn leads to thicker polymer brush films. Film thickness in the dry state is proportional to the grafting density.

Polymer brushes and polymer brush diblocks of novel post-polymerisation anthracene-modified PHEMA and PDMAEMA have been successfully grown on silicon wafers and glass slides by both standard ATRP and ARGET-ATRP, with a view to using the diblocks of these polymers as effective photovoltaic devices. This is in light of their excellent fluorescence properties, displaying a clear ability to move electrons between energy levels to emit light. The kinetics of the growth of both polymers by ARGET and ATRP methods were studied to determine the degree to which each polymerisation is living; to determine that diblock growth would be possible. PHEMA brushes were noticeably more controlled then their PDMAEMA counterparts. PHEMA brushes were successfully modified with a range of polyaromatic acid chlorides. Focussing on anthracene, this attachment was further confirmed by a range of techniques, before successfully growing a brush diblock of the unfunctionalised and functionalised polymers.

Functionalised monomers were synthesised from either the corresponding alcohol and methacryloyl chloride or the chloro-precursor and sodium methacrylate. The sodium methacrylate approach is favoured, as when conducted in N,N-dimethylformamide the reaction proceeds cleanly and in respectable 65% yield via an $S_{N}2$ reaction mechanism. Homopolymers of these polyaromatic monomers have been elusive by several methods, due to problems with anthracene acting as a radical trap.$^{348,349}$
Chapter 6: Conclusions

Initially, several syntheses towards monomers for poly(phenyl isocyanide) and poly(quinoxaline-2,3-diyl) were undertaken. EDCI-assisted formylations of amines to form corresponding amides were both unreliable and irreproducible. Lewis acid-catalysed synthesis of the amides from the amines was incompatible with 1,2-phenylamines, but the literature method was repeatable for aniline. Dehydrations of the resulting amides were carried out using trichloromethyl chloroformate and phosphorus(V) oxychloride. These yielded impure and unisolatable products. Phase-transfer Hofmann carbylamine reactions gave some success, but again with no ability to isolate the required product. The desired monomers were quite obviously forming to some degree, identified by their pungent odour, in all the reactions attempted but their isolation and purification proved to be a stumbling block.

Attention was turned to the synthesis of poly(thiophene)s by Kumada catalyst-transfer polymerisation. The synthesis of a suitable monomer was attempted. Several methods were tried with varying success. The best method for Grignard-based monomer production was found to be using magnesium turnings at reflux in THF with elemental iodine as an activator, as this reacted successfully with a stock aldehyde. When attempting the polymerisation, some film growth had evidently occurred but it was very inhomogeneous (9% polymer coverage). It is thought that the air and moisture sensitivities of both the Grignard monomer and bis(1,5-cyclooctadiene)nickel(0) are responsible for the inconsistent results seen. More stringent anhydrous/oxygen-free conditions need to be used (e.g. glovebox), or reagents that are more tolerant to atmospheric conditions (e.g. palladium(0) catalysts) could be used instead.

After this, ring-opening metathesis polymerisation was explored as a possible avenue. The successful synthesis of several cyclopropenes (up to 55% yield) for use as monomers was carried out. However, the ROMP of these monomers failed and this was believed to be due to the inherent ester functionality incorporated into these monomers ligating with the Grubbs’ catalyst and hindering the subsequent formation of metalloccyclobutane intermediates.

ROMP of unsubstituted norbornene was successful. 20 mmol of Grubbs’ second generation catalyst in 2 mL of dichloromethane was determined as the best concentration for initiating substrates for ROMP. XPS studies suggested that vapour deposition of SAMs gave homogenous monolayers. Solution-phase depositions appear prone to depositing inhomogeneous multilayers. Vapour deposited SAMs give better grafting densities at lower
deposition pressures, leading to thicker polymer brushes. Promising initial results for vapour-phase ROMP yield film thicknesses in excess of 270 nm for poly(norbornene) in 1 min.

Finally, atom transfer radical polymerisation methods were investigated. ARGET-ATRP was determined as the favoured method as it uses lower quantities of copper. It is also more robust under normal conditions; the reaction mixture does not have to be rigorously dried or deoxygenated (although this is still good practice). Any contact with oxygen is counteracted by the reducing agent, and the copper(I) species are easily regenerated.

Functionalised ATRP monomers were synthesised in two ways, using either an alcohol and methacryloyl chloride or a novel approach utilising chlorinated species and sodium methacrylate. When the sodium methacrylate approach is conducted in N,N-dimethylformamide the reaction proceeds cleanly and in good (65%) yield via an S\textsubscript{N}2 reaction mechanism. Homopolymers of anthracene-functionalised methacrylate monomers have been difficult to synthesise by both copper-mediated ATRP and AIBN initiation due to problems with anthracene acting as a radical trap.\textsuperscript{348,349}

Polymer brushes and polymer brush diblocks of novel anthracene-derivatised post-polymerisation modified PHEMA and PDMAEMA have been successfully grown on silicon wafers and glass slides by both standard ATRP and ARGET-ATRP, with a view to using the diblocks of these polymers as effective photovoltaic devices. This is in light of their excellent fluorescence properties, displaying a clear ability to move electrons between energy levels to emit light in the blue region (450-490 nm). The kinetics of the growth of both polymers by the ARGET (PHEMA, 241 nm/ 24 h) and ATRP (PDMAEMA, 119 nm/ 24 h) methods were studied to determine the degree to which each polymerisation is living, to determine if diblock growth would be plausible. PHEMA brushes were noticeably more controlled and thicker than their PDMAEMA counterparts. Anthracene attachment (ca. 200% increase in thickness, slightly higher than MW increase) was confirmed by a range of techniques, before successfully growing a novel brush diblock of both the unfunctionalised (PHEMA-b-PDMAEMA) and functionalised (PAnt-HEMA-b-PDMAEMA) polymers.
Chapter 7: Experimental

All $^1$H and $^{13}$C NMR spectra were measured at 400.13 and 100.62 MHz respectively with a Bruker (Coventry, West Midlands, UK) DPX 400 MHz spectrometer, in the deuterated solvent quoted, using tetramethylsilane as the internal reference. Chemical shifts are given in parts per million (ppm) and J values are given in Hertz (Hz).

Infrared spectra were measured with either a Perkin-Elmer (Cambridge, Cambridgeshire, UK) Paragon 1000 FT-IR spectrophotometer, a Perkin-Elmer Spectrum 65 FT-IR spectrophotometer or a Perkin-Elmer Spectrum 100 FT-IR spectrophotometer. Thin film IR spectra were acquired using sodium chloride plates. Surface-attached spectra (for polymer brushes) were acquired without plates. Measurements were taken in transmittance mode using an initiator coated silicon wafer as a background. Samples were fixed with magnets against a steel sample plate with an aperture created from aluminium foil to eliminate parts of the IR beam that had not passed through the sample.

Raman spectra were collected on a Horiba Jobin Yvon (Stanmore, Middlesex, UK) LabRAM HR800 spectrometer using a 632.8 nm HeNe laser with 600 grating and 50x objective. 50% of the monochromatic light was filtered out. The hole size used was 300 μm and the slit aperture 150 μm. Multiscan collections were performed, with each scan comprising of 2 accumulations, each of 5 s exposure. The full range of each scan was 100-1200cm$^{-1}$. Data was analysed using LabSpec software v 5.25.

Mass spectra were recorded on a Thermo Fisher (Basingstoke, Hampshire, UK) Exactive with an ion max source and ESI probe fitted with an Advion triversa nanomate. The instrument has a mass range of 20-2,000 AMU.

Melting points were determined using a Stuart (Stone, Staffordshire, UK) SMP-3 melting point apparatus and are uncorrected.

Ellipsometry studies were conducted using a Gaertner Scientific (Skokie, Illinois, USA) L116-B rotating analyser ellipsometer, equipped with a 1 mW 632.8 nm helium-neon laser at an angle of incidence of 70°. The polariser was fixed at 45° for ellipsometry measurements. A refractive index of 1.5 was assumed$^{361,335}$ for the grafted polymer chains when processing the Ψ and Δ.
values with WVASE32 (J. A. Woolham Co., Inc., Lincoln, New England, USA). Calculated thicknesses are quoted in nanometres (nm).

XPS spectra were obtained using a VG Scientific (East Grinstead, West Sussex, UK) Escalab 5 Mark II X-Ray Photoelectron Spectrophotometer, with an unmonochromated aluminium X-Ray source. Shirley background correction\(^{362}\) was applied, and high-resolution peaks were fitted using XPSPEAK 4.1 (Raymund Kwok, The Chinese University of Hong Kong, Sha Tin, New Territories, Hong Kong).

Microwave reactions were performed in a Biotage (Uppsala, Uppsala County, Sweden) Initiator EXP 8 reactor in 2-5 or 20-25 mL crimped vials.

UV-Ozone cleaning of wafers was performed in a UVP Inc. (Cambridge, Cambridgeshire, UK) PR-100 UV-Ozone photo reactor.

Polymers were freeze-dried on a VirTis (Ipswich, Suffolk, UK) Benchtop “K” Series SLC freeze drier, capable of condenser temperatures from -55 °C to -105 °C.

All chromatographic manipulations used silica gel as the adsorbent unless otherwise stated. Reactions were monitored using thin layer chromatography (TLC) on aluminium-backed plates coated with Merck (Beeston, Nottinghamshire, UK) Kieselgel 60 F254 silica gel. TLC plates were visualized by UV radiation at a wavelength of 254 nm, or stained by exposure to an ethanolic solution of phosphomolybdic acid (acidified with concentrated sulfuric acid), followed by charring where appropriate. If any other visualisation method has been used it is stated within the experimental procedure to which it is relevant. Purification by column chromatography used Merck Kiesel 60 H silica adsorbent.

Silicon wafers (<100> orientation, boron-doped, 0-100 Ω.cm, ~500 μm thickness) were purchased from Compart Technology (Peterborough, Cambridgeshire, UK).

All reagents were obtained from Sigma-Aldrich (Gillingham, Dorset, UK), Alfa Aesar (Heysham, Lancashire, UK) or Fisher Scientific (Loughborough, Leicestershire, UK) unless otherwise stated and were used without further purification, unless specified in the appropriate procedure or detailed below.

Petroleum ether (bp 40-60 °C) and ethyl acetate were distilled from calcium chloride prior to use. Dichloromethane was distilled over calcium hydride, and in flame dried glassware under nitrogen if there was an anhydrous requirement. Anhydrous tetrahydrofuran was distilled from the sodium/benzophenone ketyl radical under an argon atmosphere in oven dried glassware.
Chapter 7: Experimental

RCA-SC-1 cleaning of silicon wafers

Silicon wafers were cut into strips approximately 1 cm wide and then cleaned and rendered hydrophilic by first washing sequentially with acetone, methanol and water, and then immersed for 15 min in a mixture of ammonia solution (35% wt., 20 mL), hydrogen peroxide solution (30% w/w, 20 mL) and distilled water (100 mL) at 75 °C. After 15 min the mixture was replaced with 100% distilled water, and then the substrates were removed, rinsed thoroughly with distilled water and dried under a stream of nitrogen gas, then transferred to a Petri dish for storage before subsequent functionalisation. Success of the cleaning was determined by visual inspection of the contact angle of the water on the silicon surface during the water rinsing. A low contact angle indicates a hydrophilic surface.

UV-Ozone cleaning of silicon wafers

Silicon wafers were cut into strips approximately 1 cm wide and then cleaned and rendered hydrophilic by placing into a UV-Ozone photoreactor approximately 1 cm away from the UV source, and then irradiating for ca. 15 min. The substrates were removed, rinsed thoroughly with distilled water and dried under a stream of nitrogen gas, then transferred to a Petri dish for storage before subsequent functionalisation. Success of the cleaning was determined by visual inspection of the contact angle of the water on the silicon surface during the water rinsing. A low contact angle indicates a hydrophilic surface.

RCA-SC-1 cleaning of silicon nanoparticles

Silicon powder (ca. 325 mesh, 1.00 g, 35.6 mmol) was placed for 15 min in a mixture of ammonia solution (20 mL, 35% wt.), hydrogen peroxide solution (20 mL, 30% w/w) and distilled water (100 mL) at 75 °C. Once cooled to room temperature the mixture was centrifuged at 2,500 rpm for 5 min before decanting the aqueous solution. The silicon powder was washed with distilled water (100 mL), and was centrifuged again at 2,500 rpm for 5 min before again decanting the aqueous solution. The silicon powder was then dried in a vacuum oven at 60 °C.
for 2 h to remove the remaining water before being stored in a vacuum desiccator (0.93 g, 32.9 mmol, 93% recovered). Raman $\nu_{\text{max}}$/cm$^{-1}$: 519.05 (Si-O).

**Functionalisation of silicon substrates with trialkoxysilanes via vacuum deposition**

RCA-SC-1 or UV-Ozone cleaned silicon substrates were placed on aluminium foil, and functionalised by exposure to a vapour of a trialkoxysilane (methoxy or ethoxy) using ca. 10 drops of the trialkoxysilane in an aluminium foil receptacle, contained within a vacuum oven or vacuum desiccator at 1-2 mbar for 30 min at room temperature. The vacuum was then broken and the substrates were then annealed in air at 110 °C for 30 min. Substrates were transferred to a Petri dish for storage before conducting subsequent reactions. Success of the deposition was determined by visual inspection of the contact angle of the water on the silicon surface during the water rinsing. The contact angle will be higher than the cleaned surface but will be relative to the hydrophilicity of the R group on the silane.

**Functionalisation of silicon substrates with trialkoxysilanes via solution deposition**

RCA-SC-1 or UV-Ozone cleaned silicon substrates were sealed in a flame dried Schlenk tube. The Schlenk tube was evacuated under reduced pressure and then purged with nitrogen. This cycle was conducted five times, and then the sealed tube was left under a slight positive pressure of nitrogen using a nitrogen filled balloon. Substrates were immersed in a solution of trialkoxysilane (methoxy or ethoxy, 1 mmol) in anhydrous toluene (20 mL), and left for 24 h. The wafers were then removed and exposed to air, washed sequentially with toluene, methanol and water. Substrates were dried under a stream of nitrogen, and then transferred to a Petri dish for storage before conducting subsequent reactions. Success of the deposition was determined by visual inspection of the contact angle of the water on the silicon surface during the water rinsing. The contact angle will be higher than the cleaned surface but will be relative to the hydrophilicity of the R group on the silane.
Chapter 7: Experimental

Functionalisation of silicon nanoparticles with (3-aminopropyl)triethoxysilane

A flame dried round bottomed flask was purged with nitrogen before being charged with RCA-SC-1 cleaned silicon nanoparticles (0.75 g, 26.7 mmol). The nanoparticles were suspended in a solution of (3-aminopropyl)triethoxysilane (6.25 mL, 5.91 g, 26.7 mmol) in anhydrous toluene (20 mL), and left for 24 h. The mixture was centrifuged at 2,500 rpm for 5 min before decanting the toluene solution. The silicon powder was washed with distilled water (100 mL), and was centrifuged again at 2,500 rpm for 5 min before decanting the aqueous solution. The silicon powder was then dried in a vacuum oven at 60 °C for 2 h to remove the remaining water before being stored in a vacuum desiccator (0.59 g, 21.0 mmol, 79% recovered). Raman $\nu_{\text{max}}/\text{cm}^{-1}$: 505.96 (Si-O), 517.86 (Si-O).

Functionalisation of substrates with 4-bromobenzoyl chloride

Substrates previously functionalised with (3-aminopropyl)triethoxysilane were sealed in a flame dried Schlenk tube. The Schlenk tube was evacuated under reduced pressure and then purged with nitrogen. This cycle was conducted five times, and then the sealed tube was left under a slight positive pressure of nitrogen using a nitrogen filled balloon. The substrate was immersed in a solution of 4-bromobenzoyl chloride (0.22 g, 1 mmol) in anhydrous tetrahydrofuran (50 mL). Triethylamine (0.14 mL, 0.10 g, 1 mmol) was dried over CaH$_2$ and then added. The reaction mixture was left for 1 h, then exposed to air. Substrates were then washed sequentially with tetrahydrofuran, methanol and water. Substrates were dried under a stream of nitrogen gas, and then transferred to a Petri dish for storage before undergoing polymerisation. It was evident that the condensation reaction had been successful as when washing with water the contact angle was high (i.e. surface is very hydrophobic).
Functionalisation of substrates with bicyclo[2.2.1]hept-5-ene-2-carbonyl chloride

Substrates previously functionalised with (3-aminopropyl)triethoxysilane were sealed in a flame dried Schlenk tube. The Schlenk tube was evacuated under reduced pressure and then purged with nitrogen. This cycle was conducted five times, and then the sealed tube was left under a slight positive pressure of nitrogen using a nitrogen filled balloon. The substrate was immersed in a solution of bicyclo[2.2.1]hept-5-ene-2-carbonyl chloride (0.16 g, 1 mmol) in anhydrous tetrahydrofuran (20 mL). Triethylamine (0.14 mL, 0.10 g, 1 mmol) was dried over CaH₂ and then added. The reaction mixture was left overnight, then exposed to air. Substrates were then washed sequentially with tetrahydrofuran, methanol and water. Substrates were dried under a stream of nitrogen gas, and then transferred to a Petri dish for storage before undergoing initiation. It was evident that the condensation reaction had been successful as when washing with water the contact angle was high (i.e. surface is very hydrophobic).

Functionalisation of substrates with 2-bromoisobutyryl bromide

Substrates previously functionalised with (3-aminopropyl)triethoxysilane were sealed in a flame dried Schlenk tube. The Schlenk tube was evacuated under reduced pressure and then purged with nitrogen. This cycle was conducted five times, and then the sealed tube was left under a slight positive pressure of nitrogen using a nitrogen filled balloon. The substrate was immersed in a solution of 2-bromoisobutyryl bromide (0.63 mL, 1.17 g, 5 mmol) in anhydrous tetrahydrofuran (50 mL). Triethylamine (0.69 mL, 0.50 g, 5 mmol) was dried over CaH₂ and then added. The reaction mixture was left for 1 h, then exposed to air. Substrates were then washed sequentially with tetrahydrofuran, methanol and water. Substrates were dried under a stream of nitrogen gas, and then transferred to a Petri dish for storage before undergoing initiation.
polymerisation. It was evident that the condensation reaction had been successful as when washing with water the contact angle was high (i.e. surface is very hydrophobic).

**Functionalisation of silicon nanoparticles with 2-bromoisobutryl bromide**

A flame dried round bottomed flask was purged with nitrogen before being charged with silicon nanoparticles previously functionalised with (3-aminopropyl)triethoxysilane (0.50 g, 17.8 mmol). The nanoparticles were suspended in a solution of triethylamine (2.49 mL, 1.80 g, 17.8 mmol) (dried over CaH$_2$) in anhydrous tetrahydrofuran (20 mL). 2-Bromoisobutryl bromide (2.20 mL, 4.02 g, 17.8 mmol) was then added. The reaction mixture was left for 1 h, then exposed to air. The silicon powder was washed with distilled water (100 mL), and was centrifuged at 2,500 rpm for 5 min before decanting the aqueous solution. The silicon powder was washed again with distilled water (100 mL), and was centrifuged again at 2,500 rpm for 5 min before again decanting the aqueous solution. The silicon powder was then dried in a vacuum oven at 60 °C for 2 h to remove the remaining water before being stored in a vacuum desiccator (0.47 g, 20.2 mmol, 96% recovered). Raman $\nu_{\max}$/cm$^{-1}$: 509.53 (Si-O), 517.86 (Si-O).

**Attempted synthesis of N-phenylformamide**

Formic acid (8.00 mL, 9.62 g, 209 mmol) was dissolved in dichloromethane (100 mL) and charged to a round bottomed flask equipped with a magnetic stirrer bar and cooled to 0 °C. Aniline (3 mL, 3.06 g, 32.8 mmol) and $N$-methylmorpholine (11.00 mL, 11.82 g, 117 mmol) were added to the reaction mixture. A small amount of white gas evolved, and the reaction mixture changed colour from colourless to amber. EDCI (19.45 g, 101 mmol) was then added in small portions over 45 min. Some more white gas evolved. The reaction mixture was left to stir at 0 °C for 1 h and then allowed to warm to room temperature overnight. The reaction mixture was quenched with concentrated hydrochloric acid (32% w/v, 20 mL). A precipitate formed and
a white gas was evolved. Distilled water (50 mL) was added followed by dichloromethane (30 mL) and the layers separated, the aqueous phase was washed with dichloromethane (2 x 30 mL). The organics were dried over anhydrous magnesium sulfate, filtered and solvent was removed under reduced pressure. No product was isolated, and starting material was recovered.

**Synthesis of N-phenylformamide**

![Synthesis of N-phenylformamide](image)

Aniline (3.00 mL, 3.06 g, 32.8 mmol) and zinc(II) chloride (0.95 g, 7.00 mmol) were charged to a round bottomed flask. Formic acid (15.00 mL, 18.06 g, 130 mmol) was added. The reaction mixture was heated at 70 °C for 18 h. The reaction mixture was then allowed to cool to room temperature and diluted with ethyl acetate (40 mL). Distilled water (40 mL) was added and the layers separated, the organic phase was washed with more distilled water (2 x 20 mL) and then brine (2 x 10 mL). The organics were dried over anhydrous magnesium sulfate, filtered and solvent was removed under reduced pressure to yield a pale yellow solid (3.57 g, 29.5 mmol, 90%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.06-7.15 (4 H, m, 1/3/4/6), 7.24-7.34 (4 H, m, 1/3/4/6), 7.54-7.56 (2 H, m, 2), 8.11 (1 H, s, 7b), 8.65 (1 H, d, $J = 11.2$ Hz, 7a), 8.93 (1 H, s, 9), 9.48 (1 H, d, $J = 10.4$ Hz, 8). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 124.6 (4/6), 125.1 (2), 128.9 (1/3), 136.7 (5), 159.5 (7b), 163.0 (7a). IR $\nu_{max}$ (CHCl$_3$)/cm$^{-1}$: 3272 (N-H), 1710 (C=O). mp: 46.1-47.2 °C. m/z (ESI): 122.0633; C$_7$H$_8$NO (M + H$^+$) requires 122.0606.

**Attempted synthesis of N,N'-(1,2-phenylene)diformamide**

![Attempted synthesis of N,N'-(1,2-phenylene)diformamide](image)

o-Phenylendiamine (1.02 g, 9.40 mmol) and zinc(II) chloride (0.30 g, 2.16 mmol) were charged to a round bottomed flask. Formic acid (5.00 mL, 6.02 g, 130 mmol) was added. The reaction mixture was heated at 70 °C for 18 h. The reaction mixture was then allowed to cool to room temperature and diluted with ethyl acetate (40 mL). Distilled water (40 mL) was added and the layers separated, the organic phase was washed with more distilled water (2 x 20 mL) and then brine (2 x 10 mL). The organics were dried over anhydrous magnesium sulfate, filtered and solvent was removed under reduced pressure to yield impure starting material.
Synthesis of N,N’-(1,2-phenylene)diformamide

Formic acid (8.00 mL, 9.62 g, 209 mmol) was dissolved in dichloromethane (100 mL) and charged to a round bottomed flask equipped with a magnetic stirrer bar and cooled to 0 °C. o-Phenylenediamine (3.59 g, 33.2 mmol) and N-methylmorpholine (11.00 mL, 11.82 g, 117 mmol) were added to the mixture. A small amount of white gas evolved, and the reaction mixture changed colour from colourless to yellow. EDCI (19.66 g, 103 mmol) was then added in small portions over 45 min. Some more white gas evolved. The reaction mixture was left to stir at 0 °C for 4 h. The reaction mixture was quenched with concentrated hydrochloric acid (32% w/v, 15 mL). The mixture turned red and an orange precipitate formed, to which distilled water (50 mL) was added followed by dichloromethane (30 mL) and the layers separated, the aqueous phase was washed with dichloromethane (2 x 30 mL) and the combined organics washed with sodium hydrogen carbonate (20 mL). The organics were dried over anhydrous magnesium sulfate, filtered and solvent was removed under reduced pressure. This product was combined with the aqueous fractions and stirred to induce crystallisation. The solution was cooled in ice and filtered to yield a white solid (1.61 g, 9.8 mmol, 30%). $^1$H NMR (400 MHz, DMSO-d$_6$): δ 7.16-7.23 (2.5 H, m, 1/2/3/6), 7.32-7.34 (1.5 H, m, 1/2/3/6), 8.27 (2 H, s, 9/10), 9.64 (2 H, s, 7/8). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 125.2 (1/2), 125.6 (3/6), 126.1 (4/5), 160.3 (9/10). IR $\nu_{\text{max}}$ (KBr)/cm$^{-1}$: 3700-3400 (N-H), 1660 (C=O). mp: 153.1-154.9 °C. m/z (ESI): 164.0562; C$_8$H$_8$N$_2$O$_2$ (M$^+$) requires 164.0586.

Attempted synthesis of isocyanobenzene

Formanilide (0.128 g, 1.06 mmol) was charged to a 20 mL microwave vial equipped with a magnetic flea. Triethylamine (0.48 mL, 0.35 g, 3.5 mmol), dichloromethane (10 mL) and cyanuric chloride (0.58 g, 3.18 mmol) were added in the prescribed order at 0 °C. The vial was sealed immediately and irradiated by microwave radiation at 50 °C for 3 min. The reaction mixture was cooled to room temperature and diluted with more dichloromethane (40 mL). The organics were washed with saturated potassium hydrogen sulfate solution (2 x 20 mL). The
organic layer was dried over anhydrous magnesium sulfate, filtered and solvent was removed under reduced pressure. $^1$H NMR and thin layer chromatography (TLC) suggested that there was no formation of the desired product.

**Attempted microwave-assisted synthesis of 1,2-diisocyanobenzene**

\[ \text{N,N'}-(1,2-\text{Phenylene})\text{diformamide} (0.089 \text{ g}, 0.53 \text{ mmol}) \text{ was charged to a 20 mL microwave vial equipped with a magnetic flea. Triethylamine (0.48 mL, 0.35 g, 3.5 mmol), dichloromethane (10 mL) and cyanuric chloride (0.58 g, 3.18 mmol) were added in the prescribed order at 0 °C. The vial was sealed immediately and irradiated by microwave radiation at 50 °C for 3 min. The reaction mixture was cooled to room temperature and diluted with more dichloromethane (40 mL). The organic solution was washed with saturated potassium hydrogen sulfate solution (2 x 20 mL). The organic layer was dried over anhydrous magnesium sulfate, filtered and solvent was removed under reduced pressure. $^1$H NMR and thin layer chromatography (TLC) suggested that there was no formation of the desired product.} \]

**Synthesis of isocyanobenzene**

\[ \text{N-Phenylformamide} (5.04 \text{ g}, 41.60 \text{ mmol}) \text{ was dissolved in anhydrous dichloromethane (100 mL) in a flame dried two-neck round bottomed flask, equipped with a rubber septum and a nitrogen bubbler. The reaction mixture was cooled to -78 °C and triethylamine (11.5 mL, 8.37 g, 82.7 mmol) was added. A solution of phosphorus(V) oxychloride (4.5 mL, 7.40 g, 48.28 mmol) in anhydrous dichloromethane (20 mL) was added dropwise over 30 min. A white gas evolved, the reaction mixture was allowed to warm to room temperature and was left to stir overnight. The reaction mixture was then cooled to -15 °C and quenched with aqueous sodium hydrogen carbonate (saturated, 100 mL), the layers separated, the aqueous phase was washed with dichloromethane (3 x 20 mL) and the combined organics washed with water (50 mL). The organics were dried over anhydrous magnesium sulfate, filtered and solvent was removed under reduced pressure to yield a dark brown oil as a crude product (2.97 g, 69.7%). $^1$H NMR and thin layer chromatography (TLC) suggested a complex mixture of products, but a} \]
distinctive isonitrile odour was observed. Attempted purification through a pad of silica and Celite® using a solvent system of 2:1 v/v petroleum ether and ethyl acetate was unsuccessful. IR ν max (CH₂Cl₂)/cm⁻¹: 2204 (R-N≡C).

**Synthesis of isocyanobenzene**

\[ \text{N-Phenylformamide (5.00 g, 41.27 mmol) was dissolved in anhydrous dichloromethane (100 mL) in a flame dried two-neck round bottomed flask, equipped with a rubber septum and a nitrogen bubbler. The reaction mixture was cooled to -78 °C and triethylamine (11 mL, 7.99 g, 78.96 mmol) was added. A solution of trichloromethyl chloroformate (4.8 mL, 7.87 g, 39.77 mmol) in anhydrous dichloromethane (10 mL) was added dropwise. A white gas was evolved during this addition. The reaction mixture was allowed to warm to room temperature and was left to stir overnight. The reaction mixture was then cooled to -15 °C and quenched with aqueous sodium hydrogen carbonate (saturated, 100 mL), the layers separated, the aqueous phase was washed with dichloromethane (3 x 20 mL) and the combined organics washed with water (50 mL). The organics were dried over anhydrous magnesium sulfate, filtered and solvent was removed under reduced pressure to yield a dark brown viscous oil (5.8 g, >100%).} \]

\[ ^1H \text{NMR and thin layer chromatography (TLC) suggested a complex mixture of products, but a distinctive isonitrile odour was observed. IR } \nu_{\max} (\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}: 2204 (\text{R-N=C}). \]

**Synthesis of 1,2-diisocyanobenzene**

\[ \text{N,N'-(1,2-Phenylene)diformamide (0.49 g, 3 mmol) was dissolved in anhydrous dichloromethane (5 mL) in a flame dried two-neck round bottomed flask, equipped with a rubber septum and a nitrogen bubbler. The reaction mixture was cooled to -78 °C and triethylamine (2.4 mL, 1.74 g, 17.2 mmol) was added. A solution of trichloromethyl chloroformate (0.5 mL, 0.82 g, 4.1 mmol) in anhydrous dichloromethane (10 mL) was added dropwise. A white gas was evolved during this addition. The reaction mixture was allowed to warm to room temperature and was left to stir overnight. The reaction mixture was then cooled to -15 °C and quenched with aqueous sodium hydrogen carbonate (saturated, 20 mL), the layers separated, the aqueous phase was washed with dichloromethane (2 x 20 mL) and the} \]
combined organics washed with water (50 mL). The organics were dried over anhydrous magnesium sulfate, filtered and solvent was removed under reduced pressure to yield a dark brown viscous oil (0.47 g). $^1$H NMR and thin layer chromatography (TLC) suggested a complex mixture of products. A 2D-TLC suggested that the product would be unstable to purification by column chromatography. A distinctive isonitrile odour was observed. IR $\nu_{\text{max}}$(CH$_2$Cl$_2$)/cm$^{-1}$: 2254 (R-N$^+$≡C$^-$).

**Synthesis of isocyanobenzene**

Powdered sodium hydroxide (60.0 g, 1.5 mol) was added in small portions to water (60 mL) at 0 °C in a three neck flask equipped with a reflux condenser and a pressure equalising addition funnel. Aniline (40 mL, 40.88 g, 0.44 mol), chloroform (16 mL, 23.87 g, 0.2 mol) and benzyltriethylammonium chloride (0.5 g, 2.3 mmol, 0.5 mol%) were dissolved in dichloromethane (60 mL) and charged to the pressure equalising addition funnel. The mixture from the addition funnel was left to add dropwise over 1 h and then left to stir for a further 3 h. The reaction mixture refluxed under its own heat. The reaction mixture was then quenched with ice water (150 mL) and the layers separated, the aqueous phase was washed with dichloromethane (2 x 50 mL) and the combined organic extracts washed with saturated potassium hydrogen sulfate (2 x 50 mL), dried over anhydrous magnesium sulfate, filtered and solvent was removed under reduced pressure to yield a crude brown oil (40.1 g, 389 mmol, 89%). Purification by distillation and column chromatography resulted in decomposition. The distinctive isonitrile odour was observed. IR $\nu_{\text{max}}$(CH$_2$Cl$_2$)/cm$^{-1}$: 2126 (R-N$^+$≡C$^-$).

**Synthesis of 1,2-diisocyanobenzene**

Powdered sodium hydroxide (16.5 g, 411 mmol) was added in small portions to water (60 mL) at 0 °C in a three neck flask equipped with a reflux condenser and a pressure equalising addition funnel. $\alpha$-Phenylenediamine (3.00 g, 27.7 mmol), chloroform (70 mL, 104.4 g, 875 mmol) and benzyltriethylammonium chloride (0.1 g, 0.4 mmol, 1.5 mol%) were charged to
the pressure equalising addition funnel. The mixture from the addition funnel was left to add dropwise over 1 h and then left to stir for a further 3 h. The reaction mixture refluxed under its own heat. The reaction mixture was quenched with ice water (150 mL) and the layers separated, the aqueous phase was washed with dichloromethane (2 x 50 mL) and the combined organics washed with saturated potassium hydrogen sulfate (2 x 50 mL). The organics were dried over anhydrous magnesium sulfate, filtered and solvent was removed under reduced pressure to yield a crude brown oil (0.7 g, 5.54 mmol, 20%). Purification by distillation and column chromatography resulted in decomposition. The distinctive isonitrile odour\(^{365}\) was observed. IR \(\nu_{\text{max}} (\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}: 2120\) (R-N\(^+\)≡C).

### Synthesis of 1,4-diisocyanobenzene\(^{283}\)

Powdered sodium hydroxide (16.5 g, 411 mmol) was added in small portions to water (60 mL) at 0 °C in a three neck flask equipped with a reflux condenser and a pressure equalising addition funnel. \(p\)-Phenylenediamine (3.00 g, 27.7 mmol), chloroform (70 mL, 104.4 g, 875 mmol) and benzyltriethylammonium chloride (0.1 g, 0.4 mmol, 1.5 mol%) were charged to the pressure equalising addition funnel. The mixture from the addition funnel was left to add dropwise over 1 h and then left to stir for a further 3 h. The reaction mixture refluxed under its own heat. The reaction mixture was quenched with ice water (150 mL) and the layers separated, the aqueous phase was washed with dichloromethane (2 x 50 mL) and the combined organics washed with saturated potassium hydrogen sulfate (2 x 50 mL). The organics were dried over anhydrous magnesium sulfate, filtered and solvent was removed under reduced pressure to yield a crude brown oil (3.7 g. Purification by distillation and column chromatography resulted in decomposition. The distinctive isonitrile odour\(^{365}\) was observed. IR \(\nu_{\text{max}} (\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}: 2254\) (R-N\(^+\)≡C).

### Synthesis of (5-iodothiophen-2-yl)magnesium chloride\(^{116}\)

A flame dried Schlenk flask was charged with 2,5-diiodothiophene (0.334 g, 1 mmol) and was evacuated under reduced pressure and then purged with nitrogen. This cycle was conducted
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five times, and was then left under a slight positive pressure of nitrogen using a nitrogen filled balloon. The 2,5-diiodothiophene was then dissolved in anhydrous tetrahydrofuran (10 mL). The reaction mixture was cooled to 0 °C, and isopropyl magnesium chloride solution (2.0M in tetrahydrofuran, 0.45 ml, 0.9 mmol) was added slowly. The reaction mixture was left to stir and warm to room temperature for 1 h. The mixture was then used crude and immediately in subsequent reactions.

Synthesis of (5-iodothiophen-2-yl)magnesium iodide

Flame dried glassware was charged with oven dried magnesium turnings (0.056 g, 2.3 mmol) and ca. 2-3 drops of 1,2-dibromoethane under a nitrogen atmosphere. 2,5-diiodothiophene (0.86 g, 2.55 mmol) was dissolved in anhydrous tetrahydrofuran (20 mL). This solution was added to the magnesium turnings and the reaction mixture was left to reflux for 1 h. The mixture was then used crude and immediately in subsequent reactions.

-Or-

Flame dried glassware was charged with oven dried magnesium turnings (0.056 g, 2.3 mmol) and five iodine crystals under a nitrogen atmosphere. 2,5-diiodothiophene (0.86 g, 2.55 mmol) was dissolved in anhydrous tetrahydrofuran (20 mL). This solution was added to the magnesium turnings and the reaction mixture was left to reflux for 1 h. The mixture was then used crude and immediately in subsequent reactions.
Attempted synthesis of (5-iodothiophen-2-yl)(4-methoxyphenyl)methanol

A crude solution of (5-iodothiophen-2-yl)magnesium chloride in tetrahydrofuran (0.9 mmol max., ca. 20 mL) prepared as described previously, was cooled to 0 °C. 4-Methoxybenzaldehyde (0.27 mL, 0.30 g, 2.2 mmol) was added slowly. The reaction mixture was allowed to stir and warm to room temperature for 1 h. The reaction mixture was quenched with sulfuric acid (1M, 6 mL, 6 mmol). The aqueous layer was diluted with distilled water (20 mL), the product was extracted with dichloromethane (20 mL). The layers separated, the aqueous phase was washed with dichloromethane (2 x 20 mL) and the combined organics were dried over anhydrous magnesium sulfate, filtered and solvent was removed

Synthesis of (1-(5-iodothiophen-2-yl)-2-methylpropan-1-ol

A crude solution of (5-iodothiophen-2-yl)magnesium iodide in tetrahydrofuran (0.9 mmol max., ca. 20 mL) prepared as described previously, was cooled to 0 °C. Isobutyraldehyde (0.10 mL, 0.08 g, 1.1 mmol) was added slowly. The reaction mixture was allowed to stir and warm to room temperature for 1 h. The reaction mixture was quenched with sulfuric acid (1M, 6 mL, 6 mmol). The aqueous layer was diluted with distilled water (20 mL), the product was extracted with dichloromethane (20 mL). The layers separated, the aqueous phase was washed with dichloromethane (2 x 20 mL) and the combined organics were dried over anhydrous magnesium sulfate, filtered and solvent was removed under reduced pressure. The crude product was purified by column chromatography (9:1 v/v petroleum ether: ethyl acetate) to yield a yellow oil (0.13 g, 0.66 mmol, 73%).
\[^{1}\text{H} \text{NMR (400 MHz, CDCl}_3\text{): } \delta \text{ 0.89 (6H, d, } J = 6.0 \text{ Hz, } 7/8\text{), 1.87 (1H, hept, } J = 4.2 \text{ Hz, } 6\text{), 2.65 (1H, br s, } 9\text{), 4.58 (1H, d, } J = 6.8 \text{ Hz, } 5\text{), 7.18-7.27 (2H, m, } 2/3\text{).} \]

\[^{13}\text{C} \text{NMR (100 MHz, CDCl}_3\text{): } \delta \text{ 19.2 (7/8), 36.4 (6), 72.1 (5), 125.3 (3), 127.2 (2), 131.6 (1), 144.0 (4).} \]

IR \( \nu_{\text{max}} \) (CH\(_2\)Cl\(_2\))/cm\(^{-1}\): 3371 (OH), 1457 (thiophene), 1411 (thiophene).

m/z (ESI): 213.0144; \( \text{C}_8\text{H}_{11}\text{OSNa} \) (M + Na\(^+\)) requires 213.0117.

**Attempted synthesis of 1-(4-methoxyphenyl)-2-methylpropan-1-ol**

\[
\text{MgCl} \quad \text{MeO} \quad \overset{\text{THF, A, 16 h}}{\text{O}} \quad \text{OMe}
\]

Isopropyl magnesium chloride solution (2.0M in tetrahydrofuran, 0.5 mL, 1 mmol) was diluted further with anhydrous tetrahydrofuran (20 mL), and was cooled to 0 °C. 4-Methoxybenzaldehyde (0.12 mL, 0.14 g, 1 mmol) was added slowly. The reaction mixture was allowed to stir, and was heated at 50 °C overnight. The reaction mixture was quenched with sulfuric acid (1 M, 6 mL, 6 mmol). The aqueous layer was diluted with distilled water (20 mL), the product was extracted with dichloromethane (20 mL). The layers separated, the aqueous phase was washed with dichloromethane (2 x 20 mL) and the combined organics were dried over anhydrous magnesium sulfate, filtered and solvent was removed under reduced pressure to yield starting material.

**Initiation of substrates with bis(1,5-cyclooctadiene)nickel(0)**

Substrates previously functionalised with 4-bromo-benzamide terminal groups were sealed in flame dried Schlenk tubes. The Schlenk tubes were evacuated under reduced pressure and then purged with nitrogen. This cycle was conducted five times, and then each sealed tube was left under a slight positive pressure of nitrogen using a nitrogen filled balloon. The substrate was immersed in a 0.05% wt. solution of bis(1,5-cyclooctadiene)nickel(0) (9 mg, 0.03 mmol)
and triphenylphosphine (39 mg, 0.14 mmol) in anhydrous toluene (10 mL). The reaction mixture was left for 16 h, then exposed to air. Substrates were then washed sequentially with toluene and methanol. Substrates were dried under a stream of nitrogen, and then transferred to a Petri dish for storage before undergoing polymerisation.

**Synthesis of poly(thiophene) brushes via SI-KCTP**

Nickel-initiated 4-bromo-benzamide silicon substrates were sealed in flame dried Schlenk tubes. The Schlenk tubes were evacuated under reduced pressure and then purged with nitrogen. This cycle was conducted five times, and then each sealed tube was left under a slight positive pressure of nitrogen using a nitrogen filled balloon. The substrate was immersed in a solution of unpurified (5-iodothiophen-2-yl)magnesium chloride in anhydrous tetrahydrofuran (5 mL). The reaction mixture was left for 16 h, then exposed to air. Substrates were then washed sequentially with 1 M hydrochloric acid then tetrahydrofuran, toluene, methanol and water. Substrates were dried under a stream of nitrogen and observed by ellipsometry. Ellips.: (HeNe, 632.8 nm; θ, 70°) 156 nm (Composition approximated to be 9% polymer coverage).

**Synthesis of methanesulfonyl azide**

Under a nitrogen atmosphere, methanesulfonyl chloride (10.14 mL, 15.00 g, 130 mmol) was dissolved in acetone (100 mL). Sodium azide (10.14 g, 156 mmol) was then added in small portions over 30 min. The reaction mixture was left to stir at room temperature for 4 h. The reaction mixture was quenched with distilled water (100 mL). The product was extracted with diethyl ether (2 x 50 mL) and the combined organics were washed with brine (20 mL), dried over anhydrous magnesium sulfate, filtered and solvent was removed under reduced pressure to yield a colourless liquid (15.11 g, 125 mmol, 96%).
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$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 3.29 (3H, s, 1). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 42.7 (1).
IR $\nu_{\text{max}}$ (CH$_2$Cl$_2$)/cm$^{-1}$: 2359 (N=N=N), 1182 (SO$_2$). m/z (ESI): 143.9838; CH$_3$SO$_2$N$_3$Na (M + Na$^+$) requires 143.9838.

**Synthesis of dimethyl 2-diazo malonate**

![Diagram of dimethyl 2-diazo malonate]

Dimethyl malonate (4.30 mL, 4.96 g, 37.56 mmol) and methanesulfonyl azide (3.10 mL, 5.00 g, 41.42 mmol) were charged to a flame dried round bottomed flask under a nitrogen atmosphere, and were dissolved in anhydrous acetonitrile (60 mL). The reaction mixture was cooled to 0 °C. Triethylamine (11.50 mL, 8.36 g, 82.64 mmol) was dried over CaH$_2$ and then added dropwise. The reaction mixture was allowed to warm to room temperature and left to stir overnight under a nitrogen atmosphere. The solution was concentrated under reduced pressure and the resulting residue was dissolved in a 1:1 v/v solution of petroleum ether and chloroform (40 mL). The resulting precipitate was removed by filtration on a Büchner funnel, and the filtrate was dried over anhydrous magnesium sulfate, filtered and solvent was removed under reduced pressure to yield a yellow liquid (5.92 g, 125 mmol, 90%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 3.84 (6H, s, 1/5). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 52.1 (1/5), 65.1 (3), 161.0 (2/4). IR $\nu_{\text{max}}$ (CH$_2$Cl$_2$)/cm$^{-1}$: 2137 (C=N=N), 1761 (C=N=N), 1695 (C=O). m/z (ESI): 181.0263; C$_5$H$_6$O$_4$N$_2$Na (M + Na$^+$) requires 181.0225.

**Synthesis of 2-phenyl-cycloprop-2-ene-1,1-dicarboxylic acid dimethyl ester**

![Diagram of 2-phenyl-cycloprop-2-ene-1,1-dicarboxylic acid dimethyl ester]

Phenylacetylene (10.40 mL, 9.70 g, 95 mmol) and rhodium acetate dimer (140 mg, 0.32 mmol) were charged to a flame dried round bottomed flask under a nitrogen atmosphere. Dimethyl 2-diazo malonate (5.00 g, 32 mmol) in anhydrous dichloromethane (50 mL) was added via syringe at a rate between 0.5 and 1.0 mL h$^{-1}$. Once addition was complete the reaction mixture was left to stir for an additional six hours, then filtrated through a pad of Celite® and silica gel, and solvent was removed under reduced pressure. The crude product was purified by column chromatography (8:1 v/v petroleum ether: ethyl acetate) to yield a pale yellow solid (4.06 g, 17.5 mmol, 55%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 3.73 (6H, s, 9/10), 6.89 (1H, s, 5),
7.43-7.46 (3H, m, 12/13/14), 7.62 (2H, dd, J = 6.4, 3.2 Hz, 7/8).
\[\text{\textsuperscript{13}C NMR (100 MHz, CDCl}_3\text{): } \delta \text{ 52.4 (9/10), 76.7 (4), 77.1 (1), 95.3 (5), 123.9 (6), 128.9 (7/8), 130.4 (12/13/14), 171.1 (2/3).}\]

**Synthesis of dimethyl 2-(4-(trifluoromethyl)phenyl) cycloprop-2-ene-1,1-dicarboxylate**

![Chemical structure](image)

1-ethyl-4-(trifluoromethyl)benzene (4.00 mL, 4.17 g, 24.5 mmol) and rhodium acetate dimer (36 mg, 0.08 mmol) were charged to a flame dried round bottomed flask under a nitrogen atmosphere. Dimethyl 2-diazomalonate (1.29 g, 8.13 mmol) in anhydrous dichloromethane (50 mL) was added via syringe at a rate between 0.5 and 1.0 mL h\(^{-1}\). Once addition was complete the reaction mixture was left to stir for an additional six hours, then filtered through a pad of Celite® and silica gel, and solvent was removed under reduced pressure. The crude product was purified by column chromatography (8:1 v/v petroleum ether: ethyl acetate) to yield an orange oil (0.75 g, 2.50 mmol, 31%). \[^1\text{H NMR (400 MHz, CDCl}_3\text{): } \delta \text{ 3.75 (6H, s, 7/8), 7.06 (1H, s, 5), 7.73 (4H, dd, J = 8.8, 17.2 Hz, 9/10/12/13).}\]

**Synthesis of dimethyl 2-(4-nitrophenyl)cycloprop-2-ene-1,1-dicarboxylate**

![Chemical structure](image)

1-ethyl-4-nitrobenzene (4.63 g, 31.5 mmol) and rhodium acetate dimer (50 mg, 0.11 mmol) were charged to a flame dried round bottomed flask under a nitrogen atmosphere. Dimethyl 2-diazomalonate (1.66 g, 10.5 mmol) in anhydrous dichloromethane (50 mL) was added via syringe at a rate between 0.5 and 1.0 mL h\(^{-1}\). Once addition was complete the reaction mixture was left to stir for an additional six hours, then filtered through a pad of Celite® and silica gel, and solvent was removed under reduced pressure. The crude product was purified by column chromatography (5:1 v/v petroleum ether: ethyl acetate) to yield an orange solid (1.68 g, 4.93 mmol, 47%). \[^1\text{H NMR (400 MHz, CDCl}_3\text{): } \delta \text{ 3.77 (6H, s, 7/8), 7.22 (1H, s, 5),}\]

\[^{13}\text{C NMR (100 MHz, CDCl}_3\text{): } \delta \text{ 32.5 (4), 52.6 (7/8), 102.3 (5), 123.6 (1), 125.9 (10/12), 127.4 (9/13), 130.6 (11), 143.1 (6), 167.9 (14), 170.7 (2/3). IR } \nu_{\text{max}} \text{ (CH}_2\text{Cl}_2/cm}^{-1} \text{ 1733 (C=O), 1293 (C-OR), 1164 (C-F), 1119 (C-F). m/z (ESI): 323.0491; C}_{14}\text{H}_{11}\text{F}_3\text{O}_4\text{Na (M + Na}^+) \text{ requires 323.0507.}\]
7.81 (2H, d, J = 8.4 Hz, 9/13), 8.31 (2H, d, J = 8.4 Hz, 10/12) \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ 33.2 (4), 52.7 (7/8), 100.6 (5), 111.1 (1), 124.2 (10/12), 130.1 (6), 131.1 (9/13), 148.7 (11), 170.7 (2/3). IR ν\textsubscript{max} (CH\textsubscript{2}Cl\textsubscript{2})/cm\textsuperscript{-1} 1723 (C=O), 1290 (C-OR), 1521 (NO\textsubscript{2}), 1341 (NO\textsubscript{2}). mp: 107.8-109.1 °C. m/z (ESI): 278.0658; C\textsubscript{13}H\textsubscript{12}NO\textsubscript{6} (M + H\textsuperscript{+}) requires 278.0659.

**Synthesis of dimethyl 2,3-diphenycycloprop-2-ene-1,1-dicarboxylate\textsuperscript{305}**

![Synthesis diagram]

2-phenyl-cycloprop-2-ene-1,1-dicarboxylic acid dimethyl ester (1.00 g, 4.31 mmol), iodobenzene (0.48 mL, 0.88 g, 4.31 mmol) and palladium(II) acetate (100 mg, 0.43 mmol) were charged to a flame dried round bottom flask under a nitrogen atmosphere and dissolved in anhydrous N,N-dimethylformamide (50 mL). Potassium carbonate (1.49 g, 10.77 mmol) was then added in small portions over 10 min. The reaction mixture was left to stir at 50 °C for 3 days, then filtered through a pad of Celite®. The product was extracted with dichloromethane (20 mL) and washed with ammonium chloride (2 x 50 mL), water (2 x 50 mL) and brine (2 x 50 mL), dried over anhydrous magnesium sulfate, filtered and solvent was removed under reduced pressure. The crude product was purified by column chromatography (10:1 v/v petroleum ether: ethyl acetate) to yield a white solid (0.63 g, 1.08 mmol, 48%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 3.73 (6H, s, 7/8), 7.43-7.48 (6H, m, 10/11/12/16/17/18), 7.74 (4H, dd, J = 4.8, 3.2 Hz, 9/13/15/19). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ 52.4 (7/8), 76.7 (4/5), 77.1 (1), 129.0 (6/14), 130.0 (9/13/15/19), 130.2 (10/11/12/16/17/18), 171.1 (2/3). IR ν\textsubscript{max} (CH\textsubscript{2}Cl\textsubscript{2})/cm\textsuperscript{-1} 1652 (C=O), 1272 (C-OR). mp: 121.3-123.1 °C. m/z (ESI): 331.0982; C\textsubscript{19}H\textsubscript{16}O\textsubscript{4}Na (M + Na\textsuperscript{+}) requires 331.0946.
Attempted synthesis of
poly(2-phenyl-cycloprop-2-ene-1,1-dicarboxylic acid dimethyl ester)

2-phenyl-cycloprop-2-ene-1,1-dicarboxylic acid dimethyl ester (0.5 g, 2.16 mmol) was charged to a flame dried round bottomed flask under a nitrogen atmosphere and was dissolved in anhydrous dichloromethane (20 mL). The reaction mixture was stirred vigorously and Grubbs' 2nd generation catalyst (20 mg, 23 µmol) in anhydrous dichloromethane (1 mL) was added via syringe. The reaction mixture was left to stir for 48 h with no obvious sign of polymerisation. The polymerisation was terminated with ethyl vinyl ether (5 mL) and solvent was removed under reduced pressure to return starting material.

Attempted synthesis of
bis(2-phenyl-cycloprop-2-ene-1,1-dicarboxylic acid dimethyl ester) copper(II)

Copper(II) chloride (46 mg, 0.34 mmol) was charged to a conical flask and dissolved in distilled water (15 mL). 2-phenyl-cycloprop-2-ene-1,1-dicarboxylic acid dimethyl ester (200 mg, 0.86 mmol) was charged to a separate conical flask and was dissolved in methanol (5 mL), and then added dropwise via pipette over 10 min to the reaction mixture whilst maintaining constant stirring. Sodium acetate (77 mg, 0.94 mmol) was dissolved in distilled water (10 mL), and was added in small portions over 5 min. The reaction mixture was heated to 80 °C whilst maintaining rapid stirring for 1 h. The reaction mixture was then cooled to 0 °C, and a blue-grey precipitate was filtered off and washed with distilled water (50 mL). The product was recrystallised from methanol and dried in a desiccator overnight, and found to be unreacted starting material only.
Attempted synthesis of (2-phenylcycloprop-ene,1,1-diyl)dimethanol

2-phenyl-cycloprop-ene,1,1-dicarboxylic acid dimethyl ester (100 mg, 0.43 mmol) was charged to a flame dried round bottomed flask under a nitrogen atmosphere and was dissolved in anhydrous tetrahydrofuran (20 mL). The reaction mixture was cooled to 0 °C, and lithium aluminium hydride solution (1.0M in tetrahydrofuran, 0.7 mL, 0.7 mmol) was added slowly. The reaction mixture was allowed to warm to room temperature and was left to stir overnight. The reaction mixture was quenched with saturated sodium potassium tartrate solution (20 mL), and the product was extracted with diethyl ether (2 x 20 mL). The combined organics were dried over anhydrous magnesium sulfate, filtered and solvent was removed under reduced pressure to yield a yellow oil.

1H NMR of the crude product suggested that the esters had been reduced but that the cyclopropene ring had either been opened or the double bond had been hydrogenated by a hydride anion in the same process.

Attempted synthesis of (2-phenylcycloprop-ene,1,1-diyl)dimethanol

2-phenyl-cycloprop-ene,1,1-dicarboxylic acid dimethyl ester (100 mg, 0.43 mmol) was charged to a flame dried round bottomed flask under a nitrogen atmosphere and was dissolved in anhydrous tetrahydrofuran (20 mL). The reaction mixture was cooled to 0 °C, and diisobutylaluminium hydride solution (25% wt. in toluene, 1.45 mL, 0.306 g, 2.15 mmol) was added slowly. The reaction mixture was allowed to warm to room temperature and was left to stir for 3 h. The reaction mixture was quenched with saturated sodium potassium tartrate solution (20 mL), and the product was extracted with dichloromethane (3 x 20 mL). The combined organics were dried over anhydrous magnesium sulfate, filtered and solvent was removed under reduced pressure to yield a yellow oil (39 mg, 0.22 mmol, 51%). 1H NMR of the crude product suggested that the esters had been reduced but that the cyclopropene ring had either been opened or the double bond had been hydrogenated by a hydride anion in the same process.
Chapter 7: Experimental

Synthesis of poly(norbornene)

Norbornene (1.88 g, 20 mmol) was charged to a flame dried round bottomed flask under a nitrogen atmosphere and was dissolved in anhydrous dichloromethane (20 mL). The reaction mixture was stirred vigorously and Grubbs’ 2nd generation catalyst (20 mg, 23 µmol) in anhydrous dichloromethane (1 mL) was added via syringe. The reaction mixture was left to stir until forming a viscous gel that prevented the stirrer bar from rotating, ca. 10 min. The flask was then washed with methanol (10 mL) to yield a white solid (1.88 g, >99%). The Grubbs’ 2nd generation catalyst can be substituted for Grubbs’ 1st generation catalyst to give identical products and yields. $^1$H NMR (400 MHz, CDCl$_3$): δ 0.97-1.09 (1 H, m, E-trans-4), 1.25-1.35 (2 H, m, E-trans-1/2), 1.77-1.88 (3 H, m, Z-cis-1/2/4), 2.44 (2 H, s, E-trans-3/5), 2.79 (2 H, s, Z-cis-3/5), 5.19-5.29 (2 H, m, Z-cis-6/7), 5.31-5.39 (2 H, m, E-trans-6/7). Ratio of integrals suggests $E:Z$ (cis:trans) $\approx$ 6:4. $^{13}$C NMR (100 MHz, CDCl$_3$): δ 32.0 (E-trans-1/2), 32.3 (E-trans-1/2), 33.2 (Z-cis-1/2), 33.4 (Z-cis-1/2), 38.7 (Z-cis-3/5), 38.8 (Z-cis-3/5), 41.5 (E-trans-4), 42.6 (Z-cis-4), 43.3 (E-trans-3/5), 43.7 (E-trans-3/5), 132.2 (E-trans-6/7), 132.6 (E-trans-6/7), 134.1 (Z-cis-6/7). IR ν$_{\text{max}}$ (ATR)/cm$^{-1}$ 1675 (C=C), 905 (C=CH), 880 (C=CH), 710 (C=C).

Synthesis of bicyclo[2.2.1]hept-5-ene-2-carbonyl chloride

Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (5.00 mL, 5.65 g, 40.86 mmol) was charged to a round bottomed flask. Thionyl chloride (30 mL, 48.93 g, 411 mmol) was added and the reaction mixture was stirred and gently heated at 50 °C. The evolution of sulfur dioxide was observed for ca. 1 h and the reaction mixture was then left to stir at 50 °C for a further 2 h. Excess thionyl chloride was removed under reduced pressure and yielded a brown oil (5.90 g, 37.65 mmol, 92%), which was used immediately without characterisation or purification.
**Synthesis of N-(3-(trimethoxysilyl)propyl)bicyclo[2.2.1]hept-5-ene-2-carboxamide**

Bicyclo[2.2.1]hept-5-ene-2-carbonyl chloride (0.89 g, 5.68 mmol) was charged to a flame dried round bottomed flask under a nitrogen atmosphere and was dissolved in anhydrous tetrahydrofuran (20 mL). The reaction mixture was cooled to 0 °C, then (3-aminopropyl)trimethoxysilane (1.00 mL, 1.02 g, 5.68 mmol) and triethylamine (0.87 mL, 0.63 g, 6.25 mmol) were added slowly to the reaction mixture via syringe. The reaction mixture was allowed to warm to room temperature and was left to stir overnight. The reaction mixture was diluted with ethyl acetate (20 mL) and the triethylamine hydrochloride precipitate was filtered off. The reaction mixture was dried over anhydrous magnesium sulfate, filtered and solvent was removed under reduced pressure to yield a brown oil (1.15 g, 3.86 mmol, 68%).

**\( ^1H \text{NMR} (400 \text{ MHz, CDCl}_3): \delta\)** 0.61-0.68 (2 H, m, 10), 1.24-1.37 (2 H, m, 6), 1.39-1.47 (1 H, m, 7), 1.55-1.67 (2 H, m, 9), 1.87-2.01 (2 H, m, 4), 2.84-2.91 (1 H, m, 5), 3.13-3.24 (1 H, m, 3), 3.25-3.29 (2 H, m, 8), 3.57 (9 H, s, 13/14/15), 5.60 (1 H, s, 11), 5.98 (1 H, q, \( J = 3.3 \text{ Hz}\), 2), 6.23 (1 H, q, \( J = 2.7 \text{ Hz}\), 1).

**\( ^{13}\text{C NMR} (100 \text{ MHz, CDCl}_3): \δ\)** 6.5 (10), 22.8 (9), 29.9 (4), 30.5 (6), 41.9 (8), 42.7 (5), 46.2 (3), 50.0 (7), 50.6 (13/14/15), 132.4 (2), 137.7 (1), 174.1 (12).

**IR \( \nu_{\text{max}} (\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}\):** 1663 (C=O), 1677 (C=C), 1294 (O-Me).

**m/z (ESI):** 300.1626; \( \text{C}_{14}\text{H}_{26}\text{NO}_{4}\text{Si} (\text{M} + \text{H}^+) \) requires 300.1581.

**Initiation of substrates with Grubbs’ catalyst**

Substrates previously functionalised with \( N\)-(3-(trimethoxysilyl)propyl)bicyclo[2.2.1]hept-5-ene-2-carboxamide were sealed in a flame dried Schlenk tube. The Schlenk tube was evacuated under reduced pressure and then purged with nitrogen. This cycle was conducted five times, and then the sealed tube was left under a slight positive pressure of nitrogen using a nitrogen filled balloon. The substrate was immersed in a solution of Grubbs’ 2\(^\text{nd}\) Generation catalyst (20 mg, 23 \( \mu\text{mol} \)) in anhydrous dichloromethane (20 mL). The reaction mixture was left for 1 h,
then removed by cannula to minimise exposure to air. Substrates were then washed under nitrogen with dichloromethane (10 x 20 mL) to remove any residual catalyst, and then used immediately for polymerisation.

**Synthesis of poly(norbornene) brushes via SI-ROMP**

![Chemical structure diagram](image)

Pre-washed ruthenium-initiated norbornyl amide silicon substrates pre-sealed in a flame dried Schlenk tube under a nitrogen atmosphere from the initiation reaction were immersed in a solution of norbornene in anhydrous dichloromethane (1.0 M, 20 mL, 20 mmol). The reaction mixture was left for 90 min, then exposed to air. Substrates were then washed sequentially with ethyl vinyl ether then dichloromethane, methanol and water. Substrates were dried under a stream of nitrogen gas and observed by ellipsometry. Ellips.: (HeNe, 632.8 nm; θ, 70°)

Norbornyl silane (multi-layered) sample (pre-polymerisation) 88.05 ±1.94 nm (MSE 0.595);
Final sample (post-polymerisation) 131.03 ±1.08 nm (MSE 9.539); Calculated polymer brush thickness 42.98 ±3.02 nm.

**Initiation of substrates with Grubbs’ catalyst**

![Chemical structure diagram](image)

Substrates previously functionalised with bicyclo[2.2.1]hept-5-ene-2-yltriethoxysilane were sealed in a flame dried Schlenk tube. The Schlenk tube was evacuated under reduced
pressure and then purged with nitrogen. This cycle was conducted five times, and then the 
sealed tube was left under a slight positive pressure of nitrogen using a nitrogen filled balloon. 
The substrate was immersed in a solution of Grubbs’ 2nd Generation catalyst (20 mg, 23 µmol) 
in anhydrous dichloromethane (20 mL). The reaction mixture was left for 1 h, then removed by 
cannula to minimise exposure to air. Substrates were then washed under nitrogen with 
dichloromethane (10 x 20 mL) to remove any residual catalyst, and then used immediately for 
polymerisation.

**Synthesis of poly(norbornene) brushes via SI-ROMP**

![Chemical structure](attachment:structure.png)

Pre-washed ruthenium-initiated norbornyl silane silicon substrates pre-sealed in a flame dried 
Schlenk tube under a nitrogen atmosphere from the initiation reaction were immersed in a 
solution of norbornene in anhydrous dichloromethane (1.0M, 20 mL, 20 mmol). The reaction 
mixture was left for 90 min, then exposed to air. Substrates were then washed sequentially with 
ethyl vinyl ether then dichloromethane, methanol and water. Substrates were dried under a 
stream of nitrogen gas and observed by ellipsometry. Ellips.: (HeNe, 632.8 nm; θ, 70°) 9.46 ±0.79 nm (MSE 1.189).

**Initiation of substrates with Grubbs’ catalyst**

![Chemical structure](attachment:structure.png)

Substrates previously functionalised with allyltriethoxysilane were sealed in a flame dried 
Schlenk tube. The Schlenk tube was evacuated under reduced pressure and then purged with 
nitrogen. This cycle was conducted five times, and then the sealed tube was left under a slight
positive pressure of nitrogen using a nitrogen filled balloon. The substrate was immersed in a solution of Grubbs' 2\textsuperscript{nd} Generation catalyst (20 mg, 23 µmol) in anhydrous dichloromethane (20 mL). The reaction mixture was left for 1 h, then removed by cannula to minimise exposure to air. Substrates were then washed under nitrogen with dichloromethane (10 x 20 mL) to remove any residual catalyst, and then used immediately for polymerisation.

**Attempted synthesis of poly(norbornene) brushes via SI-ROMP\textsuperscript{5}**

Pre-washed ruthenium-initiated allylsilane silicon substrates pre-sealed in a flame dried Schlenk tube under a nitrogen atmosphere from the initiation reaction were immersed in a solution of norbornene in anhydrous dichloromethane (1.0M, 20 mL, 20 mmol). The reaction mixture was left for 90 min, then exposed to air. Substrates were then washed sequentially with ethyl vinyl ether\textsuperscript{367} then dichloromethane, methanol and water. Substrates were dried under a stream of nitrogen gas and observed by ellipsometry. No notable growth was observed.

**Initiation of substrates with Grubbs' catalyst\textsuperscript{5}**

Substrates previously functionalised with vinyltriethoxysilane were sealed in a flame dried Schlenk tube. The Schlenk tube was evacuated under reduced pressure and then purged with nitrogen. This cycle was conducted five times, and then the sealed tube was left under a slight positive pressure of nitrogen using a nitrogen filled balloon. The substrate was immersed in a solution of Grubbs' 2\textsuperscript{nd} Generation catalyst (20 mg, 23 µmol) in anhydrous dichloromethane (20 mL). The reaction mixture was left for 1 h, then removed by cannula to minimise exposure to air. Substrates were then washed under nitrogen with dichloromethane (10 x 20 mL) to remove any residual catalyst, and then used immediately for polymerisation.
Attempted synthesis of poly(norbornene) brushes via Si-ROMP

Pre-washed ruthenium-initiated vinylsilane silicon substrates pre-sealed in a flame dried Schlenk tube under a nitrogen atmosphere from the initiation reaction were immersed in a solution of norbornene in anhydrous dichloromethane (1.0M, 20 mL, 20 mmol). The reaction mixture was left for 90 min, then exposed to air. Substrates were then washed sequentially with ethyl vinyl ether then dichloromethane, methanol and water. Substrates were dried under a stream of nitrogen gas and observed by ellipsometry. No notable growth was observed.

Synthesis of poly(norbornene) brushes via Vapour-Phase SI-ROMP

Pre-washed ruthenium-initiated norbornyl silane silicon substrates were pre-sealed in a flame dried Schlenk tube under a nitrogen atmosphere from the initiation reaction. A few drops of an anhydrous dichloromethane solution of norbornene (3.0M, ca. 0.3 mL, 1.0 mmol) was injected into the Schlenk tube, down the sides of the glass taking care not to contact the initiated surface of the wafer. Polymerisation was evident within seconds (ca. 10-300 nm) and the brushes were left to grow for a further 10 min. The substrates were then exposed to air and washed sequentially with ethyl vinyl ether then dichloromethane, methanol and water. Substrates were dried under a stream of nitrogen gas and observed by ellipsometry.
Ellips.: (HeNe, 632.8 nm; θ, 70°) Monolayer, 9.46 ±0.80 (MSE 1.189); Polymer 131.3 ±2.86 nm (MSE 26.61); Thickness increase, 121.8 ±2.97 nm.

Attempted synthesis of poly(norbornene) brushes via Vapour-Phase SI-ROMP, utilising specialist reactor setup

Using the apparatus illustrated in Figure 60 (p. 118), pre-washed ruthenium-initiated norbornyl silane silicon substrates were pre-sealed in a flame dried Schlenk flask (A) under a nitrogen atmosphere from the initiation reaction. Schlenk flask B was also flame dried and then charged with norbornene (5.00 g, 53.1 mmol) and placed under a nitrogen atmosphere using tap 8. Flask B was heated to 100 °C to melt the norbornene. Ensuring all taps were closed, polymerisation was attempted by pulling a vacuum and opening taps 1, 2 and 3 to reduce the pressure in flask A. Once the pressure in flask A had reached 3 mbar, taps 5 and 6 were opened to attempt to draw the norbornene vapour across. Unfortunately, the norbornene solidified on the cold glassware and was just pulled across in the solid state.

Synthesis of poly(2-hydroxyethyl methacrylate)

2-Hydroxyethyl methacrylate (9.32 mL, 10.0 g, 76.8 mmol) was charged to a round-bottomed flask and dissolved in anhydrous toluene (50 mL). This solution was deoxygenated by bubbling with nitrogen gas for ca. 15 min. 2,2'-Azobisbutyronitrile (AIBN, 80 mg, 0.5 mmol) was added to the reaction mixture and the flask was sealed and placed under a nitrogen atmosphere. The reaction mixture was heated to reflux and left to stir for 10 min. The reaction mixture was then cooled and the polymer began to precipitate. The reaction mixture was exposed to air and solvent was removed under reduced pressure. Polymer was further dried in a vacuum oven at 60 °C/1 mbar for 30 min to yield a white solid (8.7 g, 66.9 mmol, 87%).

$^1$H NMR (400 MHz, CD$_3$OD): δ 1.03 (3H, br d, J = 66.4 Hz, 3), 2.00 (2H, br, J = 27.2 Hz, 1), 3.79 (2H, s, 6), 4.05 (2H, s, 5). $^{13}$C NMR (100 MHz, CD$_3$OD): δ 17.8-20.0 (3), 46.3-46.7 (2), 53.6-55.8 (1), 60.9-61.0 (6) 68.04 (5) 179.0-180.0 (4). IR $\nu_{\text{max}}$ (KBr)/cm$^{-1}$ 3431 (O-H), 1727 (C=O), 1277 (C-OR), 1161 (C-OR), 1077 (C-OH).
Chapter 7: Experimental

Synthesis of poly(2-hydroxyethyl methacrylate)

2-Hydroxyethyl methacrylate (9.32 mL, 10.0 g, 76.8 mmol) was charged to a round-bottomed flask and dissolved in anhydrous toluene (50 mL). This solution was deoxygenated by bubbling with nitrogen gas for ca. 15 min. 1,1'-Azobis(cyclohexanecarbonitrile) (ABCN, 120 mg, 0.5 mmol) was added to the reaction mixture and the flask was sealed and placed under a nitrogen atmosphere. The reaction mixture was heated to reflux and left to stir for 10 min. The reaction mixture was then cooled and the polymer began to precipitate. The reaction mixture was exposed to air and solvent was removed under reduced pressure. Polymer was further dried in a vacuum oven at 60 °C/1 mbar for 30 min to yield a white solid (8.3 g, 63.8 mmol, 83%).

^1^H NMR (400 MHz, CD_3^OD): δ 1.03 (3H, br d, J = 66.4 Hz, 3), 2.00 (2H, br, J = 27.2 Hz, 1), 3.79 (2H, s, 6), 4.05 (2H, s, 5). ^13^C NMR (100 MHz, CD_3^OD): δ 17.8-20.0 (3), 46.3-46.7 (2), 53.6-55.8 (1), 60.9-61.0 (6) 68.04 (5) 179.0-180.0 (4).

IR ν\text{max} (KBr)/cm\textsuperscript{-1} 3431 (O-H), 1727 (C=O), 1277 (C-OR), 1161 (C-OR), 1077 (C-OH).

Synthesis of poly(2-hydroxyethyl methacrylate) via ATRP

2-Hydroxyethyl methacrylate (20 mL, 21.46 g, 165 mmol) was charged to a round-bottomed flask and mixed with distilled water (10 mL) and methanol (10 mL) as co-solvents. This reaction mixture was deoxygenated by bubbling with nitrogen gas for ca. 15 min. Copper(I) bromide (213 mg, 1.50 mmol), copper(II) bromide (32 mg, 0.15 mmol) and 2,2'-bipyridine (576 mg, 3.69 mmol) were added to the reaction mixture. The flask was sealed and placed under a nitrogen atmosphere. This mixture was left to stir for 5 min, before ethyl 2-bromoisobutyrate (0.22 mL, 0.30 g, 1.52 mmol) was added. The reaction mixture was left to stir for 3 h. The reaction mixture was diluted with methanol (250 mL) and the methanol solution was double filtered over a plug of Celite® and silica gel to remove the copper salts (evident when the solution runs colourless, not pink). The methanol solution was poured into diethyl ether (200 mL) to precipitate the polymer. The organic solvents were decanted and the polymer was swollen with water. The polymer was evaporated to dryness using a freeze drier to yield a white...
solid (8.48 g, 64.4 mmol, 39%). ¹H NMR (400 MHz, CD₃OD): δ 1.03 (3H, br d, J = 66.4 Hz, 3), 2.00 (2H, br, J = 27.2 Hz, 1), 3.79 (2H, s, 6), 4.05 (2H, s, 5). ¹³C NMR (100 MHz, CD₃OD): δ 17.8-20.0 (3), 46.3-46.7 (2), 53.6-55.8 (1), 60.9-61.0 (6) 68.04 (5) 179.0-180.0 (4). IR νmax (KBr)/cm⁻¹ 3431 (O-H), 1727 (C=O), 1277 (C-OR), 1161 (C-OR), 1077 (C-OH). IR νmax (ATR)/cm⁻¹ 3406 (O-H), 1719 (C=O), 1246 (C-OR), 1152 (C-OR), 1072 (C-OH).

**Synthesis of poly(2-hydroxyethyl methacrylate) via ARGET-ATRP**

2-Hydroxyethyl methacrylate (20 mL, 21.46 g, 165 mmol) was charged to a round-bottomed flask and mixed with distilled water (10 mL) and methanol (10 mL) as co-solvents. This reaction mixture was deoxygenated by bubbling with nitrogen gas for ca. 15 min. Copper(II) bromide (8 mg, 0.04 mmol), 2,2'-bipyridine (12 mg, 0.08 mmol) and ascorbic acid (100 mg, 0.57 mmol) were added to the reaction mixture. The flask was sealed and placed under a nitrogen atmosphere. This mixture was left to stir for 5 min, before ethyl 2-bromoisobutyrate (0.22 mL, 0.30 g, 1.52 mmol) was added. The reaction mixture was left to stir for 30 min, and became very viscous. Once viscosity had reached the point where the resistance caused by the reaction mixture prevented stirring, the reaction mixture was diluted with methanol (500 mL). The methanol solution was triple filtered over a plug of Celite® and silica gel to remove the copper salts (evident when the solution runs colourless, not pink). The methanol solution was poured into diethyl ether (400 mL) to precipitate the polymer. The organic solvents were decanted and the polymer was swollen with water. The polymer was evaporated to dryness using a freeze drier to yield a white solid (14.07 g, 107.3 mmol, 65%). ¹H NMR (400 MHz, CD₃OD): δ 1.02 (3H, br d, J = 66.8 Hz, 3), 1.99 (2H, br, J = 27.6 Hz, 1), 3.78 (2H, s, 6), 4.04 (2H, s, 5). IR νmax (KBr)/cm⁻¹ 3436 (O-H), 1728 (C=O), 1279 (C-OR), 1163 (C-OR), 1077 (C-OH). IR νmax (ATR)/cm⁻¹ 3406 (O-H), 1718 (C=O), 1246 (C-OR), 1152 (C-OR), 1072 (C-OH).
Synthesis of anthracene-9-carbonyl chloride

Anthracene-9-carboxylic acid (0.50 g, 2.25 mmol) was charged to a round bottomed flask. Thionyl chloride (20 mL, 32.62 g, 275 mmol) was added and the reaction mixture was stirred and gently heated at 50 °C. The evolution of sulfur dioxide was observed for ca. 1 h and the reaction was then left to stir at 50 °C for a further 1 h. Excess thionyl chloride was removed under reduced pressure and yielded a brown oil (0.52 g, 2.16 mmol, 96%), which was used immediately without characterisation or purification.

Synthesis of 2-(methacryloyloxy)ethyl anthracene-9-carboxylate

2-Hydroxyethyl methacrylate (1.51 mL, 1.62 g, 12.5 mmol) was charged to a flame dried round bottomed flask under a nitrogen atmosphere and was dissolved in anhydrous tetrahydrofuran (20 mL). Triethylamine (3.47 mL, 2.52 g, 25.0 mmol) was dried over CaH₂ and then added. Anthracene-9-carbonyl chloride (3.00 g, 12.5 mmol) in tetrahydrofuran (15 mL) was added to the reaction mixture and left to stir overnight. The reaction was then exposed to air and extracted with dichloromethane (20 mL). The organic fraction was washed with distilled water (2 x 20 mL) and brine (1 x 20 mL), dried over anhydrous magnesium sulfate, filtered and solvent was removed under reduced pressure. The crude product was purified by column chromatography (9:1 v/v petroleum ether: ethyl acetate) to yield an orange viscous oil (0.32 g, 0.87 mmol, 7%). ¹H NMR (400 MHz, CDCl₃): δ 1.99 (3H, s, 21), 4.61 (2H, t, J = 4.6 Hz, 16), 4.88 (2H, t, J = 4.6 Hz, 17), 5.64 (1H, s, cis-20), 6.23 (1H, s, trans-20), 7.47-7.54 (4H, m, 1/2/12/13), 8.06 (4H, dd, J = 20.2, 8.2 Hz, 3/6/11/14), 8.55 (1H, s, 7). ¹³C NMR (100 MHz, CDCl₃): δ 18.3 (21), 56.1 (17), 59.7 (16), 127.0 (2/12), 127.5 (20), 128.4 (1/13), 128.9 (7), 129.1 (6/14), 129.6 (10), 131.0 (3/11), 131.6 (5/9), 133.1 (4/8), 137.7 (19), 166.0 (15), 167.2 (18). IR ν max (CH₂Cl₂)/cm⁻¹ 1723 (C=O), 1704 (C=O),
1252 (C-OR), 1152 (C-OR), 1136 (C-OR), 1073 (C-OR). m/z (ESI): 357.1109; C_{21}H_{18}O_{4}Na (M + Na^+) requires 357.1103.

**Attempted synthesis of poly(2-(methacryloyloxy)ethyl anthracene-9-carboxylate)**

![Diagram of attempted synthesis](image)

2-(Methacryloyloxy)ethyl anthracene-9-carboxylate (0.32 g, 0.96 mmol) was charged to a round-bottomed flask and dissolved in anhydrous toluene (50 mL). This solution was deoxygenated by bubbling with nitrogen gas for ca. 15 min. 1,1-Azobis(cyclohexanecarbonitrile) (ABCN, 10 mg, 0.04 mmol) was added to the reaction mixture and the flask was sealed and placed under a nitrogen atmosphere. The reaction mixture was heated to reflux and left to stir overnight. The reaction mixture was then exposed to air and solvent was removed under reduced pressure to yield starting material (2-(methacryloyloxy)ethyl anthracene-9-carboxylate) and decomposed ABCN.

**Synthesis of anthracen-9-ylmethanol**

![Diagram of synthesis](image)

Sodium borohydride (9.06 g, 240 mmol) was charged to a flame dried three-necked round bottomed flask equipped with a reflux condenser and addition funnel. The sodium borohydride was placed under a nitrogen atmosphere and suspended in tetrahydrofuran (250 mL). Anthracene carboxaldehyde (19.75 g, 95 mmol) was placed in the addition funnel and dissolved in tetrahydrofuran (200 mL). The reaction mixture was heated at reflux, then the anthracene carboxaldehyde solution was added slowly over 15 min. The reaction was then left to reflux overnight. The reaction was cooled and exposed to air, washed with distilled water (500 mL), before being extracted with dichloromethane (2 x 250 mL), dried over anhydrous magnesium sulfate, filtered and solvent removed under reduced pressure to yield a yellow solid (17.9 g, 86 mmol, 90%). ¹H NMR (400 MHz, CDCl₃): δ 1.74 (1H, br s, 17), 5.68 (2H, s, 7), 7.56 (4H, ddd, J = 30.4, 14.8, 0.8 Hz, 10/11/14/15), 8.03 (2H, d, J = 8.0 Hz, 12/13),
8.42 (2H, d, 8.8 Hz, 9/16), 8.47 (1H, s, 3/16). 13C NMR (100 MHz, CDCl3): δ 55.2 (7), 124.6 (11/14), 124.8 (10/15), 125.5 (3), 127.5 (9/16), 128.4 (12/13), 128.9 (2/4), 129.1 (1/5), 129.6 (6). IR νmax (CH2Cl2)/cm⁻¹ 3071 (O-H), 1270 (C-OH). mp: 161.1-163.9 °C. m/z (ESI): 209.0994; C15H13O (M + H⁺) requires 209.0966.

**Synthesis of anthracen-9-ylmethyl methacrylate**

Anthracen-9-ylmethanol (490 mg, 2.35 mmol) and 4-dimethylaminopyridine (2 mg, 0.02 mmol) were charged to a flame dried round bottomed flask under a nitrogen atmosphere and were dissolved in anhydrous dichloromethane (5 mL) and anhydrous toluene (5 mL). Anhydrous pyridine (0.29 mL, 0.28 g, 3.60 mmol) was added to the reaction mixture using a syringe. The reaction mixture was left to stir for 15 min, then methacryloyl chloride (0.26 mL, 0.28 g, 2.64 mmol) was added dropwise. The reaction was left to stir overnight. The reaction was then exposed to air and diluted with ethyl acetate (20 mL) and washed with distilled water (3 x 30 mL). The organics were then dried over anhydrous magnesium sulfate, filtered and solvent was removed under reduced pressure to yield a yellow oil (0.32 g, 1.17 mmol, 49%). 1H NMR (400 MHz, CDCl3): δ 1.92 (3H, s, 18), 5.51 (1H, t, J = 1.4 Hz, cis-17), 6.05 (1H, s, trans-17), 6.23 (2H, s, 19), 7.50 (2H, t, J = 7.4, 2/12), 7.58 (2H, ddd, J = 9.0, 6.4, 1.3 Hz, 1/13), 8.04 (2H, d, J = 8.4 Hz, 3/11), 8.38 (2H, d, J = 9.2 Hz, 6/14), 8.52 (1H, s, 7). IR νmax (CH2Cl2)/cm⁻¹ 1715 (C=O), 1291 (C-OR). m/z (ESI): 299.1042; C19H16O2Na (M + Na⁺) requires 299.1043.

**Synthesis of 9-(chloromethyl) anthracene**

Anthracen-9-ylmethanol (5.00 g, 24.0 mmol) was charged to a flame dried three-necked round bottomed flask equipped with a reflux condenser and addition funnel. The anthracen-9-ylmethanol was placed under a nitrogen atmosphere and dissolved in chloroform (100 mL). Thionyl chloride (1.75 mL, 2.86 g, 24.0 mmol) was placed in the addition funnel and
diluted with chloroform (20 mL). The reaction mixture was heated at reflux, then the thionyl chloride solution was added slowly over 45 min. The reaction was then left to reflux overnight. The reaction was cooled and exposed to air, dried over anhydrous magnesium sulfate, filtered and solvent and excess thionyl chloride were removed under reduced pressure to yield a yellow solid (5.33 g, 23.5 mmol, 98%). ^1H NMR (400 MHz, CDCl₃): δ 5.63 (2H, s, 7), 7.51 (2H, ddd, J = 8.0, 6.6, 1.0 Hz, 11/14), 7.62 (2H, ddd, J = 8.4, 6.6, 1.2 Hz, 10/15), 8.04 (2H, d, J = 8.4 Hz, 12/13), 8.32 (2H, d, 8.8 Hz, 9/16), 8.50 (1H, s, 3).

^13C NMR (100 MHz, CDCl₃): δ 39.0 (7), 123.4 (9/16), 125.2 (11/14), 126.9 (10/15), 127.7 (1/5), 129.3 (3), 129.3 (12/13), 130.0 (2/4), 131.5 (6). IR νmax (CH₂Cl₂)/cm⁻¹ 768 (C–Cl).

mp: 136.2–138.8 °C. m/z (ESI): 191.0853; C₁₅H₁₁ (M–Cl) requires 191.0855.

Synthesis of anthracen-9-ylmethyl methacrylate

Sodium methacrylate (0.24 g, 2.20 mmol) was charged to a flame dried round bottomed flask under a nitrogen atmosphere and was dissolved in anhydrous N,N-dimethylformamide (20 mL). 9-(chloromethyl) anthracene (0.50 g, 2.20 mmol) was added to the reaction mixture and left to stir overnight. The reaction was then exposed to air and diluted with ethyl acetate (20 mL). The organic fraction was washed with distilled water (2 x 20 mL) and brine (6 x 50 mL), dried over anhydrous magnesium sulfate, filtered and solvent was removed under reduced pressure to yield a red viscous oil (0.40 g, 1.43 mmol, 65%). ^1H NMR (400 MHz, CDCl₃): δ 1.92 (3H, s, 18), 5.51 (1H, t, J = 1.6 Hz, cis-17), 6.05 (1H, s, trans-17), 6.22 (2H, s, 19), 7.50 (2H, t, J = 8.4, 2/12), 7.58 (2H, t, J = 8.4 Hz, 1/13), 8.04 (2H, d, J = 8.4 Hz, 3/11), 8.38 (2H, d, J = 8.4 Hz, 6/14), 8.52 (1H, s, 7).

^13C NMR (100 MHz, CDCl₃): δ 18.4 (18), 59.1 (19), 124.0 (6/14), 125.1 (2/12), 126.0 (17), 126.6 (1/13), 129.1 (7), 129.1 (3/11), 129.3 (10), 131.1 (5/9), 131.4 (4/8), 136.1 (16), 167.6 (15). IR νmax (CH₂Cl₂)/cm⁻¹ 1715 (C=O), 1291 (C-OR), 1155 (C-OR). m/z (ESI): 299.1038; C₁₉H₁₆O₂Na (M + Na⁺) requires 299.1043.
Chapter 7: Experimental

**Attempted synthesis of poly(anthracen-9-ylmethyl methacrylate)**

![Diagram]

Anthracen-9-ylmethyl methacrylate (0.32 g, 1.17 mmol) was charged to a round-bottomed flask and dissolved in anhydrous toluene (50 mL). This solution was deoxygenated by bubbling with nitrogen gas for ca. 15 min. 2,2'-Azobisbutyronitrile (10 mg, 0.06 mmol) was added to the reaction mixture and the flask was sealed and placed under a nitrogen atmosphere. The reaction mixture was heated to 60 °C and left to stir overnight. The reaction mixture was then exposed to air and was poured into diethyl ether (300 mL) to attempt precipitate the polymer to no avail. The organics were then dried over anhydrous magnesium sulfate, filtered and solvent was removed under reduced pressure to yield starting material (anthracen-9-ylmethyl methacrylate).

**Attempted synthesis of poly(anthracen-9-ylmethyl methacrylate) via ARGET-ATRP**

![Diagram]

Anthracen-9-ylmethyl methacrylate (0.32 g, 1.17 mmol) was charged to a round-bottomed flask and mixed with distilled water (10 mL) and methanol (10 mL) as co-solvents. This reaction mixture was deoxygenated by bubbling with nitrogen gas for ca. 15 min. Copper(II) bromide (8 mg, 0.04 mmol), 2,2'-bipyridine (61 mg, 0.40 mmol) and ascorbic acid (130 mg, 0.74 mmol) were added to the reaction mixture. The flask was sealed and placed under a nitrogen atmosphere. This mixture was left to stir for 5 min, before ethyl 2-bromoisobutyrate (0.01 mL, 1.8 mg, 9.0 μmol) was added. The reaction mixture was left to stir overnight. The reaction mixture was diluted with methanol (100 mL) and the methanol solution was triple filtered over a plug of Celite® and silica gel to remove the copper salts (evident when the solution runs colourless, not pink). The methanol solution was poured into diethyl ether (200 mL) to attempt precipitate the polymer to no avail. The organics were then dried over anhydrous magnesium
sulfate, filtered and solvent was removed under reduced pressure to yield starting material (anthracen-9-ylmethyl methacrylate).

Synthesis of poly(2-(methacryloyloxy)ethyl anthracene-9-carboxylate)

Poly(2-hydroxyethyl methacrylate) (0.78 g, 6.0 mmol) was charged to a flame dried round bottomed flask under a nitrogen atmosphere and was dissolved in anhydrous N,N-dimethylformamide (50 mL). Triethylamine (1.66 mL, 1.21 g, 12.0 mmol) was dried over CaH$_2$ and then added. Anthracene-9-carbonyl chloride (1.44 g, 6.0 mmol) in anhydrous N,N-dimethylformamide (10 mL) was added to the reaction mixture and left to stir overnight. The reaction was then cooled and exposed to air. The product precipitated on cooling and was filtered and washed with water (50 mL) and brine (3 x 50 mL) to yield a yellow solid (1.41 g, 4.2 mmol, 70%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.25 (3H, s, 20), 1.59 (2H, br s, 21) 2.89 (2H, s, 16), 2.96 (2H, s, 17), 7.47-7.54 (4H, m, 1/2/12/13), 8.12 (4H, dd, $J = 20.0, 8.0$ Hz, 3/6/11/14), 8.51 (1H, s, 7). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 22.7 (20), 31.4 (21), 42.8 (19), 55.3 (17), 59.2 (16), 125.0 (2/12), 126.4 (1/13), 126.8 (7), 127.0 (6/14), 127.5 (10), 128.4 (3/11), 129.2 (5/9), 130.7 (4/8), 167.3 (15), 175.1 (18). IR $\nu_{\text{max}}$ (ATR)/cm$^{-1}$ 1787 (C=O), 1722 (C=O), 1264 (C-OR), 1232 (C-OR), 1178 (C-OR), 1159 (C-OR). UV-Vis $\lambda_{\text{max}}$ (CHCl$_3$)/nm 327, 345, 363, 383. Fluorescence emission $\lambda_{\text{max}}$ (CHCl$_3$, 300 nm)/nm 440, 447, 451, 482.
Attempted synthesis of poly(2-(methacryloyloxy)ethyl anthracene-9-carboxylate) using coupling agents

Poly(2-hydroxyethyl methacrylate) (0.16 g, 1.21 mmol) was charged to a flame dried round bottomed flask under a nitrogen atmosphere and was dissolved in anhydrous N,N-dimethylformamide (10 mL). Triethylamine (0.34 mL, 0.24 g, 2.42 mmol) was dried over CaH₂ and then added. Anthracene-9-carboxylic acid (0.27 g, 1.21 mmol) and N,N'-dicyclohexylcarbodiimide (0.50 g, 2.42 mmol) in anhydrous N,N-dimethylformamide (10 mL) was added to the reaction mixture and left to stir overnight. The reaction was then cooled and exposed to air. The reaction mixture was extracted with dichloromethane (20 mL), washed saturated sodium hydrogen carbonate (20 mL), brine (3 x 20 mL) and water (50 mL), dried over anhydrous magnesium sulfate, filtered and solvent was removed under reduced pressure to yield starting materials.

Poly(2-hydroxyethyl methacrylate) (0.16 g, 1.21 mmol) was charged to a flame dried round bottomed flask under a nitrogen atmosphere and was dissolved in anhydrous N,N-dimethylformamide (20 mL). Triethylamine (0.34 mL, 0.24 g, 2.42 mmol) was dried over
CaH$_2$ and then added. Anthracene-9-carboxylic acid (0.27 g, 1.21 mmol) and PyBOP (1.26 g, 2.42 mmol) in anhydrous $N,N$-dimethylformamide (20 mL) was added to the reaction mixture and left to stir overnight. The reaction was then cooled and exposed to air. The reaction mixture was extracted with dichloromethane (20 mL), washed saturated sodium hydrogen carbonate (20 mL), brine (3 x 20 mL) and water (50 mL), dried over anhydrous magnesium sulfate, filtered and solvent was removed under reduced pressure to yield starting materials.

**Attempted synthesis of anthracen-9-yl methacrylate**

Anthrone (500 mg, 2.57 mmol) was charged to a flame dried round bottomed flask under a nitrogen atmosphere and was dissolved in anhydrous tetrahydrofuran (5 mL). Anhydrous pyridine (1.04 mL, 1.02 g, 12.87 mmol) was added and the reaction mixture was warmed to 35 °C. Methacryloyl chloride (0.30 mL, 0.32 g, 3.09 mmol) was added dropwise. The reaction was then heated to 50 °C and was left to stir overnight. The reaction was then exposed to air and diluted with diethyl ether (20 mL). The ethereal solution was washed with 1 M hydrochloric acid (1 x 10 mL), saturated sodium carbonate (2 x 10 mL) distilled water (2 x 10 mL) and brine (1 x 10 mL). The ethereal solution was then dried over anhydrous magnesium sulfate, filtered and solvent was removed under reduced pressure to yield a yellow solid. The yellow solid was determined as anthrone (0.424 g).

**Synthesis of anthracen-9-yl methacrylate**

Anthrone (500 mg, 2.57 mmol) was charged to a flame dried round bottomed flask under a nitrogen atmosphere and was dissolved in anhydrous tetrahydrofuran (5 mL). In a separate flask, sodium hydride (60% dispersion in mineral oil, 0.20 g, 5.14 mmol) was sealed under a nitrogen atmosphere and suspended in anhydrous tetrahydrofuran (5 mL). This solution was cooled in an ice bath. The anthrone solution was added to the sodium hydride suspension slowly using a syringe. The reaction mixture was left to stir for 5 min, then methacryloyl chloride (0.30 mL, 0.32 g, 3.09 mmol) was added dropwise. The reaction was left to stir overnight. The
reaction was then exposed to air and excess sodium hydride was quenched by adding ethanol dropwise until no further evolution of hydrogen gas occurred. The reaction was diluted with ethyl acetate (20 mL) and washed with distilled water (2 x 10 mL) and brine (1 x 10 mL). The organics were then dried over anhydrous magnesium sulfate, filtered and solvent was removed under reduced pressure to yield an orange solid (0.58 g, 2.18 mmol, 85%).

\[\text{H NMR (400 MHz, CDCl}_3\text{): } \delta \text{ 2.42 (3H, s, } \text{18), 5.98 (1H, s, cis-17), 6.70 (1H, s, trans-17), 7.77 (4H, dd, } J = 6.2, 3.0 \text{ Hz, } \text{12/13), 8.29 (4H, dd, } J = 5.8, 3.4 \text{ Hz, } \text{6/11/14).}\]

\[\text{13C NMR (100 MHz, CDCl}_3\text{): } \delta \text{ 18.6 (18), 127.0 (6/14), 128.1 (17), 128.5 (7), 131.9 (10), 133.5 (2/12), 133.7 (3/11), 134.2 (1/13), 135.5 (16), 139.9 (5/9), 142.3 (4/8), 166.1 (15).}\]

IR $\nu_{\max}$ (CH$_2$Cl$_2$)/cm$^{-1}$: 1736 (C=O), 1170 (C-OR), 1122 (C-OR).

Synthesis of poly(methacrylic acid sodium salt)

Sodium methacrylate (10.0 g, 92.58 mmol) was charged to a round-bottomed flask and dissolved in anhydrous methanol (100 mL). This solution was deoxygenated by bubbling with nitrogen gas for ca. 15 min. 2,2'-Azobisbutyronitrile (100 mg, 0.61 mmol) was added to the reaction mixture and the flask was sealed and placed under a nitrogen atmosphere. The reaction mixture was heated to 60 °C and left to stir overnight. The precipitated polymer was then filtered under vacuum and washed with methanol (3 x 50 mL) before drying under reduced pressure to yield an off-white solid (9.04 g, 83.7 mmol, 90%).

\[\text{H NMR (400 MHz, D}_2\text{O): } \delta \text{ 1.31 (3H, s, } \text{2), 1.62 (2H, t, } J = 7.0 \text{ Hz, } \text{1), 1.96 (2H, t, } J = 7.0 \text{ Hz, } \text{1).}\]

\[\text{13C NMR (100 MHz, D}_2\text{O): } \delta \text{ 18.6 (2), 19.8 (2), 47.0 (3), 47.8 (3), 54.4 (1), 56.6 (1), 187.1 (4), 187.4 (4).}\]

IR $\nu_{\max}$ (KBr)/cm$^{-1}$: 1552 (C=O), 1243 (C-ONa).

Attempted synthesis of poly(benzyl methacrylate)

Poly (methacrylic acid sodium salt) (0.50 g, 4.63 mmol) was charged to a round bottomed flask was dissolved in absolute ethanol (100 mL). Benzyl chloride (0.59 g, 4.63 mmol) was added to the reaction mixture and left to stir over 3 days at room temperature. The reaction was then
diluted with dichloromethane (50 mL). The organic fraction washed with distilled water (2 x 50 mL) and brine (2 x 50 mL), dried over anhydrous magnesium sulfate, filtered and solvent was removed under reduced pressure to yield the starting material (benzyl chloride).

**Synthesis of 9-methylacridine**

Diphenylamine (9.95 g, 58.8 mmol) was first recrystallised from petroleum ether and then recrystallised again from methanol and dried under vacuum, before being charged to a flame dried three-neck round bottomed flask fitted with a thermometer and reflux condenser. Zinc(II) chloride (40.1 g) and acetic acid (>99.99%, 10.0 mL, 10.6 g, 176.5 mmol) were added to the reaction mixture. The reaction mixture was placed under a nitrogen atmosphere and heated to 180 °C at which point the temperature stabilised. The reaction was left to heat for 48 h before carefully adding 1M sulfuric acid (25 mL, 25 mmol) down the condenser. This was left to reflux for a further 18 h, before allowing the reaction mixture to cool. Once at room temperature, the reaction mixture was neutralised with concentrated ammonia solution. The resulting precipitate was removed by gravity filtration. The filtrate was extracted with chloroform (600 mL). The organics were washed with saturated sodium hydrogen carbonate (5 x 100 mL), dried over anhydrous magnesium sulfate, filtered and solvent was removed under reduced pressure. The crude product was purified by column chromatography (9:1 v/v petroleum ether: ethyl acetate) to yield a green-brown solid (3.75 g, 19.4 mmol, 33%).

**1H NMR (400 MHz, CDCl₃):** δ 2.96 (3H, s, 14), 7.45 (2H, t, J = 7.6 Hz, 1/12), 7.70 (2H, t, J = 7.6 Hz, 2/11), 8.14 (4H, dd, J = 30.6, 8.6 Hz, 3/6/10/13).

**13C NMR (100 MHz, CDCl₃):** δ 13.5 (14), 124.5 (3/10), 125.3 (1/12), 125.4 (5/8), 129.7 (2/11), 130.2 (6/13), 142.2 (9), 148.3 (4/7). IR ν_max (KBr)/cm⁻¹ 1613 (acridine), 1564 (acridine), 1519 (acridine), 1441 (acridine), 1382 (acridine). mp: 111.2-113.4 °C. m/z (ESI): 193.0874; C₁₄H₁₁N (M⁺) requires 193.0891.

**Attemped synthesis of 9-chloromethylacridine**

Diphenylamine (9.95 g, 58.8 mmol) was first recrystallised from petroleum ether and then recrystallised again from methanol and dried under vacuum, before being charged to a flame.
dried three-neck round bottomed flask fitted with a thermometer and reflux condenser. Zinc(II) chloride (40.1 g) and chloroacetic acid (16.68 g, 176.5 mmol) were added to the reaction mixture. The reaction mixture was placed under a nitrogen atmosphere and heated to 230 °C. The reaction was left to heat for 48 h before carefully adding 1 M sulfuric acid (30 mL, 30 mmol) down the condenser. This was left to reflux for a further 24 h, before allowing the reaction mixture to cool. Once at room temperature, the reaction mixture was neutralised with concentrated ammonia solution. The resulting precipitate was removed by gravity filtration. The filtrate was extracted with chloroform (600 mL). The organics were washed with saturated sodium hydrogen carbonate (5 × 100 mL), dried over anhydrous magnesium sulfate, filtered and solvent was removed under reduced pressure. The crude product was purified by column chromatography (9:1 v/v petroleum ether: ethyl acetate) to yield starting materials.

**Attempted radical chlorination of 9-methylacridine**

\[
\text{N-Chlorosuccinimide (1.04 g, 7.76 mmol) was first recrystallised from toluene and dried under vacuum}\text{, before being charged to a flame dried round bottomed flask fitted with a reflux condenser. Cyclohexane (20 mL) and 9-methylacridine (1.00 g, 5.17 mmol) were added to the reaction mixture. The reaction mixture was placed under a nitrogen atmosphere and was left to reflux for 48 h before cooling the reaction mixture to 0 °C. 1M Sodium hydroxide was then added to the reaction mixture. The reaction mixture was extracted with dichloromethane (2 × 50 mL). The organics were washed with 1M sodium hydroxide (20 mL), water (2 × 20 mL) and brine (2 × 20 mL), dried over anhydrous magnesium sulfate, filtered and solvent was removed under reduced pressure. The crude product was purified by column chromatography (9:1 v/v petroleum ether: ethyl acetate) to yield starting materials.}
\]

**Synthesis of acetylferrocene**

Ferrocene (3.00 g, 16.1 mmol) was charged to a flame dried round bottomed flask under a nitrogen atmosphere, and dissolved in acetic anhydride (10 mL, 10.22 g, 106.0 mmol).
Concentrated phosphoric acid (2 mL, 38.47 mmol) was added dropwise over 15 min. The reaction mixture was heated over a steam bath for 20 min. Whilst still hot, the reaction mixture was poured over crushed ice (100 g). The ice slush was left to melt and the resulting aqueous solution was neutralised with sodium hydrogen carbonate. The resulting precipitate was filtered, and then recrystallised from petroleum ether to yield an orange solid (1.44 g, 6.3 mmol, 39%).

\[
\text{\textsuperscript{1}H NMR (400 MHz, CDCl}_3\text{): } \delta 2.40 \text{ (3H, s, 12)}, 4.21 \text{ (5H, s, 1/2/3/4/5)}, 4.51 \text{ (2H, t, } J = 2.0 \text{ Hz, 7/8)}, 4.78 \text{ (2H, t, } J = 1.8 \text{ Hz, 6/9}). \text{\textsuperscript{13}C NMR (100 MHz, CDCl}_3\text{): } \delta 68.7 \text{ (1/2/3/4/5)}, 69.1 \text{ (7/8)}, 70.5 \text{ (6/9)}, 76.2 \text{ (10)}, 172.2 \text{ (11)}. \text{IR } \nu_{\text{max}} \text{ (CH}_2\text{Cl}_2)/\text{cm}^{-1} 1654 \text{ (C=O)}, 1456 \text{ (Fc), 1280 (Fc).mp: 80.3-81.6 °C. m/z (ESI): 228.0243; C}_{12}\text{H}_{12}\text{OFe (M\textsuperscript{+}) requires 228.0238.}
\]

### Synthesis of 1-(ferrocenyl)ethanol

Acetylferrocene (2.00 g, 8.77 mmol) was charged to a flame dried round bottomed flask under a nitrogen atmosphere, and dissolved in anhydrous ethanol (50 mL). The reaction was cooled to 0 °C and then powdered sodium borohydride (3.3 g, 87.7 mmol) was added in small portions over 30 min. The reaction mixture was allowed to warm to room temperature and then left to stir for 2 h. The reaction was then cooled back to 0 °C and quenched with distilled water (50 mL). The reaction mixture was extracted with diethyl ether (2 x 50 mL) and the combined organic extracts were washed with brine (2 x 50 mL) and distilled water (50 mL), dried over anhydrous magnesium sulfate, filtered and solvent was removed under reduced pressure. The crude product was recrystallised from petroleum ether to yield an orange solid (1.94 g, 8.42 mmol, 96%).

\[
\text{\textsuperscript{1}H NMR (400 MHz, CDCl}_3\text{): } \delta 1.44 \text{ (3H, d, } J = 6.4 \text{ Hz, 12)}, 1.64 \text{ (1H, br s, 13)}, 4.17 \text{ (1H, q, } J = 1.8 \text{ Hz, 11)} 4.20 \text{ (5H, s, 1/2/3/4/5)}, 4.51 \text{ (2H, t, } J = 2.0 \text{ Hz, 7/8)}, 4.77 \text{ (2H, t, } J = 2.0 \text{ Hz, 6/9}). \text{\textsuperscript{13}C NMR (100 MHz, CDCl}_3\text{): } \delta 25.2 \text{ (12)}, 66.0 \text{ (11), 67.1 (7/8)}, 69.2 \text{ (6/9)}, 69.8 \text{ (1/2/3/4/5)}, 96.1 \text{ (10). IR } \nu_{\text{max}} \text{ (CH}_2\text{Cl}_2)/\text{cm}^{-1} 3435 \text{ (O-H), 1453 (Fc), 1277 (Fc).mp: 74.8-76.9 °C. m/z (ESI): 230.0389; C}_{12}\text{H}_{14}\text{OFe (M\textsuperscript{+}) requires 230.0394.}
Synthesis of (2-chlorobenzyl)ferrocene\textsuperscript{360}

Ferrocene (1.86 g, 10.0 mmol) was charged to a flame dried round bottomed flask under a nitrogen atmosphere. 2-chlorobenzoyl chloride (1.27 mL, 1.75 g, 10.0 mmol) in dichloromethane (100 mL) was added to dissolve the ferrocene. The reaction mixture was cooled to 0 °C, and then aluminium chloride (1.46 g, 11.0 mmol) was added in small portions over 30 minutes whilst maintaining a temperature below 5 °C. The appearance of a deep blue colour indicated that the reaction was occurring, as indicated by Reeves\textsuperscript{360}. Upon completion of the addition, stirring continued at 0 °C for 30 min and then for 2 h at room temperature. The reaction mixture was cooled again to 0 °C, and was quenched with distilled water (200 mL). This two-phase mixture was stirred vigorously for 30 min, before transferring to a separating funnel. The layers were separated, the aqueous layer was extracted with dichloromethane (2 x 30 mL). The combined dichloromethane solutions were washed with distilled water (50 mL), and 1M sodium hydroxide (2 x 100 mL), dried over anhydrous magnesium sulfate, filtered and solvent was removed under reduced pressure to yield a red solid (2.94 g, 8.6 mmol, 86%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 4.27 (5H, s, 1/2/3/4/5), 4.59 (2H, t, J = 2.0 Hz, 7/8), 4.74 (2H, t, J = 1.8 Hz, 6/9), 7.34-7.47 (4H, m, 14/15/16/17). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ 70.2 (1/2/3/4/5), 71.1 (7/8), 72.9 (6/9), 78.5 (10), 126.2 (16), 128.6 (14), 130.3 (17), 130.7 (12), 131.0 (15), 139.5 (13), 198.7 (11). IR ν\textsubscript{max} (CH\textsubscript{2}Cl\textsubscript{2})/cm\textsuperscript{-1}: 1647 (C=O), 1445 (Fc), 1292 (Fc). mp: 98.7-101.4 °C. m/z (ESI): 289.0322; C\textsubscript{17}H\textsubscript{13}OClFe (M–Cl) requires 289.0315.

Attempted synthesis of ferrocene carboxylic acid\textsuperscript{360}

Potassium tert-butoxide (4.61 g, 41.1 mmol) was charged to a flame dried round bottomed flask under a nitrogen atmosphere. 1,2-Dimethoxyethane (100 mL) and purified water (reagent grade, 0.22 mL, 0.22 g, 12.0 mmol) were added to the reaction vessel, and then finally (2-chlorobenzyl)ferrocene (2.94 g, 8.6 mmol) was added. The reaction was heated to reflux for 2 h. The reaction mixture was cooled again to room temperature, and was quenched with distilled water (100 mL). The aqueous phase was extracted with diethyl ether (4 x 75 mL). The combined organic solutions were washed with 1 M sodium hydroxide (2 x 100 mL), before
attempting to precipitate the desired product by acidifying the organic extracts with concentrated hydrochloric acid (1 mL). The resulting precipitate was filtered and traces of solvent were removed under reduced pressure to yield the starting material ((2-chlorobenzyl)ferrocene). Reeves notes that the molar ratio of potassium tert-butoxide to water is critical, and the amounts specified in the original paper represent optimum quantities for cleavage of 100 mmol of ketone\(^\text{360}\). These were scaled down accordingly but with no success after several attempts.

**Synthesis of ferrocene carboxylic acid\(^{370}\)**

Ferrocene (5.00 g, 26.9 mmol) was charged to a flame dried round bottomed flask under a nitrogen atmosphere, and dissolved in tetrahydrofuran (100 mL). \(n\)-Butyllithium (1.7 M in hexane, 40 mL, 68 mmol) was added dropwise over 1 h via a syringe pump. The reaction mixture was left to stir for 15 min before slowly flushing with gaseous carbon dioxide until saturated. The reaction mixture was extracted with diethyl ether (100 mL) and washed with distilled water (3 x 100 mL), before acidifying the organic extracts with concentrated hydrochloric acid (1 mL). The resulting precipitate was filtered through a pad of silica, charcoal and Celite, before traces of solvent were removed under reduced pressure to yield a brown solid (1.86g, 8.1 mmol, 30%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta \) 4.26 (5H, s, 1/2/3/4/5), 4.48 (2H, t, \(J = 2.0\) Hz, 7/8), 4.86 (2H, t, \(J = 1.8\) Hz, 6/9). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta \) 68.7 (1/2/3/4/5), 69.1 (7/8), 70.5 (6/9), 76.2 (10), 172.2 (11). IR \(\nu_{\text{max}} (\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}\): 3584 (O-H), 1654 (C=O), 1472 (Fc), 1283 (Fc). mp: 204.1-208.3 °C. m/z (ESI): 230.0028; \(C_{11}H_{10}O_2Fe\) (M\(^+\)) requires 230.0031.
Substrates initiated with 2-bromoisobutryl bromide were cut into squares (ca. 1 cm²) and sealed in individual flame dried Schlenk tubes. The Schlenk tubes were evacuated under reduced pressure and then purged with nitrogen. This cycle was conducted five times, and then each sealed tube was left under a slight positive pressure of nitrogen using a nitrogen filled balloon. A 1:1 v/v solution of 2-hydroxyethyl methacrylate (10.00 mL, 10.73g, 82.45 mL) and methanol (10 mL) was deoxygenated by bubbling with nitrogen gas for 15 min. Copper(II) bromide (2 mg, 0.01 mmol), 2,2’-bipyridyl (4 mg, 0.03 mmol) and sodium ascorbate (185 mg, 0.934 mmol) were then added to the methanol solution. This solution was then injected in 5 mL aliquots into each Schlenk tube. After the prescribed period, substrates were removed from the polymerisation solution, washed with methanol and distilled water and dried under a stream of nitrogen gas. Substrates were then observed by ellipsometry. Ellips.: (HeNe, 632.8 nm; θ, 70°) 1 h, not detectable; 4 h, 47.3 ±2.1 nm (MSE 1.05); 7 h, 50.5 ±1.3 nm (MSE 0.61); 24 h, 100.8 ±5.1 nm (MSE 2.29). IR ν_max (SiO2)/cm⁻¹ 3424 (O-H), 1725 (C=O), 1279 (C-OH), 1159 (C-OR), 1077 (C-OR).

Synthesis of poly(2-(methacyroyloxy)ethyl anthracene-9-carboxylate) brushes

Substrates previously functionalised with poly(2-hydroxyethyl methacrylate) were sealed in a flame dried Schlenk tube. The Schlenk tube was evacuated under reduced pressure and then purged with nitrogen. This cycle was conducted five times, and then the sealed tube was left
under a slight positive pressure of nitrogen using a nitrogen filled balloon. The substrate was immersed in anhydrous tetrahydrofuran (20 mL). Triethylamine (0.31 mL, 0.23 g, 2.25 mmol) was dried over CaH$_2$ and then added. Freshly prepared anthracene-9-carbonyl chloride (0.52 g, 2.16 mmol) was dissolved in the minimum amount of anhydrous tetrahydrofuran and this solution was injected into the Schlenk tube. The reaction mixture was left overnight, then exposed to air. Substrates were then washed sequentially with tetrahydrofuran, methanol and water. Substrates were dried under a stream of nitrogen gas, and observed by ellipsometry.

Ellips.: (HeNe, 632.8 nm; θ, 70°) PHEMA, 44.8 ± 1.3 nm (MSE 0.679); Anth 1 h, 51.2 ± 3.9 nm (MSE 1.788); 18 h, Δ < 180° (*see footnote), 131.5 ± 5.8 nm (MSE 18.03); Δ > 180°, 134.4 ± 1.6 nm (MSE 18.03). Average thickness increase, 1 h, 6.4 ± 4.1 nm; 18 h, 88.2 ± 3.9 nm. 

IR $\nu$$_{max}$ (SiO$_2$/cm$^{-1}$) 1711 (C=O), 1141 (C-O). UV-Vis $\lambda$$_{max}$ (glass)/nm 329, 348, 365, 385. Fluorescence emission $\lambda$$_{max}$ (glass, 300 nm)/nm 437, 442, 449, 474.
Synthesis of 1-naphthoyl chloride

1-naphthoic acid (1.00 g, 5.80 mmol) was charged to a round bottomed flask. Thionyl chloride (20 mL, 32.62 g, 275 mmol) was added and the reaction mixture was stirred and gently heated at 50 °C. The evolution of sulfur dioxide was observed for ca. 1 h and the reaction was then left to stir at 50 °C for a further 1 h. Excess thionyl chloride was removed under reduced pressure and yielded a brown oil (1.04 g, 5.34 mmol, 94%), which was used immediately without characterisation or purification.

Condensation of 1-naphthoyl chloride onto PHEMA-functionalised silicon substrates

Substrates previously functionalised with poly(2-hydroxyethyl methacrylate) were sealed in a flame dried Schlenk tube. The Schlenk tube was evacuated under reduced pressure and then purged with nitrogen. This cycle was conducted five times, and then the sealed tube was left under a slight positive pressure of nitrogen using a nitrogen filled balloon. The substrate was immersed in anhydrous tetrahydrofuran (10 mL). Triethylamine (0.80 mL, 0.58 g, 5.80 mmol) was dried over CaH₂ and then added. Freshly prepared 1-naphthoyl chloride (1.04 g, 5.43 mmol) was dissolved in the minimum amount of anhydrous tetrahydrofuran and this solution was injected into the Schlenk tube. The reaction mixture was left overnight, then exposed to air. Substrates were then washed sequentially with tetrahydrofuran, methanol and water. Substrates were dried under a stream of nitrogen gas, and observed by ellipsometry. Ellips.: (HeNe, 632.8 nm; θ, 70°) PHEMA, 44.8 ±1.3 nm (MSE 0.679); Naphthyl, 102.8 ±22.2 nm (MSE 10.77). Thickness increase, 58.0 ±22.3 nm. IR ν_max (SiO₂)/cm⁻¹ 1731 (C=O), 1631 (C=O), 1242 (C-O), 1196 (C-O), 1148 (C-O).
Chapter 7: Experimental

Synthesis of 4-cyanobenzoyl chloride

![Chemical structure of 4-cyanobenzoyl chloride]

4-Cyanobenzoic acid (0.50 g, 3.40 mmol) was charged to a round bottomed flask. Thionyl chloride (20 mL, 32.62 g, 275 mmol) was added and the reaction mixture was stirred and gently heated at 50 °C. The evolution of sulfur dioxide was observed for ca. 1 h and the reaction was then left to stir at 50 °C for a further 1 h. Excess thionyl chloride was removed under reduced pressure and yielded a brown oil (0.56 g, 3.40 mmol, >99%), which was used immediately without characterisation or purification.

Synthesis of poly(2-(methacryloyloxy)ethyl 4-cyanobenzoate) brushes

![Chemical structure of poly(2-(methacryloyloxy)ethyl 4-cyanobenzoate) brushes]

Substrates previously functionalised with poly(2-hydroxyethyl methacrylate) were sealed in a flame dried Schlenk tube. The Schlenk tube was evacuated under reduced pressure and then purged with nitrogen. This cycle was conducted five times, and then the sealed tube was left under a slight positive pressure of nitrogen using a nitrogen filled balloon. The substrate was immersed in anhydrous tetrahydrofuran (20 mL). Triethylamine (0.47 mL, 0.34 g, 3.40 mmol) was dried over CaH$_2$ and then added. Freshly prepared 4-cyanobenzyol chloride (0.56 g, 3.40 mmol) was dissolved in the minimum amount of anhydrous tetrahydrofuran and this solution was injected into the Schlenk tube. The reaction mixture was left overnight, then exposed to air. Substrates were then washed sequentially with tetrahydrofuran, methanol and water. Substrates were dried under a stream of nitrogen gas, and observed by ellipsometry.

Ellips.: (HeNe, 632.8 nm; θ, 70°) PHEMA, 44.8 ±1.3 nm (MSE 0.679); Cyano, 104.6 ±17.5 nm (MSE 9.067). Thickness increase, 59.8 ±17.5 nm. IR $\nu_{\text{max}}$(SiO$_2$)/cm$^{-1}$ 2233 (C≡N), 1764 (C=O), 1729 (C=O), 1277 (C-O), 1244 (C-O), 1178 (C-O), 1106 (C-O).
Synthesis of 4-bromobenzoyl chloride

\[
\text{Br} \quad \text{OH} \quad \overset{\text{Cl-S-Cl}}{\text{neat, } 50 \, ^\circ\text{C, 2 h}} \quad \text{Br} \quad \text{O} \quad \\
\]

4-Bromobenzoic acid (0.50 g, 2.49 mmol) was charged to a round bottomed flask. Thionyl chloride (20 mL, 32.62 g, 275 mmol) was added and the reaction mixture was stirred and gently heated at 50 °C. The evolution of sulfur dioxide was observed for ca. 1 h and the reaction was then left to stir at 50 °C for a further 1 h. Excess thionyl chloride was removed under reduced pressure and yielded a brown oil (0.54 g, 2.46 mmol, 99%), which was used immediately without characterisation or purification.

Synthesis of poly(2-(methacryloyloxy)ethyl 4-cyanobenzoate) brushes

Substrates previously functionalised with poly(2-hydroxyethyl methacrylate) were sealed in a flame dried Schlenk tube. The Schlenk tube was evacuated under reduced pressure and then purged with nitrogen. This cycle was conducted five times, and then the sealed tube was left under a slight positive pressure of nitrogen using a nitrogen filled balloon. The substrate was immersed in anhydrous tetrahydrofuran (10 mL). Triethylamine (0.30 mL, 0.22 g, 2.46 mmol) was dried over CaH₂ and then added. Freshly prepared 4-bromobenzoyl chloride (0.54 g, 2.46 mmol) was dissolved in the minimum amount of anhydrous tetrahydrofuran and this solution was injected into the Schlenk tube. The reaction mixture was left for the prescribed period, then exposed to air. Substrates were then washed sequentially with tetrahydrofuran, methanol and water. Substrates were dried under a stream of nitrogen gas, and observed by ellipsometry. Ellips.: (HeNe, 632.8 nm; θ, 70°) PHEMA, 172.1 ±4.5 nm (MSE 1.610); 1 h, 216.1 ±1.4 nm (MSE 0.669); 4 h, 336.85 ±5.0 nm (MSE 1.645); 7 h, 365.1 ±2.2 nm (MSE 0.807); 10 h, 348.0 ±15.9 nm (MSE 4.558); 24 h, 177.9 ±6.3 nm (MSE 1.940). IR ν_{max} (SiO₂)/cm⁻¹ 1726 (C=O), 1591 (C=O), 1274 (C-O), 1175 (C-O), 1156 (C-O), 756 (C-Br).
Synthesis of pyrazine-2-carbonyl chloride

![Chemical structure of pyrazine-2-carbonyl chloride]

Pyrazine-2-carboxylic acid (1.00 g, 8.06 mmol) was charged to a round bottomed flask. Thionyl chloride (20 mL, 32.62 g, 275 mmol) was added and the reaction mixture was stirred and gently heated at 50 °C. The evolution of sulfur dioxide was observed for ca. 1 h and the reaction was then left to stir at 50 °C for a further 1 h. Excess thionyl chloride was removed under reduced pressure and yielded a brown oil (1.06 g, 7.42 mmol, 92%), which was used immediately without characterisation or purification.

Synthesis of poly(2-(methacryloyloxy)ethyl pyrazine-2-carboxylate) brushes

![Chemical structure of poly(2-(methacryloyloxy)ethyl pyrazine-2-carboxylate)]

Substrates previously functionalised with poly(2-hydroxyethyl methacrylate) were sealed in a flame dried Schlenk tube. The Schlenk tube was evacuated under reduced pressure and then purged with nitrogen. This cycle was conducted five times, and then the sealed tube was left under a slight positive pressure of nitrogen using a nitrogen filled balloon. The substrate was immersed in anhydrous tetrahydrofuran (10 mL). Triethylamine (2.25 mL, 1.63 g, 16.12 mmol) was dried over CaH$_2$ and then added. Freshly prepared pyrazine-2-carbonyl chloride (1.06 g, 7.42 mmol) was dissolved in the minimum amount of anhydrous tetrahydrofuran and this solution was injected into the Schlenk tube. The reaction mixture was left overnight, then exposed to air. Substrates were then washed sequentially with tetrahydrofuran, methanol and water. Substrates were dried under a stream of nitrogen gas, and observed by ellipsometry. Ellips.: (HeNe, 632.8 nm; θ, 70°) PHEMA, 44.8 ±1.3 nm (MSE 0.679); Pyrazine, 80.5 ±5.3 nm (MSE 1.520). Thickness increase, 35.7 ±5.5 nm. IR ν$_\text{max}$ (SiO$_2$/cm$^{-1}$) 1732 (C=O), 1453 (Pyrazine), 1398 (Pyrazine), 1306 (C-O), 1282 (C-O), 1139 (C-O).
Synthesis of 9:1 benzoyl chloride: anthracene-9-carbonyl chloride mixture

Anthracene-9-carboxylic acid (0.22 g, 1.00 mmol) and benzoic acid (1.10 g, 9.0 mmol) were charged to a round bottomed flask. Thionyl chloride (20 mL, 32.62 g, 275 mmol) was added and the reaction mixture was stirred and gently heated at 50 °C. The evolution of sulfur dioxide was observed for ca. 1 h and the reaction was then left to stir at 50 °C for a further 1 h. Excess thionyl chloride was removed under reduced pressure and yielded a brown oil (1.43 g, 8.55/0.95 mmol, 95%), which was used immediately without characterisation or purification.

Synthesis of 9:1 poly(2-(methacryloyloxy)ethyl benzoate)-co-poly(2-(methacryloyloxy)ethyl anthracene-9-carboxylate) brushes

Substrates previously functionalised with poly(2-hydroxyethyl methacrylate) were sealed in a flame dried Schlenk tube. The Schlenk tube was evacuated under reduced pressure and then purged with nitrogen. This cycle was conducted five times, and then the sealed tube was left under a slight positive pressure of nitrogen using a nitrogen filled balloon. The substrate was immersed in anhydrous tetrahydrofuran (20 mL). Triethylamine (2.79 mL, 2.02 g, 20 mmol) was dried over CaH$_2$ and then added. A freshly prepared mixture of 9:1 benzoyl chloride: anthracene-9-carbonyl chloride (1.43 g, 8.55/0.95 mmol) was dissolved in the minimum amount of anhydrous tetrahydrofuran and this solution was injected into the Schlenk tube. The reaction
mixture was left overnight, then exposed to air. Substrates were then washed sequentially with
tetrahydrofuran, methanol and water. Substrates were dried under a stream of nitrogen gas,
and observed by ellipsometry. Ellips.: (HeNe, 632.8 nm; θ, 70°)
PHEMA, 44.8 ±1.3 nm (MSE 0.679); Post-modified, 76.4 ±9.9 nm (MSE 2.869).
Thickness increase, 31.6 ±9.9 nm. IR ν\text{max} (SiO\textsubscript{2}/cm\textsuperscript{-1}) 1732 (C=O), 1456 (C-O), 1278 (C-O),
1152 (C-O). The sample was viewed under an ultraviolet light but no fluorescence was
observed.

Synthesis of ferrocene carbonyl chloride

\[
\begin{align*}
\text{Fe} & \quad \text{OH} \\
\text{Cl} & \quad \text{S} - \text{Cl}
\end{align*}
\]

Ferrocene carboxylic acid (1.00 g, 4.35 mmol) was charged to a round bottomed flask and
dissolved in chloroform (50 mL). Thionyl chloride (3.2 mL, 5.18 g, 43.5 mmol) was added and
the reaction mixture was stirred and gently heated at 50 °C. The evolution of sulfur dioxide was
observed for ca. 1 h and the reaction was then left to stir at 50 °C for a further 1 h. Excess
thionyl chloride and chloroform were removed under reduced pressure and yielded a brown oil
(1.05 g, 4.23 mmol, 97%), which was used immediately without characterisation or purification.

Synthesis of poly(2-(methacryloyloxy)ethyl ferrocene-2-carboxylate) brushes

\[
\begin{align*}
\text{Br} & \quad \text{O} \quad \text{OH} \\
\text{N} & \quad \text{Fe} \quad \text{Cl} \\
\text{Si} & \quad \text{O} \quad \text{S} \quad \text{O}
\end{align*}
\]

Substrates previously functionalised with poly(2-hydroxyethyl methacrylate) were sealed in a
flame dried Schlenk tube. The Schlenk tube was evacuated under reduced pressure and then
purged with nitrogen. This cycle was conducted five times, and then the sealed tube was left
under a slight positive pressure of nitrogen using a nitrogen filled balloon. The substrate was
immersed in anhydrous tetrahydrofuran (10 mL). Triethylamine (0.60 mL, 0.44 g, 4.35 mmol)
was dried over CaH\textsubscript{2} and then added. Freshly prepared ferrocene carbonyl chloride (1.08 g,
4.35 mmol) was dissolved in the minimum amount of anhydrous tetrahydrofuran and this
solution was injected into the Schlenk tube. The reaction mixture was left for the prescribed
period, then exposed to air. Substrates were then washed sequentially with tetrahydrofuran,
methanol and water. Substrates were dried under a stream of nitrogen gas, and observed by ellipsometry. Ellips.: (HeNe, 632.8 nm; θ, 70°) PHEMA, 167.3 ±6.3 nm (MSE 2.171); 1 h, 209.3 ±5.6 nm (MSE 2.289); 4 h, 201.5 ±3.9 nm (MSE 1.334); 7 h, 186.1 ±13.0 nm (MSE 3.717); 10 h, 186.5 ±9.1 nm (MSE 2.609); 24 h, 180.3 ±9.6 nm (MSE 2.841). IR νₘₐₓ (SiO₂)/cm⁻¹ 1726 (C=O), 1487 (Fc), 1448 (Fc), 1274 (C-O), 1250 (C-O), 1159 (C-O).

Synthesis of poly[(2-dimethylamino) ethyl methacrylate] brushes via SI-ATRP

Substrates initiated with 2-bromoisobutyryl bromide were cut into squares (ca. 1 cm²) and sealed in individual flame dried Schlenk tubes. The Schlenk tubes were evacuated under reduced pressure and then purged with nitrogen. This cycle was conducted five times, and then each sealed tube was left under a slight positive pressure of nitrogen using a nitrogen filled balloon. 2-Dimethylamino ethyl methacrylate (DMAEMA, 25.0 mL, 23.35 g, 148.6 mmol) was pulled through a short column of basic alumina (ca. 5 cm length, 2.5 cm column diameter, 25 cm³ total packed volume) before being added to a solution of distilled water (5.00 mL, 5.00 g, 277.5 mmol) and isopropanol (20.0 mL, 15.7 g, 332.8 mmol). The solution was deoxygenated by bubbling with nitrogen gas for 15 min. Copper(I) bromide (88.5 mg, 0.617 mmol), copper(II) bromide (13.8 mg, 0.061 mmol) and 1,1,4,7,10,10-hexamethyl-triethylenetetramine (HMTETA, 313 mg, 1.36 mmol) were then added to the solution. This solution was then injected in 5 mL aliquots into each Schlenk tube. After the prescribed period (between 1 h and 24 h), substrates were removed from the polymerisation solution, washed with isopropanol and distilled water and dried under a stream of nitrogen gas. Ellips.: (HeNe, 632.8 nm; θ, 70°) 2 h, 44.3 ±2.2 nm (MSE 1.18); 4 h, 93.6 ±5.8 nm (MSE 2.03); 7 h, 153.8 ±9.4 nm (MSE 6.56); 24 h, 138.3 ±3.8 nm (MSE 7.39). IR νₘₐₓ (SiO₂)/cm⁻¹ IR νₘₐₓ (SiO₂)/cm⁻¹ 1728 (C=O), 1157 (C-O), 1063 (C-N).
Synthesis of poly[(2-dimethylamino) ethyl methacrylate] brushes via Si-ARGET-ATRP

Substrates initiated with 2-bromoisobutyryl bromide were cut into squares (ca. 1 cm²) and sealed in individual flame dried Schlenk tubes. The Schlenk tubes were evacuated under reduced pressure and then purged with nitrogen. This cycle was conducted five times, and then each sealed tube was left under a slight positive pressure of nitrogen using a nitrogen filled balloon. 2-Dimethylamino ethyl methacrylate (DMAEMA, 25.0 mL, 23.35 g, 148.6 mmol) was pulled through a short column of basic alumina before being added to a solution distilled water (5.00 mL, 5.00 g, 277.5 mmol) and isopropanol (20.0 mL, 15.7 g, 332.8 mmol). The solution was deoxygenated by bubbling with nitrogen gas for 15 min. Copper(II) bromide (13.3 mg, 0.059 mmol), 1,1,4,7,10,10-hexamethyl-triethylenetetramine (HMTETA, 68.3 mg, 0.297 mmol) and ascorbic acid (104 mg, 0.593 mmol) were then added to the solution. This solution was then injected in 5 mL aliquots into each carousel tube. After the prescribed period (between 1 h and 24 h), substrates were removed from the polymerisation solution, washed with isopropanol and distilled water and dried under a stream of nitrogen gas. Ellips.: (HeNe, 632.8 nm; θ, 70°) 2 h, 18.1 ±0.1 nm (MSE 0.15); 4 h, 20.7 ±0.6 nm (MSE 0.57); 18.5 h, 23.6 ±0.2 nm (MSE 0.15); 24 h, 25.0 ±0.1 nm (MSE 7.39). IR ν max (SiO)/cm⁻¹ IR ν max (SiO)/cm⁻¹ 1728 (C=O), 1157 (C-O), 1063 (C-N).
Attempted synthesis of poly(N-(anthracen-9-ylmethyl)-2-(methacryloyloxy)-N,N-dimethylethanaminium) brushes

Substrates previously functionalised with poly[(2-dimethylamino) ethyl methacrylate] were sealed in a flame dried Schlenk tube. The Schlenk tube was evacuated under reduced pressure and then purged with nitrogen. This cycle was conducted five times, and then the sealed tube was left under a slight positive pressure of nitrogen using a nitrogen filled balloon. The substrate was immersed in anhydrous toluene (5 mL). 9-(Chloromethyl)anthracene (0.23 g, 1.00 mmol) in anhydrous toluene (5 mL) was injected into the Schlenk tube. The reaction mixture was left for 24 h at 65 °C, then exposed to air. Substrates were then washed sequentially with toluene, methanol and water. Substrates were dried under a stream of nitrogen gas, and observed by ellipsometry. There was no observable thickness increase and the IR suggested the brushes had not been successfully quaternised. Exposure to UV light at 365 nm saw no fluorescent activity.
Synthesis of poly(2-hydroxyethyl methacrylate)-poly[(2-dimethylamino) ethyl methacrylate] diblock brushes via SI-ATRP

Substrates functionalised with poly(2-hydroxyethyl methacrylate) were sealed in individual flame dried Schlenk tubes. The Schlenk tubes were evacuated under reduced pressure and then purged with nitrogen. This cycle was conducted five times, and then each sealed tube was left under a slight positive pressure of nitrogen using a nitrogen filled balloon. 2-Dimethylamino ethyl methacrylate (25.0 mL, 23.35 g, 148.6 mmol) was pulled through a short column of basic alumina before being added to a solution distilled water (5.00 mL, 5.00 g, 277.5 mmol) and isopropanol (20.0 mL, 15.7 g, 332.8 mmol). The solution was deoxygenated by bubbling with nitrogen gas for 15 min. Copper(I) bromide (88.5 mg, 0.617 mmol), copper(II) bromide (13.8 mg, 0.061 mmol) and 1,1,4,7,10,10-hexamethyl-triethylenetetraamine (313 mg, 1.36 mmol) were then added to the solution. This solution was then injected in 5 mL aliquots into each carousel tube. After 24 h, substrates were removed from the polymerisation solution, washed with isopropanol and distilled water and dried under a stream of nitrogen gas. Substrates were then observed by ellipsometry. Ellips.: (HeNe, 632.8 nm; θ, 70°) PHEMA, 251.0 ±0.2 nm (MSE 0.27); Diblock, 321.6 ±11.2 nm (MSE 5.10). IR ν_{max} (SiO\textsubscript{2})/cm\textsuperscript{-1} 3392 (O-H), 1727 (C=O), 1635 (C=O), 1480 (C-N), 1470 (C-N), 1452 (C-N), 1239 (C-OH), 1157 (C-OR), 1082 (C-OR).
Substrates previously functionalised with a diblock of poly(2-hydroxyethyl methacrylate) and poly[(2-dimethylamino) ethyl methacrylate] were sealed in a flame dried Schlenk tube. The Schlenk tube was evacuated under reduced pressure and then purged with nitrogen. This cycle was conducted five times, and then the sealed tube was left under a slight positive pressure of nitrogen using a nitrogen filled balloon. The substrate was immersed in anhydrous toluene (5 mL). 9-(Chloromethyl)anthracene (0.23 g, 1.00 mmol) in anhydrous toluene (5 mL) was injected into the Schlenk tube. The reaction mixture was left for 24 h at 65 °C, then exposed to air. Substrates were then washed sequentially with toluene, methanol and water. Substrates were dried under a stream of nitrogen gas, and observed by ellipsometry. There was no observable thickness increase and the IR suggested the brushes had not been successfully quaternised. Exposure to UV light at 365 nm saw no fluorescent activity.
Synthesis of poly(2-(methacryloyloxy)ethyl anthracene-9-carboxylate)-poly[(2-dimethylamino) ethyl methacrylate] diblock brushes via SI-ATRP

Substrates functionalised with poly(2-(methacryloyloxy)ethyl anthracene-9-carboxylate) were sealed in individual flame dried Schlenk tubes. The Schlenk tubes were evacuated under reduced pressure and then purged with nitrogen. This cycle was conducted five times, and then each sealed tube was left under a slight positive pressure of nitrogen using a nitrogen filled balloon. 2-Dimethylamino ethyl methacrylate (25.0 mL, 23.35 g, 148.6 mmol) was pulled through a short column of basic alumina before being added to a solution distilled water (5.00 mL, 5.00 g, 277.5 mmol) and isopropanol (20.0 mL, 15.7 g, 332.8 mmol). The solution was deoxygenated by bubbling with nitrogen gas for 15 min. Copper(II) bromide (13.3 mg, 0.059 mmol), 1,1,4,7,10,10-hexamethyl-triethylenetetramine (68.3 mg, 0.297 mmol) and ascorbic acid (104 mg, 0.593 mmol) were then added to the solution. This solution was then injected in 5 mL aliquots into each carousel tube. After the prescribed period (between 1 h and 24 h), substrates were removed from the polymerisation solution, washed with isopropanol and distilled water and dried under a stream of nitrogen gas. Substrates were then observed by ellipsometry. Ellips.: (HeNe, 632.8 nm; θ, 70°) PAanth-HEMA, 386.8 ±5.4 nm (MSE 4.45); Diblock, 569.7 ±1.1 nm (MSE 0.89). IR $\nu_{\text{max}}$(SiO$_2$)/cm$^{-1}$ 1718 (C=O), 1606 (C=O), 1444 (C-N), 1381 (C-N), 1238 (C-OR), 1148 (C-OR), 1055 (C-OR), 1013 (C-OR).
Chapter 7: Experimental

At tempted synthesis of poly(2-(methacryloxy)ethyl anthracene-9-carboxylate)-poly(N-(anthracen-9-ylmethyl)-2-(methacryloxy)-N,N-dimethylethanolaminium) diblock brushes

Substrates previously functionalised with a diblock of poly(2-(methacryloxy)ethyl anthracene-9-carboxylate) and poly[(2-dimethylamino) ethyl methacrylate] were sealed in a flame dried Schlenk tube. The Schlenk tube was evacuated under reduced pressure and then purged with nitrogen. This cycle was conducted five times, and then the sealed tube was left under a slight positive pressure of nitrogen using a nitrogen filled balloon. The substrate was immersed in anhydrous toluene (5 mL). 9-(Chloromethyl)anthracene (0.23 g, 1.00 mmol) in anhydrous toluene (5 mL) was injected into the Schlenk tube. The reaction mixture was left for 24 h at 65 °C, then exposed to air. Substrates were then washed sequentially with toluene, methanol and water. Substrates were dried under a stream of nitrogen gas, and observed by ellipsometry. There was no observable thickness increase and the IR suggested the brushes had not been successfully quaternised. Exposure to UV light at 365 nm saw no fluorescent activity.
Synthesis of poly(methacrylic acid sodium salt) brushes via SI-ATRP

Substrates initiated with 2-bromoisobutyryl bromide were cut into squares (ca. 1 cm²) and sealed in individual flame dried Schlenk tubes. The Schlenk tubes were evacuated under reduced pressure and then purged with nitrogen. This cycle was conducted five times, and then each sealed tube was left under a slight positive pressure of nitrogen using a nitrogen filled balloon. A solution of sodium methacrylate (10.80 g, 100 mmol), distilled water (12.5 mL, 700 mmol) and 2,2'-bipyridyl (390 mg, 2.5 mmol) was adjusted to pH 9.0 ±0.1 using a small volume of 1M hydrochloric acid, added dropwise. The solution was deoxygenated by bubbling with nitrogen gas for 15 min. Copper(II) bromide (45 mg, 0.2 mmol) and copper(I) bromide (144 mg, 1 mmol) were then added to the degassed solution. This solution was then injected in 5 mL aliquots into each Schlenk tube. After 3 h, substrates were removed from the polymerisation solution, washed with distilled water and dried under a stream of nitrogen gas. Substrates were then observed by ellipsometry. Ellips.: (HeNe, 632.8 nm; θ, 70°) 75.9 ±6.4 nm (MSE 1.87). IR ν_max(SiO2)/cm⁻¹ 1546 (C=O).
Attempted synthesis of poly(anthracen-9-ylmethyl methacrylate) brushes

Substrates previously functionalised with poly(methacrylic acid sodium salt) were sealed in a flame dried Schlenk tube. The Schlenk tube was evacuated under reduced pressure and then purged with nitrogen. This cycle was conducted five times, and then the sealed tube was left under a slight positive pressure of nitrogen using a nitrogen filled balloon. 9-(Chloromethyl)anthracene (0.57 g, 2.5 mmol) was dissolved in N,N-dimethylformamide (10 mL) and this solution was injected into the Schlenk tube. The reaction mixture was left for 24 h, then exposed to air. Substrates were then washed sequentially with N,N-dimethylformamide, methanol and water. Substrates were dried under a stream of nitrogen gas. Data obtained suggests conversion to poly(methacrylic acid).

Ellips.: (HeNe, 632.8 nm; θ, 70°) PNaMA, 44.8 ±1.3 nm (MSE 0.679); product 57.5 ±1.3 nm (MSE 1.352). IR ν_{max} (SiO\textsubscript{2})/cm\textsuperscript{-1} 3606 (O-H), 1699 (C=O), 1256 (C-O).

UV-Vis λ_{max} (glass)/nm Nothing observed.
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