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Synthesis of Novel Water Soluble Conjugated Polymers Based on Poly-Phenylene Vinylene and Poly-Phenylene Ethynylene

Mona Damavandi

A thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry

The University of Auckland

2016
Abstract

This thesis focuses on the synthesis using atom transfer radical polymerisation ATRP, and the photophysical characterisation of novel grafted PPV and PPE derivatives with various solubilities. Initially a series of functionalised monomers 2.4, 2.5, 2.10 and 2.11 were successfully synthesised from hydroquinone 2.7. Heck and Sonogashira polymerisation methods were then used on these monomers to give hydroxyl functionalised polymers PPVOH 2.2 and PPEOH 2.3. Then, bromoester functionalised PPV and PPE were prepared through the post polymerisation esterification using α-bromoisobutyryl bromide 2.35 which successfully gave PPVMI 3.1 but a poor yield of PPEMI 3.2.1. Using a bromoester functionalised monomer 2.11 and the use of the Sonogashira polymerisation, directly synthesised PPEMI 3.2.2 was achieved in higher yield than post polymerisation esterification.

Functionalisation of these macroinitiators PPV 3.1 and PPE 3.2.2 using ARGET ATRP was found to be successful and allow the synthesis of both PPV and PPE grafted PnBA polymers both of, which have enhanced photoluminescence properties. Further synthesis of cationic grafted PPV and PPE using 2-trimethylaminoethylmethacrylate (TMAEMA) was successful again using ARGET ATRP. Both low and high molecular weight PPV-g-PTMAEMA (5.7 and 5.8) and PPE-g-PTMAEMA (5.9 and 5.10) were able to be prepared. The grafting polymerisation of anionic sulfopropyl acrylate (SPA) was also achieved using phase transfer complexation, using 18-crown-6, and then ARGET ATRP was again implemented for the synthesis of low and high molecular weight anionic grafted polymers PPV-g-PSPA (6.2 and 6.3) and PPE-g-PSPA (6.4 and 6.5).

The antibacterial activities of the nongrafted and grafted polymers were tested against wide spectrum of bacteria, which indicated activity for all of the cationic grafted polymers with the best activity for the high molecular weight PPE derivative 5.10.

Anion sensing was also explored using the more soluble low molecular weight cationic PPV 5.7 and it showed its sensing capability with enhanced selectivity towards iodide ions.
This thesis is honourably dedicated to Maryam Farahmand, Davoud Damavandi and Reza Jafarzadeh, my everlasting beloved mother, father and husband; you mean everything to me.
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Firstly I would like to thank my supervisor, Assoc. Prof. David Barker for all his help through my PhD. You have been mentor, a friend and someone I have always looked up to. Your kind understanding nature have kept me motivated. I could not have asked for a better supervisor. It has been a privilege to work for you.

To Prof. Jadranka Travas-Sejdic, thank you for all your guidance over the years and for the supportive advises.

Thank you to Dr. Katheryn Whitehead at the Manchester Metropolitan University, UK, for biological testing of the compounds. Also thank you for Dr. Viji Sarojini for the initial biological testing.

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for the belief you have in me and for telling me that I can do anything I put my mind and effort
to. Reza thank you so much for giving me, love, such strength and belief that everything should
be pacified. All I want is to make you all proud and to be someone who deserves the love and
belief you have for me, everything I am and all that I have achieved is because of your constant
love and support.
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<th>Definition</th>
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<tbody>
<tr>
<td>ADMET</td>
<td>acyclic diene metathesis</td>
</tr>
<tr>
<td>°C</td>
<td>degree celsius</td>
</tr>
<tr>
<td>µg</td>
<td>microgram(s)</td>
</tr>
<tr>
<td>µL</td>
<td>microlitre(s)</td>
</tr>
<tr>
<td>µM</td>
<td>micromolar</td>
</tr>
<tr>
<td>µmol</td>
<td>micromole(s)</td>
</tr>
<tr>
<td>¹³C NMR</td>
<td>carbon nuclear magnetic resonance</td>
</tr>
<tr>
<td>¹H NMR</td>
<td>proton nuclear magnetic resonance</td>
</tr>
<tr>
<td>A</td>
<td>optical density</td>
</tr>
<tr>
<td>A. baumannii</td>
<td>acinetobacter.baumannii</td>
</tr>
<tr>
<td>a.u.</td>
<td>arbitrary unit</td>
</tr>
<tr>
<td>act.</td>
<td>activation</td>
</tr>
<tr>
<td>AFM</td>
<td>atomic-force microscopoy</td>
</tr>
<tr>
<td>ARGET</td>
<td>activator regenerated by electron transfer</td>
</tr>
<tr>
<td>ARGET ATRP</td>
<td>activator regenerated by electron transfer atom transfer radical polymerisation</td>
</tr>
<tr>
<td>ATRA</td>
<td>atom transfer radical addition</td>
</tr>
<tr>
<td>ATRP</td>
<td>atom transfer radical polymerisation</td>
</tr>
<tr>
<td>B. subtilis</td>
<td>Bacillus subtilis</td>
</tr>
<tr>
<td>BIBB</td>
<td>α-bromo isobutyrylbromide</td>
</tr>
<tr>
<td>BPED</td>
<td>N1,N2-dimethyl-N1,N2-bis(pyridin-2-ylmethyl)ethane-1,2-diamine</td>
</tr>
<tr>
<td>Bpy</td>
<td>2,2′-bipyridine</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>BSA</td>
<td>bovine serum albumin</td>
</tr>
<tr>
<td>c</td>
<td>velocity of light</td>
</tr>
<tr>
<td>CPs</td>
<td>conjugated polymers</td>
</tr>
<tr>
<td>CRP</td>
<td>controlled radical polymerisation</td>
</tr>
<tr>
<td>DEATGPPV</td>
<td>poly(2,5-bis(diethylaminetetraethylene glycol)phenylene vinylene)</td>
</tr>
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<td>DEATG-PPV</td>
<td>poly[2,5-bis(diethylaminetetraethylene glycol)phenylene vinylene]</td>
</tr>
<tr>
<td>DIPA</td>
<td>diisopropylamine</td>
</tr>
<tr>
<td>DL</td>
<td>detection limit</td>
</tr>
<tr>
<td>DLS</td>
<td>dynamic light scattering</td>
</tr>
<tr>
<td>DMAEMA</td>
<td>2-(dimethylamino)ethyl methacrylate</td>
</tr>
<tr>
<td>DMAP</td>
<td>4-dimethylaminopyridine</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N-dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>dimethyl sulfoxide</td>
</tr>
<tr>
<td>DP</td>
<td>degree of polymerisation</td>
</tr>
<tr>
<td>E</td>
<td>optical band gap</td>
</tr>
<tr>
<td>E. coli</td>
<td><em>Escherichia coli</em></td>
</tr>
<tr>
<td>E. faecium</td>
<td><em>Enterococcus faecium</em></td>
</tr>
<tr>
<td>EBiB</td>
<td>ethyl α-bromoiso butyrate</td>
</tr>
<tr>
<td>eq.</td>
<td>equivalent(s)</td>
</tr>
<tr>
<td>Et₂O</td>
<td>diethyl ether</td>
</tr>
<tr>
<td>Et₃N</td>
<td>trimethylamine</td>
</tr>
<tr>
<td>Et₆TREN</td>
<td>N1,N1'-(ethane-1,2-diyl)bis(N2-ethyl-N1-(2-(ethylamino)ethyl)ethane-1,2-diamine)</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>EtOAc</td>
<td>ethyl acetate</td>
</tr>
<tr>
<td>EtOH</td>
<td>ethanol</td>
</tr>
<tr>
<td>eV</td>
<td>electron Volt</td>
</tr>
<tr>
<td>F</td>
<td>fluorophore</td>
</tr>
<tr>
<td>F*</td>
<td>excited fluorophore</td>
</tr>
<tr>
<td>FETs</td>
<td>field-effect transistors</td>
</tr>
<tr>
<td>F-Q</td>
<td>non-fluorescent complex</td>
</tr>
<tr>
<td>FRET</td>
<td>fluorescence resonance energy transfer</td>
</tr>
<tr>
<td>FT-IR</td>
<td>fourier transform-infrared</td>
</tr>
<tr>
<td>g</td>
<td>gram(s)</td>
</tr>
<tr>
<td>GPC</td>
<td>gel permeation chromatography</td>
</tr>
<tr>
<td>GTP</td>
<td>group transfer polymerisation</td>
</tr>
<tr>
<td>h</td>
<td>hours</td>
</tr>
<tr>
<td>(\hbar)</td>
<td>Planck's constant</td>
</tr>
<tr>
<td>HMTETA</td>
<td>(N_1,N_1'-(\text{ethane-1,2-diyl})\text{bis}(N_1,N_2,N_2'-\text{trimethylethane-1,2-diamine}))</td>
</tr>
<tr>
<td>HMw</td>
<td>high molecular weight</td>
</tr>
<tr>
<td>I</td>
<td>measured integrated emission intensity</td>
</tr>
<tr>
<td>IOAc</td>
<td>iodoacetate</td>
</tr>
<tr>
<td>Ir</td>
<td>initiation ratio</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
</tr>
<tr>
<td>K.Pneumoniae</td>
<td>\textit{Klebsiella Pneumoniae}</td>
</tr>
<tr>
<td>KATRP</td>
<td>atom transfer radical polymerisation rate constant</td>
</tr>
<tr>
<td>L.monocytogenes</td>
<td>\textit{Listeria monocytogenes}</td>
</tr>
<tr>
<td>LCDs</td>
<td>liquid crystalline displays</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>LCP</td>
<td>living carbocationic polymerisation</td>
</tr>
<tr>
<td>LECs</td>
<td>light emitting electrochemical cells</td>
</tr>
<tr>
<td>LEDs</td>
<td>light-emitting diodes</td>
</tr>
<tr>
<td>LM&lt;sub&gt;w&lt;/sub&gt;</td>
<td>low molecular weight</td>
</tr>
<tr>
<td>m</td>
<td>multiplet</td>
</tr>
<tr>
<td>M&lt;sup&gt;+&lt;/sup&gt;</td>
<td>parent molecular ion</td>
</tr>
<tr>
<td>MBC</td>
<td>minimum bacteria concentration</td>
</tr>
<tr>
<td>Me&lt;sub&gt;6&lt;/sub&gt;TREN</td>
<td>hexamethyl 3,3',3'',3'''',3'''''-((nitrilotris(ethane-2,1-diyl))tris(azanetriyl))hexapropionate</td>
</tr>
<tr>
<td>MeOH</td>
<td>methanol</td>
</tr>
<tr>
<td>mg</td>
<td>milligram(s)</td>
</tr>
<tr>
<td>MHz</td>
<td>megahertz</td>
</tr>
<tr>
<td>MIC</td>
<td>minimum inhibitory concentration</td>
</tr>
<tr>
<td>min</td>
<td>minute(s)</td>
</tr>
<tr>
<td>mL</td>
<td>millilitre(s)</td>
</tr>
<tr>
<td>mM</td>
<td>millimolar(s)</td>
</tr>
<tr>
<td>mm</td>
<td>millimetre(s)</td>
</tr>
<tr>
<td>Mn</td>
<td>number-average molecular weight</td>
</tr>
<tr>
<td>mol</td>
<td>mol(s)</td>
</tr>
<tr>
<td>mp</td>
<td>melting point</td>
</tr>
<tr>
<td>MRSA</td>
<td>methicillin-resistant <em>Staphylococcus aureus</em></td>
</tr>
<tr>
<td>MS</td>
<td>molecular sieves or mass</td>
</tr>
<tr>
<td>MV&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>methyl viologen</td>
</tr>
<tr>
<td>Mw</td>
<td>average molecular weight</td>
</tr>
</tbody>
</table>
\( n \) refractive index of solvent

\( \text{N}_4 \) tetradaentate

\( n\text{BA} \) normal-butylacrylate

NCPs non-ionic water soluble conjugated polymers

\( n\)-hexanes normal-hexanes

\( \text{nm} \) nanometre

NMR nuclear magnetic resonance

NPPMI (E)-\( N \)-methyl-1-(pyridin-2-yl)methanimine

\( P. \text{aeruginosa} \) \textit{Pseudomonas aeruginosa}

PA polyacetylene

PAEs poly(arylene ethynylene)s

PANI polyaniline

\( \text{Pd(OAc)} \) palladium(II)acetate

\( \text{Pd(PPh3)}4 \) tetrakis(triphenylphosphine)palladium(0)

PEMDETA \( \text{N}_1\text{-}(2\text{-}(\text{dimethylamino})\text{ethyl})\text{-N}_2\text{,N}_2\text{,N}_2\text{-trimethylethane-1,2-diamine} \)

PF polyfluorene

PL photoluminescence

PMEHPPV poly(2-methoxy-5-(20-ethylhexylloxy))-1,4-phenylene vinylene

PPE poly(\textit{para}-phenylene ethynylene)

PPEMI \((2\text{-}((2\text{-}5\text{-bis}(2\text{-}(\text{methoxymethoxy})\text{ethoxy})\text{-}4\text{-}(\text{prop-1-yn-1-yl})\text{phenyl})\text{ethynyl})\text{-}5\text{-}(\text{prop-1-yn-1-yl})\text{-}1,4\text{-phenylene})\text{bis}(\text{oxy})\text{bis}(\text{propane-3,1-diyl})\text{bis}(2\text{-bromo-2-methylproanoate})\)

PPEOH \(3,3'\text{-}((2\text{-}((2\text{-}5\text{-bis}(2\text{-}(\text{methoxymethoxy})\text{ethoxy})\text{-}4\text{-}(\text{prop-1-yn-}
1-yl)phenyl)ethynyl)-5-(prop-1-yn-1-yl)-1,4-phenylene)bis(oxy))bis(propan-1-ol)

ppm  parts per million

PPP  poly(para-phenylene)

PPV  poly(para-phenylene vinylene)

PPVMI  poly ((2-(E))-2,5-bis(2-(methoxymethoxy)ethoxy)-4-(E)-prop-1-en-1-yl)styryl)-5-((E))-prop-1-en-1-yl)-1,4-phenylene)bis(oxy))bis(propane-3,1-diyl) bis(2-bromo-2-methylpropanoate)

PPVOH  poly(3-(5-(E))-2,5-bis(2-(methoxymethoxy)ethoxy)-4-(E)-prop-1-en-1-yl)styryl)-4-(2-hydroxyethoxy)-2-(E)-prop-1-en-1-yl)phenoxy)propan-1-ol)

PPy  polypyrrole

PRE  persistent radical effect

PSPA  poly 3-(acryloyloxy)propane-1-sulfonate

PT  polythiophene

PTC  phase transfer complexation

PTMAEMA  poly N,N,N-trimethylaminoethylmethacrylate

Q  quencher molecule

q  quartet

QL  quencher-ligand

RAFT  reversible addition-fragmentation chain transfer polymerisation

RDP  reversible-deactivation polymerisation

ROMP  ring-opening metathesis polymerisation

RP  radical polymerisation

rt  room temperature
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tr>
<td>s</td>
<td>singlet</td>
</tr>
<tr>
<td>S. epidermidis</td>
<td><em>Staphylococcus epidermidis</em></td>
</tr>
<tr>
<td>S₀</td>
<td>ground singlet electronic state</td>
</tr>
<tr>
<td>S₁</td>
<td>singlet excited electronic state</td>
</tr>
<tr>
<td>S₈₁</td>
<td>nucleophilic substitution (unimolecular)</td>
</tr>
<tr>
<td>S₈₂</td>
<td>nucleophilic substitution (bimolecular)</td>
</tr>
<tr>
<td>SPA</td>
<td>3-(acyrlyloxy)propane-1-sulfonate</td>
</tr>
<tr>
<td>SPMA</td>
<td>sulfopropyl methacrylate</td>
</tr>
<tr>
<td>SRMP</td>
<td>stable-radical-mediated polymerisation</td>
</tr>
<tr>
<td>STM</td>
<td>scanning tunnelling microscopy</td>
</tr>
<tr>
<td>t</td>
<td>triplet</td>
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<tr>
<td>TBDMS</td>
<td>tert-butyltrimethylsilane</td>
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<tr>
<td>TBDMScI</td>
<td>tert-butyl-dimethylsilyl chloride</td>
</tr>
<tr>
<td>'BuOK</td>
<td>potassium tert-butoxide</td>
</tr>
<tr>
<td>'BuONa</td>
<td>sodium tert-butoxide</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TMAEMA</td>
<td>N,N,N-trimethylaminoethylmethacrylate</td>
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<tr>
<td>TMS</td>
<td>tetramethylsilane</td>
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<tr>
<td>TPEDA</td>
<td>N₁,N₁,N₂,N₂-tetakis(pyridin-2-ylmethyl)ethane-1,2-diamine</td>
</tr>
<tr>
<td>TPMA</td>
<td>tris(pyridin-2-ylmethyl)amine</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>VRE</td>
<td>vancomycin-resistant <em>enterococci</em></td>
</tr>
<tr>
<td>ZI</td>
<td>zone of inhibition</td>
</tr>
<tr>
<td>δ</td>
<td>chemical shift</td>
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<tr>
<td>λ</td>
<td>cut-off wavelength</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
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</tr>
<tr>
<td>$\lambda_{\text{max abs}}$</td>
<td>maximum absorption wavelength</td>
</tr>
<tr>
<td>$\lambda_{\text{max em}}$</td>
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Chapter 1: Introduction
Up to 40 years ago, all carbon based polymers were mainly considered to be insulators. The idea of carbon based polymers being conductive polymers arose from an experimental error in Hideki Shirakawa’s lab in 1967 when the semiconducting polyacetylene (PA) was obtained by the accidental addition of 1000 times excess of catalyst. Furthered by doping of electron acceptors and electron donors in PA, the conductivity of this polymer was increased by 10 million times in 1977.

Since then, conjugated polymers (CPs) have developed into an entirely new field of chemistry which resulted in the awarding of a Nobel Prize to three polymer scientists in 2000. CPs display attractive optical, electrical and magnetic properties due to their delocalised \(\pi\)-electron systems, which has resulted in an abundance of investigations by a large number of scientists around the world.

Conjugated polymers are a growing class of materials, with a wide range of applications, such as in light-emitting diodes (LEDs), light emitting electrochemical cells (LECs), plastic lasers, solar cells and field-effect transistors (FETs). One of the most recent area of focus for CPs is their utilisation as chemical or biological sensors. The chemical structure of CPs, lend them to have many properties desired for a sensor, particularly with regard to their sensitivity. In particular, the delocalized electronic structure of CPs means these polymers are able to exhibit potential absorption and substantial emission. Hence they are able to produce amplified signal changes while interacting with different analytes. Rapid transport of electronic excitation and coupling between optoelectronic segments can result in an increase in sensitivity of CPs. CP-based sensors may be characterised based on the observed signal type; sensors may be categorised as conductometer (electrical conductivity as the detecting signal), potentiometer (chemical potential as the detecting signal), colorimeter (absorption characteristic as the detecting signal) and fluorometers (fluorescence characteristic as the detecting signal).

Examples of the most commonly investigated CPs are poly(\textit{para}-phenylene) (PPP), poly(\textit{para}-phenylene vinylene) (PPV), poly(\textit{para}-phenylene ethynylene) (PPE), polythiophene (PT), polypyrrole (PPy), polyaniline (PANI) and polyfluorene (PF) (Fig 1.1).
Most CPs of this type are synthesised using palladium-catalyzed cross-coupling polymerisation methods. This method of polymerisation is often chosen because palladium-catalysed reaction conditions are generally considered to be mild and may be used with a wide range of functional groups, as well as solvent compatibility.23

Within the CP family, poly(para-phenylene ethynylene)s (PPEs) and poly(para-phenylene vinylene)s (PPVs) are the most recently investigated polymers for biological applications.24 Due to the 180° bond angle between the phenyl carbon and sp’ alkyne carbon and the lower-molecular-weight of PPEs, these polymers may also be useful in several applications, such as in nonlinear optical fibers,25 liquid-crystal displays26 and molecular wires to bridge nanoelectrodes.27 Compared with PPVs, PPEs exhibit an extended electronic structure and also higher quantum yield. Arising from this, PPEs have been widely studied in sensing and potential transducing.28

Solubility in aqueous media is a desirable factor for CPs to interact with analytes, particularly for biological application. Solubility can be imparted by sidechain functionality, and in the case of organic soluble components, alkyl chains could be appended to the monomers. Water-soluble CPs may also be produced by incorporating ionic functional groups onto the conjugated backbone, with the resulting polymers known as conjugated polyelectrolytes (CPEs). Furthermore, introducing a large number of ionic sites by grafting polymerisation on to a CP backbone, to produce grafted molecular brushes, not only tackles the water solubility concern of the CPs but also introduces a further wide range of applications.29–32 Ionic CP molecular brushes are a new class of CPs; their processability and applications are of great interest in recent years, particularly as chemical sensors and other biological applications.33–36
1.1 Poly(para-phenylene vinylene) (PPV)

1.1.1 Overview

Poly(para-phenylene vinylene) (PPV) is considered to be a copolymer consisting of para-phenylene and trans-vinylene. The unsaturated property of PPV results in an optical band gap around 2.6 mV. Quantitatively, this optical capability is located between poly para-phenylene (PPP) and polyacetylene. The unsaturation in PPV also enables it to have electrical conductivity. PPVs has been widely studied as a doped film for which the conductivity is estimated to be around 10-500 SCm⁻¹. The optical properties of PPV and its derivatives make them one of the most applicable groups of material for polymer-based LEDs.

Within the PPV family, the addition of alkoxy groups on to the backbone result in a large increase of photocurrent ability, which enables such PPV derivatives to be used for solar cell applications. The generally trans configuration of PPVs result in extremely rigid polymers which are capable of thermal liquid crystallisation.

PPVs generally have large dielectric constants, which is a common feature in all types of CPs. This results in limited solubility in common organic solvents. This can be overcome by introducing suitable functional groups in order to improve polymer solubility. Water-solubility, which is desired for PPV applications in biological and biomedical fields, has been tackled through the introduction of hydrophilic side chains on the PPV backbone. The resulting PPVs have shown a wide range of biological applications such as biological sensing ability as well as antiseptic efficiencies.
1.1.2 Synthesis Routes of Polyphenylene Vinylene Derivatives

Summarised below are some of the common and most important methods to prepare PPVs.

1.1.2.1 PPV Synthesis via Diene Metathesis

Acyclic diene metathesis (ADMET) is an exclusive type of olefin metathesis synthesis that can be used to polymerise divinylbenzenes. The ADMET synthesis pathway using dialkyl-divinylbenzene 1.1 is presented in Scheme 1.1.

Ethylene gas 1.2 is the by-product of this polymerisation method, which is removed from the reaction with the aid of vacuum.

It is observed that the ADMET polymerisation method mostly results in the synthesis of PPV oligomers with a degree of polymerisation (DP) of around 8.55

Using the ADMET polymerisation route, several soluble PPV derivatives have been reported. It was found that increased polarity in the side chains inhibits the metathesis cycle, therefore most of the reported soluble PPVs using ADMET synthesis are non-polar, alkyl substituted, PPVs such as 1.4 (Scheme 1.1).55,56
Scheme 1.1. ADMET polymerisation (diagram adapted from Haque et al.).
1.1.2.2 PPV Synthesis via Conventional Organic Routes

PPV was initially synthesised using condensation reactions such as the Wittig, Knoevenagel, Wurtz-Wittig, or McMurry reactions, as well as through the various dehydrohalogenation reactions. These condensation reactions to form PPVs mainly resulted in PPVs with low molecular weights or the formation of PPV oligomers.

Of all the above-mentioned condensation reactions, Wurtz-Wittig is the most frequently used method, first reported in 1960. As is shown in Scheme 1.2 in the Wittig polymerisation method the polymer synthesis is based on the condensation of dialdehyde monomers 1.5 with bis-phosphonium salts 1.6.

![Scheme 1.2. PPV synthesis via Wurtz-Wittig reaction.](image)

The Wurtz-Wittig polymerisation method has a low reactivity, which consequently results in PPVs with low DP. Despite the limitation in polymer molecular weight, Wittig polymerisation has been used for synthesis of various soluble and insoluble PPV derivatives such as 1.7 (Scheme 1.2).
The Knoevenagel condensation is also one of the classical condensation reactions. This condensation reaction is often a base catalyzed reaction between a dialdehyde 1.8 and an arene 1.9, where the arene has two sites of acidic protons (Scheme 1.3). In the Knoevenagel condensation mechanism, deprotonation of arene forms a nucleophile 1.10, which is able to attack an activated dialdehyde monomer 1.11 (often activated as an iminium ion) resulting in an elimination sequence. Several PPVs and derivatives with cyano group have been synthesised using the Knoevenagel polymerisation.45,61–64 Although PPV derivatives with a cyano group have less electron conductivity due to the electron withdrawing nature of the cyano group, they have become essential materials for creating LEDs. Comparing LEDs based on cyano substituted PPVs with non-substituted PPVs, the cyano substituted PPVs exhibited more than 4 % improvement in the LEDs efficiency.62

Scheme 1.3. Schematic structure of Knoevenagel polymerisation reaction.65
The McMurray reaction is another condensation reaction, which has been employed to synthesise PPVs.\textsuperscript{65,66} As can be observed in Scheme 1.4, this polymerisation is a coupling of a dialdehyde 1.8, which is performed in the presence of titanium chloride and a reducing agent. It has been shown that the McMurray reaction proceeds through either pinacol 1.12 or metallocarbenoid 1.13 intermediates which are both depicted in Scheme 1.4.

The formation of titanium oxides in the McMurray reaction drives the elimination of the oxygen in the carbonyl groups, giving the desired PPV.
1.1.2.3 PPV Synthesis via Precursor Method

The indirect or “precursor” polymerisation route is known as one of the most general methods for the synthesis of PPV and its derivatives. This polymerisation route has been widely employed for the synthesis of other heteroaromatic vinylenes\textsuperscript{65,68–75} is performed through either anionic or radical pathways. \textit{p}-Quinodimethane is the active propagation monomer in all the precursor routes which is formed while introducing an appropriate base to the precursor monomers, which are generally di-substituted 1,4-dimethylbenzenes\textsuperscript{76} along with the elimination of the leaving group.

After introduction of the base to the precursor monomer, the reaction mechanism could proceed through the anionic pathway\textsuperscript{76–80} while eliminating the leaving group. Further dimerisation of the monomer can also proceed through a radical mechanism after forming a diradical species.\textsuperscript{81} It is understood that a radical pathway tends to produce high molecular weight PPVs while the anionic pathway affords low molecular weight polymers. It is also observed that in some cases both mechanisms occur at the same time which results in a PPV with high polydispersity.

Several precursor routes have been developed, of which the most common ones are Gilch,\textsuperscript{82} Wessling-Zimmerman,\textsuperscript{68,83} Xanthate\textsuperscript{84} and the sulfinyl precursor routes\textsuperscript{73,85,86}, by all of which are briefly described below (Scheme 1.5).
1.1.2.4 Gilch Route

In order to achieve PPV through the polymerisation of symmetrical di-chloro \( p \)-xylene 1.14, the Gilch precursor method was developed while using an excess amount of potassium tert-butoxide (\( \text{tBuOK} \)) in an organic solvent.\(^82\) Within the Gilch method dehydrohalogenation of the monomer starts with the formation of the precursor and it is widely believed that this follows the radical mechanism rather than the ionic pathway.\(^87\) It has also been shown, that controlling the amount of base within the Gilch reaction in order to prevent incomplete elimination process is important. Most of the Gilch based PPVs are of high molecular weight and are organic soluble, which makes this method suitable for industrial purposes.\(^88\) However, there are some drawbacks to the Gilch precursor route. The main disadvantage being, that as the reaction requires high temperatures generally above 100 °C, gel formation may occur. Formation of the head-head and tail-tail structures within the propagation step, when using non-symmetrical monomers, is another drawback of the Gilch polymerization, which could significantly affect the opto-electrical properties of resulting PPV.\(^89\)
1.1.2.5 Wessling-Zimmerman Route

Bissulfonium salts (such as 1.15) are used as a monomer in the Wessling-Zimmerman polymerisation reaction. They are dissolved in polar protic solvents in the presence of the base (commonly NaOH). It is thought that the initial monomer concentration is an essential aspect of this polymerisation method. Determined by the monomer, the solvent and base being used in the polymerization reaction, it may undergo either an anionic or radical mechanism.76

The synthesis of various PPV derivatives with different side chains has been reported through the utilisation of the Wessling-Zimmerman route90, however this route has some disadvantages. The main drawback of this polymerization is that it only works for aromatic systems with substituents that are electron acceptors.91,92 Furthermore, the reactivity of the sulfonium groups in the precursor can result in the formation of gels and incomplete elimination which can result in permanent conjugation defects within the polymer backbone.93,94 Insolubility of the sulfonium precursor in common organic solvents also limits this polymerization.76

Additionally to obtain the final polymer in Wessling-Zimmerman route, hydrogen chloride needs to be eliminated through heating at temperatures higher than 170 °C, which means the overall process is experimentally involved.95

1.1.2.6 Sulfinyl Route

PPV synthesis following the sulfinyl route uses an asymmetric monomer 1.16 in the presence of a base which is usually sodium tert-butoxide (BuONa). The synthesis of this asymmetric monomer is often an involved method which is the main drawback of this polymerisation route.96 Apart from this, the sulfinyl polymerisation route can be implemented in a variety of solvents which broadens the scope of substituents in the monomer precursors.76

The sulfinyl route most likely proceeds through a radical mechanism, although depending on the choice of monomer, solvent and base the anionic mechanism is also possible.78–81

It has also been observed that the PPVs synthesised using the sulfinyl route have structural advantages due to the asymmetric structure of the precursor monomer, which results in only head to tail propagation.81 Furthermore the elimination step of the precursor polymer in the
sulfinyl route can be performed at a lower temperatures, compared to the Wessling-Zimmerman route.97

### 1.1.2.7 Xanthate Route

The Xanthate route was developed to tackle the drawbacks of the Wessling and Gilch routes. The symmetrical dixanthate 1.17 is used as a monomer in the presence of a base (usually 'BuOK) in THF. The xanthate route has an advantage over the other routes in that there is high solubility of the monomer precursor in common organic solvents. Further, it is evidenced that the PPVs achieved through the xanthate route show better electroluminescence properties compared to PPV products from the other precursor routes.98 However, it has been reported that PPVs produced using the xanthate route have high polydispersities which generally due to in structural defects.76

### 1.1.2.8 PPV Synthesis via Heck Reaction

The Heck or Mizoroki-Heck reaction is a palladium-catalysed olefin arylation reaction which has been used for several years to form C-C bonds.99,100 As shown in Scheme 1.6, through the usage of palladium catalysts (usually phosphine-ligand based) 1.18, aryl halides 1.19 may be coupled with an alkene 1.20 in the presence of a base (most commonly an alkyl amine base).
In order to synthesis PPV and its derivatives, the Heck reaction can be used based on three main methodologies, which are presented in Scheme 1.7.
Obtaining PPV via method I, ethylene gas is bubbled through a solution of substituted dibromo or diiodobenzene 1.21 containing the palladium catalyst. The reaction of both a divinyl substrate 1.22 and dihaloaryl species in the presence of palladium catalyst can give PPV in the synthesis based on method II. In method III, a difunctional monomer 1.23 may self-polymerise in the presence of the palladium catalyst to form the desired PPV.

Utilising dihalophenyl substituted monomers in Heck polymerisation using method I, a number of substituted PPVs and their copolymers have been reported (1.24-1.28), examples of which are shown in Fig 1.2.101,102

![Fig 1.2. Reported PPV derivatives utilising the Heck polymerisation method.](image)

Utilising the second Heck reaction based methodology, a number of thermotropic liquid crystalline PPV derivatives have been synthesised (1.29-1.33) which are shown in Fig 1.3.52 Analysing these PPV derivatives using X-ray diffraction illustrated the semi-crystalline structure that may dramatically changes through heating above 100 °C.

![Fig 1.3. Reported PPV derivatives synthesised using Heck reaction method II.](image)
1.2 Poly(para-phenylene ethynylene) (PPE)

1.2.1 Overview

Of the unsaturated class of polymer materials, poly(arylene ethynylene)s (PAEs) are one of the most prominent conjugated polymers. Poly(phenylene ethynylene)s (PPEs), a type of PAE, are one of the most common groups, in which benzene represents the aromatic component. As PPEs are able to have a wide range of functional groups, they can be seen to provide a number of advantages over other PAEs. To date, PPEs with different substituents such as alkyl,\textsuperscript{103} alkoxy,\textsuperscript{104} carboxylate\textsuperscript{105} and phosphonate\textsuperscript{28} have been reported.

PPEs may serve a wide range of applications, as they exhibit high quantum yields in solution, a narrow emission and a wide band gap which results in blue emission. Appropriate substitution of the PPE backbone has resulted in PPEs use in liquid crystalline displays (LCD).\textsuperscript{26,106} Furthermore, PPEs have also been reported to be used in biological applications such as in biosensing.\textsuperscript{107} Because the CPs have molecular wire capability (which drives signal amplification) they also serve as a candidates for use as signal amplifier sensors which have superiority over independently functioning chemical sensors.

One example is the sensing of protease activity with the aid of an anionic PPE derivative which was reported based on both turn-on and turn-off assays (see below for explanation and also section 1.7.4).\textsuperscript{108}

PPEs can be grouped into three types of structural configuration, (Fig 1.4) these are meta, para and ortho linked phenylene ethynylene. It has been established that the PPE configuration affects the photophysical properties of the resulted polymer.

![Fig 1.4. Molecular configurations of PPE backbone.\textsuperscript{19}](image)
Para-linked PPEs are most common and various PPEs have been synthesised and utilised as optoelectronics materials. Self-assembly in para-substituted PPEs is high and studies have been conducted to investigate configurations and chain lengths. Studies have included light scattering techniques coupled with chromatography techniques which showed a strong structural dependency to the PPE’s molecular weight. Further studies using scanning tunnelling microscopy (STM) confirms the dependency of rigid structure in the self-assembled PPEs to the molecular weight.

Meta and ortho linked PPEs have not been extensively studied for their applications, however, the folding properties of these shapes has been studied. In order to study folding efficiency and its effect on photophysical properties of resulting polymers, meta and ortho shaped PPEs were studied using 1H NMR, UV-Vis, fluorescence spectroscopy as well as through computational modelling. Consequently it has been concluded that the folding property of the meta and ortho shaped PPEs is directly dependent on the polymer chain length, temperature and solvent polarity of the polymer solution.

1.2.3 Synthetic Routes towards Poly(Aryleneethynylene) Derivatives

There are several different synthetic routes reported for the synthesis of PPEs. Self-polymerisation of functionalised cupreous acetylides through a multistep procedure is a well reported synthesis of PPE (Scheme 1.8). Elemental analysis determined the chain length for the resulting PPE to be around 12 monomer units.

![Scheme 1.8. Self-polymerisation synthetic route.](image)
Electrochemical reduction of \textit{para}-xylene is another synthetic route which has been employed for the synthesis of non-substituted PPEs. Through this route, generally hexachloro-\textit{p}-xylene \textbf{1.35} is electropolymerised using a copper electrode (\textbf{Scheme 1.9}). PPE films based on this method have been reported for battery device applications.\textsuperscript{118,119}

\begin{center}
\textbf{Scheme 1.9. Electrochemical synthesis route.}\textsuperscript{117}
\end{center}

Another synthetic route to produce PPE films is the dehydro-bromination method which requires a PPV precursor polymer \textbf{1.14}.\textsuperscript{120} By this method, PPV films are brominated, which is usually done using chloroform as a solvent. The brominated material \textbf{1.36} then needs to be heated to 300 °C resulting in elimination of 2 moles of HBr (\textbf{Scheme 1.10}).

\begin{center}
\textbf{Scheme 1.10. De-hydro-bromination synthesis route.}\textsuperscript{117}
\end{center}

To make the dehydro-bromination reaction process milder, with regard to the high temperatures required, the use of different bases has been examined, and shown to promote thermal elimination at lower temperatures.\textsuperscript{120}

Synthesis of PPE and its derivatives has also been reported utilising a polycondensation method which was conducted using dihaloaryl \textbf{1.37} substrates and disodium acetylene \textbf{1.38}.\textsuperscript{121,122} It was essential to perform the polycondensation reaction in an inert solvent with a high boiling point, such as hexadecane. As it is shown in \textbf{Scheme 1.11}, 1,4-dibromobenzene \textbf{1.37} was heated near 300 °C and gave the desired PPE.
Another alternative synthetic route is a nucleophilic substitution method which has been used in the synthesis of perfluorinated PPE (Scheme 1.12). An anionic allene 1.40 formed from a phenylacetylene 1.39 undergoes polymerisation through a stepwise reaction condition. The produced perfluorinated PPEs 1.41 are insoluble, and therefore they can be simply precipitated for the further characterisation.

Alkyne metathesis is another method reported to produce polyarylene ethynlenes. Molybdenum or tungsten-based complexes 1.42 are typically used as the catalyst. The catalyst system that was first used was Mo(CO)$_6$, which produced a basis for tungsten and molybdenum alkylidenes to be developed by Schrock and co-workers. These catalysts are structurally defined as (RO)$_3$M≡C-CMe$_3$, where M is either W or Mo and R is t-butyl or aryl groups. Utilising Schrock’s catalysts, several PPEs with high degree of polymerisation (DP) have been synthesised (Scheme 1.13).
Despite of the potential advantages of this method in synthesis of high molecular weight polyarylene ethynlenes it still suffers from some drawbacks. The used catalysts are not stable towards moisture and air and show low compatibility with a wide range of substituents.\textsuperscript{128}

\subsection*{1.2.4 Pd-Catalysed Coupling Route}

The Pd-catalysed coupling reaction, which is also known as the Sonogashira-Hagihara coupling, between an aryl dibromides or diiodides and terminal alkynes is an extensively used method for the synthesis of poly(aryleneethynylene)s including PPEs.\textsuperscript{129,130} The utilisation and mechanism of the Pd-catalysed coupling reaction has been extensively studied.\textsuperscript{129,131} The mechanism of this reaction route is depicted in Scheme 1.14. Along with the monomers, the reaction mixture typically contains different components in catalytical amounts.
Most Pd-catalysed coupling reactions, (e.g. the Heck coupling), required elevated temperature.\textsuperscript{131,132} However, utilising copper(I)iodide in the Sonogashira reaction as a co-catalyst allows milder reaction conditions and lowers the reaction temperature, even as low as room temperature.
The Sonogashira coupling reaction mechanism is shown in Scheme 1.14. It is initiated using a Pd(0) active catalyst 1.43 which itself is achieved through the reduction of the Pd(II) species with either solvent or other reducing agents. The Pd(0) species then undergoes oxidative addition to the dihaloaryl substrate 1.44. Further synchronism of the Pd-catalyst cycle A with the Cu-co-catalyst cycle B results in the transmetalation of a Cu-acetylene 1.45 to the Pd-catalytic cycle. Within the copper catalytic cycle, the copper acetylide intermediate 1.45 is formed using an appropriate base 1.46 (which is normally a secondary amine). Finally, the acetylene coupled compound 1.47 is obtained through the reductive elimination step, which also regenerates the active Pd(0) catalyst.

In many reported Sonogashira reactions, Pd[(PPh₃)₂]Cl₂ is used as the Pd catalyst as it is commercially available. Sometimes homocoupling of the acetylene species creates diacetylene compounds as byproducts. This consumption of the acetylene monomer may disrupt the stoichiometry of the polymerisation reaction which consequently results in polymers with lower molecular weight than expected.¹⁹ To prevent this, several different methods have been employed, such as adding more equivalents of acetylene monomer¹³³ as well as adding additional triphenylphosphine to stabilise the Pd(0) complex.¹⁹ However when the less active Pd[PPh₃]₄ is employed, polymers that are closer to the expected molecular weight are frequently obtained.

### 1.3 Ionic Water Soluble Conjugated Polymers

The conducting and optical properties of CPs has led to their use in a variety of applications.¹⁰,¹⁰⁷ Water soluble CPs allow them to be used as sensors in aqueous solutions. To enable this water solubility, the hydrophobic conjugated backbones in CPs must be counteracted. This has been achieved by introducing ionic groups, such as sulfonic,¹³⁴ carboxylic¹³⁵ and ammonium¹³⁶ groups as pendants, on the CP backbone to achieve conjugated polyelectrolytes (CPEs). The amphiphilic efficiency as well as the electrostatic repulsions of such CPEs allow then to be soluble in an aqueous media.

Considering the importance of the water solubility for the biological applications, CPEs have been reported to be widely used as biological sensors.²⁴,¹³⁶–¹³⁸ Moreover, a new class of sensors has been developed, focusing on the electrostatic complexation ability of CPEs. This recently
observed property of the CPEs can affect the fluorescence efficiency (Fig 1.5). For example, when a series of anionic PPV derivatives with sulfonate substituted groups were synthesised, such as anionic PPV 1.48, fluorescence behaviour in response to the cationic analyte, methylviologen (MV$^{2+}$) was studied, it was observed that the formation of polymer/MV$^{2+}$ might be reliant on electrostatic repulsion. Furthermore, a strong fluorescence quenching was also observed (which in turn also confirmed the fluorescent reversibility within the anionic PPV derivatives) when removing the analyte.\textsuperscript{104}

Regarding biological applications of CPEs, several studies have been conducted on protein sensing, based on amplification quenching using anionic CPEs 1.49.\textsuperscript{137} Further, DNA sensing was also studied using cationic CPE derivatives based on the FRET mechanism (1.50 and 1.51) (further explained below).\textsuperscript{10}

Although CPEs have been successfully applied to different biological applications, they still have some deficiencies. It is noted that several solution factors such as pH, ionic strength and temperature may directly affect the polymer's conformation, changes which subsequently influence the fluorescence quenching process.\textsuperscript{139} Further nonspecific electrostatic interactions between CPEs and biomolecules might also affect specific target detection.\textsuperscript{24,140,141}
Fig 1.5. Chemical structure of some reported ionic water soluble conjugated polymers (CPEs)
Non-ionic, water soluble, CPs have also been shown to be effective in specific biological applications; their developments are briefly described in the next section.

1.4 Non-Ionic Water Soluble Conjugated Polymers

In the previous section ionic, water soluble, conjugated polymers were reviewed; it is noted that despite their various useful applications, they still show some limitations. To address the limitations of CPEs for their use in further specific applications, non-ionic water soluble conjugated polymers (NCPs) were designed. To achieve such components, highly polar side chains such as polyhydroxyl (1.52),142 branched ethylene glycol (1.53)143 and sugars (1.54, 1.55 and 1.56)144 were introduced as pendants to the conjugated backbones; some examples of such synthesised NCPs are shown in Fig 1.6.

Hydroxyl and amide functionalised PPEs were amongst the first synthesised NCPs,143 both using the Sonogashira cross-coupling reaction to achieve the desired NCPs. It was observed that the resulting PPE derivatives were fully soluble in water with no further treatments (heating, pH deviations) required. Water solubility was not observed in PPEs that were less densely functionalised. Further studies of the optical properties of these PPE derivatives has revealed a lower intensity of both excitation and emission spectra as well as low quantum efficiency in water. Although the theory behind these observations has not been properly investigated, it still infers an unfavourable polymer conformation in water.

Considering the above mentioned limitations of the hydroxyl and amide functionalised PPE derivatives, studies were conducted towards the synthesis of other PPE derivatives with oligo-ethylene glycol substituted side chains, (1.53).143 Due to the inherent non-ionic and non-protic properties of these substituted side chains, they are able to form a shield for the polymer backbone and consequently improve water solubility.139,145–148 Further studies indicated the quantum yield of these polymers in water was not affected, as well as structural resistance towards both pH and charge deviations in the solvent.
Further studies on the NCPs were more focused on specific targeting abilities. Mannose substituted PPE derivatives (such as 1.54, 1.55 and 1.56) were specifically designed for the detection of concanavalin A (a specific mannose binding protein) while using bovine serum albumin (BSA) as a control.\textsuperscript{149} It was observed that polymer aggregation predominantly takes place in the presence of concanavalin A while low aggregation occurs within BSA.\textsuperscript{147,148} Mannose substituted PPE showed the best efficiency when applying longer linkers between monomer groups and the CP backbone.

Recently, biotin functionalised polyfluorene (1.57) has been reported and was specifically designed for the detection of streptavidine, through its binding to the biotin.\textsuperscript{150} Further studies revealed good water solubility and quantum efficiency of the biotin functionalised polyfluorene as well as desired streptavidine selectivity.
Fig 1.6. Chemical structure of some reported non-ionic water soluble conjugated polymers (NCPs)
1.5 Graft Polymers

Graft polymers are copolymers which generally have a linear backbone and a designed distribution of branches. In this class of copolymers, the polymer backbone and grafted branches are chemically different and each has its own chemical composition.

Grafted copolymers have been synthesised for many decades and their applications are known in several fields such as resistance material, thermoplastic elastomers, compatibilisers and emulsifiers, and more recent application in the alloy industry.151

Over the years, there has been several different routes used for grafting polymerisation, some of which are more common, and therefore more reported, for the synthesis of these materials. These syntheses include atom transfer radical polymerisation (ATRP), ring-opening metathesis polymerisation (ROMP), anionic and cationic polymerisations and free radical living polymerisation. Additionally there are other routes including radiation-induced polymerisation152,153 and polycondensation routes,154 which are less frequently used. Many studies have been conducted to define better preparation methods of these copolymers. These methods are generally defined as “grafting onto”, “grafting from” and “grafting through” which are used to construct grafted copolymers with specific physical and structural properties.155,156 The concepts of the defined grafting methods are briefly explained below.

1.5.1 Grafting Through

“Grafting through”, which is also termed as the “macro-monomer method” is one of the easiest methods in synthesising grafted copolymers with properly designated side chains. As is schematically depicted in Scheme 1.15, in the “grafting through” method, low molecular weight monomers 1.58 are generally copolymerised with a functionalised macro-monomer 1.59. Further utilisation of another polymerisation route (in this example, controlled radical polymerisation) on the initiated backbone will result in the final grafted polymer 1.60.
Also in the grafting through methodology, the reactivity and distribution of the initiated groups within the polymer backbone directly controls the distribution of the grafted brushes.\textsuperscript{158,159}
1.5.2 Grafting From

The primary step in the “grafting from” methodology is the synthesis of a macromolecule with highly distributed initiating sites \(^\text{1.61}\). These initiating sites can then be used in radical post-polymerisation to achieve the desired grafted copolymer \(^\text{1.62.160}\).

Within the “grafting from” methodology several densely grafted copolymers have been reported. The post-polymerisation step of this methodology is shown in **Scheme 1.16**.\(^\text{161,162}\)

![Scheme 1.16. Schematic mechanism of “grafting from”.\(^\text{163}\)](image)

1.5.3 Grafting To

Another method for the synthesis of grafted copolymers is the “grafting to” method which utilise a polymer backbone \(^\text{1.63}\) with randomly distributed functional groups.\(^\text{164}\) This recent grafting methodology has become more useful in synthesis of grafted copolymers using click chemistry. The grafting copolymerisation initiates from the coupling reaction between the functional sites of the initiated backbone \(^\text{1.63}\) and the active end-group on the branches \(^\text{1.64}\) (the reaction mechanism is schematically shown in **Scheme 1.17**). It is noteworthy that in this methodology, the polymer backbone must be chemically modified to be capable for the further coupling copolymerisation.\(^\text{165}\)
Copolymerisation using the “grafting onto” method have been reportedly performed utilising free-radical polymerisation, anionic polymerisation, atom transfer radical polymerisation (ATRP) and living polymerisation synthetic routes.
1.6 Fundamental Concepts of Living Polymerisation

Living polymerisation is a term generally used to define any chain propagation which continues without any chain termination or transfer reactions. Such a condition for living polymerisation enables this method to be utilised practically for the synthesis of a wide range of macromolecules such as block copolymers, star shape polymers, uniform-grafted copolymers and end-functional polymers.

Living polymerisation was initially observed by Zigler, Abkin and Medvev and the capability of living polymerisation was first demonstrated by Szwarc and coworkers. Using the living polymerisation route, the Szwarc group successfully copolymerised styrene and butadiene with an active simultaneous propagation mechanism for the first time.

Optimising polymerisation conditions to fix the rate of initiation to be comparable or even more than the rate of propagation, copolymers with narrow molecular weight can be formed. Such a narrow polydispersity is a distinct advantage of living polymerisation. Various living polymerisation methods have developed and show characteristics such as a narrow molecular weight and polydispersity and the end group control of the block copolymers. Some of these new developed polymerisation methods are classed as group transfer polymerisation (GTP), living carbocationic polymerisation (LCP) and controlled/living radical polymerisations, this latest method is itself a type of stable-radical-mediated polymerisation (SRMP), (ATRP) and reversible addition-fragmentation chain transfer polymerisation (RAFT).

The main difference between these newly developed polymerisation methods is their reversible terminations. Generally, such functionality is defined as a reversible-deactivation polymerisation (RDP) which differ such methods from the more general classification in the living radical polymerisation.
1.6.1 Controlled Radical Polymerisation (CRP)

Although conventional radical polymerisation (RP), controlled radical polymerisation (CRP) and ATRP are mechanistically similar, there are several critical differences between them. Compared to conventional RP systems, CRP systems typically show extended growing lifetimes as well as fast initiation process which prevents free radical initiators remaining. Therefore, the proportion of dead chains is lower in CRP systems.

ATRP is one of the most used CRP methods, and has allowed the synthesis of numerous designed polymers, through the addition of desired monomers to the initiated species. Taking the advantage of the ATRP method, a wide range of polymers has been synthesised with site specific functionality, tailored to their use in different applications. Amongst these applications, ATRP based polymers have been successfully synthesised for coatings and adhesives. More recently, ATRP formed polymers are being focused for the medical and environmental utilisations.193–201

As previously described, ATRP and other CRP methods, are fundamentally different from the conventional RP. Within ATRP, the application of an appropriate catalyst enables monomer addition to the initiated species which results in chain growth and the synthesis of a predefined polymer. Considering the simplicity of ATRP method, its process-ability in an industrial scale has also been successfully trialled. Some examples of ATRP utilisations in an industrial field are, inject printing,202–204 cosmetics205,206 and self-cleaning windows.205–209 Furthermore, application of ATRP in pharmaceutical and medical applications has been also evaluated for drug delivery methods,210–212 coating of cardiovascular stents,212–216 scaffolding for bone and tissue engineering and biocidal surfaces.217–220

1.6.1.1 Fundamental Aspects of ATRP

The ATRP mechanism is related to the transition metal mediated atom transfer radical addition (ATRA) reaction.221 However, in ATRP polymerisation the presence of the alkyl halide (as an initiator) and the unsaturated species (as a monomer) is essential for the further formation of radicals which proceed by monomer addition in a propagation step (Scheme 1.18).188 An example of the ATRP process is seen in the synthesis of polystyrene-PPV copolymer 1.65 (Scheme 1.18).
First order kinetics as well as the linear increase in the polymer molecular weight confirms the living processability of the ATRP reaction. The activation process should be slower than the deactivation process in order to form less reactive radicals, which results in less radical-radical terminations.²²³

It is understood that this polymerisation is an inner electron transfer process²²⁴ which includes reversible halogen transfer between a dormant species 1.66 while added into an initiator or dormant propagated chain 1.67 in an initiation step. This then continues with the transition of metal complex in the lower oxidation state 1.69 which consequently results in the formation of propagating radicals 1.68²²⁵ and the metal complex 1.70. It is also possible to calculate the rate constants for each step of the polymerisation. Considering this, K_{act} is denoted as the activation step and subsequently K_p and the K_{deact} are denoted to be the propagation and deactivation steps. In ATRP a persistent radical effect (PRE) is in play where a dormant polymer chain or initiating...
site can be reactivated by the metal catalysts. The PRE results in controlled polymer growth and less terminations and overall greater conversion and larger chain lengths.\textsuperscript{226–228}

Generally four main variables affect the overall ATRP rate constant ($K_{ATRP}$), temperature,\textsuperscript{229} solvent,\textsuperscript{230} alkyl halide (initiator) and catalyst.\textsuperscript{231} In the case of the metal complex, the addition of a transition metal in a higher oxidation state generates the PRE prior to initiation which may increase initiation efficiency while reducing termination.\textsuperscript{232,233}

With respect to the main ATRP variables, numerous alkyl halides of either high or low molecular weight can be used as initiators. In the case of the catalyst, a wide range of different metals have been used for ATRP reactions such as Ti,\textsuperscript{234} Mo,\textsuperscript{235–237} Re,\textsuperscript{238,239} Fe,\textsuperscript{240,241} Ru,\textsuperscript{187,242} Os,\textsuperscript{243,244} Rh,\textsuperscript{245,246} Co,\textsuperscript{247} Ni\textsuperscript{248,249} and Pd,\textsuperscript{250} Cu is most reportedly used.\textsuperscript{251} Copper is mainly used for the synthesis of a wide range of ATRP based polymers, however there are still concerns for its utilisation in an industrial scale with respect to its cost and environmental implications of its use.\textsuperscript{252} As such, iron based ATRP catalysts have been recently reported in industrial applications.\textsuperscript{240,253,254} It is also noted that utilising iron as a catalyst in the presence of polar solvents means the polymerisation occurs with no ligand requirement.\textsuperscript{245} However, the transition metal complex should be or at least be partially soluble in the solvent for reactions to occur.\textsuperscript{255}

There are other influential variables in the ATRP reaction, including temperature which has been varied from room temperature to 150 °C. Also, the ATRP reaction can perform in a wide spectrum of solvents as well as in water.\textsuperscript{230} It is also shown that the dentate number of ligands might also affect the ATRP constant ratio (further discussed below).\textsuperscript{256}

Initiator choice is also among the important variables in ATRP reactions. Macro initiators are functionalised macromolecules in which the functionalised sites can be at the terminal end or spread along the macromolecule. Such functionality distribution further determines the resulting molecular structure of the final polymer.\textsuperscript{257}

The rate constant of ATRP reactions vary due to different aspects of the initiators. The influential aspects include the degree of initiator substitution (1.71, 1.72 and 1.73), leaving group (1.74, 1.75 and 1.76) at the initiator sites and the radical stabilising groups (1.77, 1.78 and 1.79).\textsuperscript{231,258,259} These effects are depicted in Fig 1.7.
Along with the four mentioned effective variables, other factors can also influence the interactions between the reagents which might then affect ATRP equilibrium.\textsuperscript{258,260} For instance, the ATRP reaction shows a limited tolerance towards oxygen, hence it is necessary to use an oxygen free reaction medium. Further, the addition order of species can be of importance; most often it is recommended to add the catalyst last. Also, a small amount of Cu(II) addition is recommended at the beginning of the ATRP reaction to reduce the termination step, which may result in great control over the reaction.\textsuperscript{261}
1.6.1.2 Structural Effect of the Ligand in ATRP

The structure of the ligand on the rate constant of ATRP reactions has been widely studied and has been shown to have influential effect as shown in Table 1.1.

<table>
<thead>
<tr>
<th>Ligand Structure</th>
<th>Ligand Name</th>
<th>$K_{act}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="NPPMI (R = n-Pr) Ligand Structure" /></td>
<td>NPPMI (R = n-Pr)</td>
<td>$2.4 \times 10^{-3}$</td>
</tr>
<tr>
<td><img src="image" alt="bpy Ligand Structure" /></td>
<td>bpy</td>
<td>0.066</td>
</tr>
<tr>
<td><img src="image" alt="PMDETA (N[2,2]) Ligand Structure" /></td>
<td>PMDETA (N[2,2])</td>
<td>2.7</td>
</tr>
<tr>
<td><img src="image" alt="HMTETA N[2,2,2] Ligand Structure" /></td>
<td>HMTETA N[2,2,2]</td>
<td>0.14</td>
</tr>
<tr>
<td><img src="image" alt="BPED Ligand Structure" /></td>
<td>BPED</td>
<td>4.5</td>
</tr>
<tr>
<td>Ligand</td>
<td>Structural Effect</td>
<td>Activation Constant Rate</td>
</tr>
<tr>
<td>---------</td>
<td>-------------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>Et₆TREN</td>
<td><img src="image1" alt="Structure of Et₆TREN" /></td>
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</tr>
<tr>
<td>Me₆TREN</td>
<td><img src="image2" alt="Structure of Me₆TREN" /></td>
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</tr>
<tr>
<td>TPMA</td>
<td><img src="image3" alt="Structure of TPMA" /></td>
<td>62</td>
</tr>
<tr>
<td>TPEDA</td>
<td><img src="image4" alt="Structure of TPEDA" /></td>
<td>10.8</td>
</tr>
</tbody>
</table>

*Table 1.1* List of ligands and its structural effect comparing activation constant rate
Bidentate ($N_2$) ligands have been reported as the smallest active ligands. Amongst these ligands, PMI and bpy ligands$^{163,262,263}$ are those most commonly applied in ATRP reactions and results have shown that the reaction rate is poorly controlled, resulting in polymers with low polydispersity.$^{264}$

Tridentate ($N_3$) ligands are another group of ligands used, with PMDETA being the most common, due to its low cost and its availability. However, it is observed that within tridentate ligands pyridine based ligands create more active catalysts than the other aliphatic substituted ligands.$^{232}$

As is shown in Table 1.1, tetradentate ($N_4$) ligands are categorised structurally into linear and branched tetradentate ligands.$^{265}$ Amongst the linear ligands, the aliphatic amine substituted ligands with only one propylene linkage show most activity due to the flexibility of the complex. Within this group, pyridine substituted ligands such as BPED generate a more active catalyst.$^{256}$

In the branched ligands, Me$_6$TREN shows the highest activity among the tetradentate ligands.$^{266}$ Substitution of the methyl groups with ethyl to give Et$_6$TREN shows $10^4$ times less activity in forming Cu complexes.$^{163}$ TPMA within this subdivision, has been found to be one of the best choices for polymerisation in aqueous media.$^{267}$ Lastly are the hexadentate ligands, which the only reported example is TPEDA which shows good activity in forming the Cu complex.$^{268,269}$

Other structurally modified ligands include cyclic ligands. Within this group of ligands it is observed that the bidentate, tridentate and linear tetradentate pyridine ligands are more active compared to the similar aliphatic-substituted example.$^{256}$ Nonetheless, within the tetradentate ligands branched pyridine examples show less activity compared to the aliphatic amine substituted ligands.$^{270}$

1.6.1.3 Solvent Effect in ATRP

When designing an ATRP procedure, the choice of solvent needs to be carefully considered along with the other previously mentioned parameters. Investigation of solvation effect requires the consideration of several complicated process such as dipolar interactions, dispersion forces, ionic interactions and hydrogen bonding. A study on the solvent effects within the ATRP reaction was undertaken using a series of Cu catalysed reactions using ethyl
α-bromoisobutyrate (EBiB) as initiator and HMTETA as a ligand to calculate the rate constant of the polymerisation reaction.\textsuperscript{271} It was observed that the higher the polarity of the solvent, the faster the activation step and the lower the deactivation step which consequently results in a higher value of $K_{\text{ATRP}}$. Overall the rate of reaction in tested solvents was DMSO > frnamide > DMF > MeOH > anisole > CH$_3$CN > acetone > autanone.

Further hydrogen bond formations within aqueous media with the Cu catalysts was also found to be influential on the measured $K_{\text{ATRP}}$.\textsuperscript{271}

1.6.2 Activator Regenerated by Electron Transfer (ARGET) ATRP

The industrial applications of any chemical synthetic pathways are usually limited to their practical application on a large scale. Such conditions considerably limit the application of control radical polymerisation routes. The exceptional properties of ATRP procedures to have control over structure and functionality of the synthesised polymers have driven the desire to commercially use this method.\textsuperscript{272–276} However, the high concentration of catalyst consumption, which results in purification and cost issues, makes the ATRP method less useful for industrial purposes. Also the need to remove oxygen from the reaction is another drawback of the ATRP method which has to be considered for large scale synthesis. Considering these features, several ATRP modifications have been developed to not only decrease the amount of catalyst but also address the oxygen issue. One of the most recent useful developed methods in this direction the activator regenerated by electron transfer (ARGET) ATRP. Using ARGET ATRP, good control over acrylate polymer synthesis has been established.\textsuperscript{277} This method has also been widely reported for surface polymerisation, using very small amounts of catalyst.\textsuperscript{278}

1.6.2.1 ARGET ATRP Mechanism

To initiate ATRP, where the activated species is generated through an electron transfer mechanism, the employment of a reducing agent is inevitable. Such a mechanism results in the constant regeneration of the ATRP activator species \textbf{1.80} which is mostly Cu(I). Cu(I) is formed through the regular reduction of Cu(II) by the aid of a reducing agent (as shown in Scheme 1.19).
As such, in the presence of an appropriate reducing agent, the amount of copper catalyst could be decreased to only a few ppm. Some of the most commonly used reducing agents which are also FDA approved are, Sn(EH)$_2$, glucose,$^{277,279}$ ascorbic acid,$^{280}$ hydrazine and phenyl hydrazine.$^{281}$ Excess amount of ligand is generally used in ARGET ATRP to satisfy the requirement of a small amount of catalyst compared to monomer, solvent and reducing agent concentrations. In the case of ligand concentration, it is observed that in the presence of monomers$^{282}$ such as 2-(dimethylamino)ethyl methacrylate (DMAEMA) the required amount of ligand would be reduced as the nitrogen ligating in the monomer can act same as the ligand itself.$^{283,284}$

Higher molecular weight polymers are another characteristic of ARGET ATRP, which is strongly related to the reduction of catalyst based side reactions.$^{278,285}$

**Scheme 1.19.** Schematic mechanism of ARGET ATRP reaction.$^{222}$
1.6.2.2 Effective Variables in ARGET ATRP

Several variables might affect ARGET polymerisation reactions, including temperature and the choice of solvent, in similar ways as what was mentioned for the ATRP reaction. However there are, other variables that are of concern for ARGET ATRP polymerisation. The choice of ligand and its concentration is one essential factor which has been studied in several ARGET ATRP reactions. Based on this research, it is known that TPMA is one of the best ligands with respect to Cu(II) complex pH stability. PMDETA was found less useful as a result of its lower stability towards pH variation.

The choice of an appropriate reducing agent, and its concentration, is another important factor which should be considered as it is quickly consumed during the start of the reaction. If too little reducing agent is used in the reaction, it may not completely initialise. Further, the consumption of an excess amount of reducing agent may result in an uncontrolled reaction, leading to loss of control over the polymer molecular weight or undesirable side reactions with the catalyst. With respect to the reducing agent concentration, a first order linear kinetic relationship was observed when using hydrazine as the reducing agent.

1.7 Basic Process of Radiation and Fluorescence Quenching

Amplified quenching which is also called “super-quenching” is one of the most useful properties of CPs that makes them strong candidates in sensing applications. Noting such a concept for CPs, it is essential to understand the background of radiation processes.

As it is shown in Jabloski diagram (Fig 1.8), photon absorption results in fluorophore (F) excitation to the singlet excited electronic state (S₁) as well as the formation of an excited fluorophore (F*). Fluorescence may occur directly when F* returns back to the ground singlet electronic state (S₀); this process is called relaxation and generates photon emission. However, relaxation may also occur via other pathways such as phosphorescence and non-radiative relaxation. The non-radiative relaxation phenomenon may also occur before radiative relaxation (explained below). In contrast to the phenomena of fluorescence is the quenching process, which competes with the radiative relaxation process. When fluorescence quenching takes place, fluorescence intensity and its lifetime reduces through the interaction of F* with a quencher molecule (Q).
Fluorescence quenching most commonly occurs through two different mechanisms called dynamic quenching (collision quenching) and static quenching. As is shown in Fig 1.8, dynamic quenching happens when $F^*$ becomes deactivated through a diffusive confrontation with Q, which would not be further chemically changed, and returning back to the $S_0$ without emission. Static quenching is also depicted in Fig 1.8, in which the formation of the non-fluorescent complex (F-Q) results in a non-radiative relaxation of this complex while retuning back to the $S_0$.

There are several methods to distinguish the mechanism of fluorescence quenching, such as changing the quencher concentration, temperature and detecting maximum absorption. It is noted that increasing the quencher concentration may also reduce fluorescence lifetime in the dynamic mechanism which will increase its lifetime in the static mechanism. Increasing temperature is in favour of dynamic quenching rather than static. Moreover, detection of the maximum absorption changes can confirm the formation of an F-Q complex as a new species which also proves the static mechanism. However, it is noteworthy to mention that dynamic and static quenching mechanisms can happen at the same time in many systems.
1.7.1 Amplified Quenching in Conjugated Polymers

The concept of amplified quenching was first understood by Swager and his co-workers in 1995.\textsuperscript{104,133} Through their experiments, they realised that intense fluorescent quenching of PPE derivatives such as 1.81 occur in the presence of methyl viologen salt 1.82 (shown in Fig 1.9).

They attributed the fluorescent decrease to the molecular wire effect. It was then realised that the molecular wire effect further enhanced fluorescence quenching of CPs due to the extended electronic communication and exciton transport through the CP chain.

Due to the molecular wire effect, rapid exciton diffusion and energy migration through the conjugated backbone of polymer quenches several repeating units therefore the quenching process is amplified greatly.

1.7.2 Amplified Quenching in Charged Conjugated Polymers

The concept of amplified quenching in water soluble CPEs was first realised by Chen and Whitten in 1999.\textsuperscript{24} They observed fluorescent quenching in anionic PPV derivatives functionalised with short chains containing SO\textsuperscript{3} groups in the presence of MV, due to a photoinduced electron progress. The amplified quenching effect within charged conjugated polymers was further studied within various charged conjugated polymers (PPE and PPV derivatives are shown in Fig 1.10).\textsuperscript{28,295–298}
Comparison of the amplified quenching results of the charged (1.83 to 1.87) and non-charged 1.88 CPs shows more intense quenching in charged polymers. It was also observed that such intense quenching in charged conjugated polymers is due to the formation of strong complexes between the charged polymers with the oppositely charged quencher.

The amplified quenching process in charged conjugated polymers, is dependent on several factors including polymer chain length, polymer aggregation and solution conditions.
1.7.3 Aggregation and Solvent Dependent Optical Properties of Conjugated Polymers

Conjugated polymer derivatives can exhibit various amphiphilic properties resulting from a range of configurations in different solvents. As the conjugated backbones of CPs are mostly organic soluble, in very polar solvents, including water, conformational changes can occur, which may affect the photophysical properties of the CPs. One of the most prominent effects of using polar solvents is aggregation, which may results in either spectral red shift or/and fluorescence intensity decrease.\textsuperscript{298,304}

A study of solvent effect have been conducted on different PPE derivatives where the results indicate sharp peaks in both UV-Vis and fluorescence spectroscopy when conducting such experiments with non-charged PPEs in organic solvents such as chloroform and tetrahydrofuran.\textsuperscript{305} Further experiments on charged PPE derivatives were conducted in methanol, methanol-water (various ratios) and water.\textsuperscript{306–308} It was observed that when using methanol as solvent, polymers show photophysical behaviours similar to the non-charged PPEs backbone. These observations were in contrast with the results of the same polymers in methanol-water and water solvent systems. With increasing water content, spectral red shift, as well as a decrease in the fluorescent intensity was observed.

The photophysical properties of the polymers were then measured using only water as a solvent; there was a dramatic fluorescent intensity reduction as well as the appearance of new small peak. It was then concluded that the photophysical behaviour of these PPE derivatives may be largely attributed to their conformational changes in various solvents. The fluorescence observations also confirms that for charged PPEs the backbone conformation in methanol is similar to the non-charged PPE backbone in less polar organic solvents. However, its characteristics in water were observed to be closer to that an aggregated form.\textsuperscript{306–308} Further, a reduction in quantum yield was observed, which was proposed to be due to polymer aggregation. This aggregation results in fluorescence quenching due to a lower radiative process of the excited chain.\textsuperscript{309,310}

Solvent dependent optical properties have been also studied with different PPV derivatives such as poly(2-methoxy-5-(20-ethylhexyloxy))-1,4-phenylene vinylene (MEHPPV) and poly(2,5-bis(diethylaminetetraethylene glycol)phenylene vinylene (DEATGPPV).\textsuperscript{311,312} It is
noted that an increase in solvent polarity using MEHPPV increase aggregation of the PPV backbone, which results in a decrease in photoluminescence quantum yield.

Solvent polarity deviation studies with DEATGPPV revealed other photophysical results; increasing the solvent polarity through the use of water, no change in spectral shifts were observed, both in maximum absorption and emission. However, a reduction in quantum efficiency was observed when both methanol and water were used. The decrease in quantum efficiency was attributed to the formation of aggregated conformations rather than extended linear ones, which is the dominant PPV backbone conformation in organic solvents.

Therefore, it is generally accepted that conformation of CPs are intrinsically correlated to solvent polarity in which measurements are made, which can be observed as changes in the polymer’s photophysical properties.\textsuperscript{313,314}

The above mentioned factors in respect to the amplified quenching, can influence a polymer’s applications and its sensing mechanism, which are described below.

\subsection*{1.7.4 Utilisation of Conjugated Based Polymers as Optical Sensors}

Several studies have been conducted over the past few decades to achieve simpler, faster and more sensitive optical sensors in which CPs have attracted more attention.\textsuperscript{11} In the field of CP based sensors, CPEs became more dominant due to their water solubility. Beyond water solubility, many CPEs exhibit advantages such as accessibility and easier synthesis as well as signal amplification which makes CPE based sensors more sensitive. They therefore respond to even a very small amounts of quencher; such a sensitivity is rare in other sensing systems.\textsuperscript{315,316}

Most of the current CPE based sensors work on the basis of a fluorometric assay. This results in high sensitivity in detecting signal changes in either their intensity, spectral changes or lifetime. CPE based sensors can be used either to measure enhanced or quenched fluorescence, which are called turn-on and turn-off sensors, respectively.
Regardless of the fluorometric quenching method, all CPE based sensors operate through one of three mechanisms; superquenching, light harvesting, through fluorescence resonance energy transfer (FRET), and conformational changes, which are all briefly described in the next section.

1.7.4.1 Superquenching

Superquenching which is also known as amplified quenching, is specifically used for chemical and biological sensing. In this mechanism, a quencher-ligand (QL) complex is designed and synthesised in which the ligand has specific quencher binding capability. Further addition of an analyte with ligand binding capability results in superquenching sensing capability.

The superquenching mechanism was first modulated based on PPV derivatives with SO$_3^-$ functionality on their side chain (PPV- SO$_3^-$) (Fig 1.11).$^{24}$
In this example the PPV-SO$_3^-$ initially interacts with a modified methyl viologen (MV) bound biotin molecule 1.90. This interaction occurs through electrostatic interactions between the negatively charged PPV and positively charged MV. In the presence of avidin 1.91, which has a strong affinity for biotin, the MV complex dissociates from the PPV increasing its fluorescence. This is called turn-on sensor. 24,317
1.7.4.2 Light Harvesting Mechanism

Fluorescence resonance energy transfer (FRET) takes place between the long dipole-dipole interactions of the electronic excited states of two different dye molecules where one acts as a donor and the other as an acceptor species. FRET transfer is directly related to the donor and acceptor distance and the overlap of donor emission spectrum and acceptor absorption spectrum. It is understood that CPEs can be appropriate candidates for the light harvesting (FRET) mechanism due to their favourable quantum efficiency and proper exciton migration. Based on the CPEs FRET efficiencies, light harvesting mechanism through FRET was first biologically applied in DNA sensing using a cationic CPE (see in Fig 1.12).\(^\text{318}\)

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**Fig 1.12.** Schematic of (A) FRET mechanism and (B) molecular structure of cationic CPE used in DNA sensing (adapted from Gaylord *et al*).\(^\text{318}\)
In this example the negative charged DNA can associate with a positively charged polyfluorene polymers. The sensing comes from addition of a neutral PNA species to which is bound a dye. If the DNA is complementary sequence to the PNA it brings the PNA-DNA complex close enough to the polymer to allow FRET. Non-complementary DNA does not associate with the PNA and no FRET occurs.

1.7.4.3 Conformation Change Mechanism

Conformational changes of CPEs in the presence of various analytes can effect both excitation and emission properties of the CP. Several cationic CPE based sensors have been developed (the most common are shown in Fig 1.13 (1.93-1.95)).

In the example shown (Fig 1.14) the binding of a negatively charged DNA aptamer to the specific protein, thrombin, can be served using a cationic polythiophene. Two conformations of the polymer are possible with depending on the association of the DNA with specific or nonspecific target. Each conformation has unique fluorescence.
The conformational change mechanism was first used for DNA hybridisation detection, which was followed by further specific protein sensing (see Fig 1.14).

1.7.5 Application of Conjugated Polymers in Ion Sensing

Careful design of CPEs can enable them to be applied as sensors for a variety of ions, such as protons (pH sensing), metal ions, metal complexes and inorganic anions. Because of the photophysical properties of CPEs, they should be able to detect oppositely charged ions through the either superquenching, energy transfer or conformational changing mechanisms which would consequently influence the optical properties of the sensor polymer.

Several CPE based ion sensors have been reported, such as carboxylate substituted PPE as a Pb^{2+} sensor which showed high sensitivity towards lead due to multivalent effect which results in an amplified quenching effect (Fig 1.15).
In addition to the above mentioned ion sensing properties of the carboxylate substituted PPE, CPEs have been widely used as pH sensors\textsuperscript{323} and for sensing $K^+$, $\text{Eu}^{2+}$, $\text{Cu}^{2+}$, $\text{Ru(bpy)}_2\text{(dppz)}^{2+}$ (bpy: 2,2'-bipyridine, dppz: [3,2-a-2'3'-c]phenazine\textsuperscript{325} and several multicationic amines.\textsuperscript{326}
1.8 Objectives

The primary objective of this project was to synthesise novel conjugated water soluble polymers based on PPV and PPE scaffolds with the view of using these polymers for a number of biological applications.

To achieve this goal, project was categorised as follows:

1) Develop a synthetic route to functionalised monomers for the formation of novel PPV and PPE backbones, as well as the macro-initiator forms of these polymers
2) Develop synthetic routes for further grafting polymerisation from the prepared PPV and PPE macro-initiators
3) Investigate the properties of PPV and PPE grafted molecular brushes, and their usage in further applications

With these objectives in mind, this thesis is composed of nine chapters. Following this introduction chapter, chapter two mainly describes the design and synthesis of novel functionalised monomers. Chapter three presents routes toward the CP backbones and their conversion to macro-initiators as well as their physicochemical characteristics. Chapters four to six present work on grafting polymerisation including optimised synthetic pathways, along with characterisation of these new grafted polymers. Chapter eight focuses on the application of the novel grafted polymers, and finally chapter nine which presents current and future works as well as a summary of results.
Chapter 2: Synthesis of Functionalised Monomers
2.1 Introduction

The main objective of this project was the synthesis of novel CPs based on poly-phenylene vinylene (PPV) and poly-phenylene ethynylene (PPE) CPs. A major focus of the polymers to be prepared was their use in biological applications where, the hydrophilicity of the polymer backbones is of importance.

Previously our research group has prepared PPVs 2.1 that contained lateral glycol substituents which assisted in the water compatibilities of the polymers (Fig 2.1).

However, the triglycol groups alone did not give complete water solubility therefore it was desired that the new PPV derivatives could have attachment points for further hydrophilic groups. Therefore the aim was to synthesis hydroxyl functionalised PPVOH 2.2 and PPEOH 2.3 which, contains not only hydrophilic triglycol groups but also oxypropan-1-ol chains which would be capable for further hydrophilic modification based on radical polymerisation (Fig 2.2).
To prepare hydroxyl functionalised PPVOH 2.2 and PEOH 2.3, a series of functionalised monomers required synthesis, which is depicted within the retrosynthesis pathway of PPVOH 2.2 and PEOH 2.3 in Scheme 2.1 and 2.2.

The proposed synthesis of PPVOH 2.2 was to construct the polymer using the Heck polymerisation from divinyl monomer 2.4 and diiodobenzene monomer 2.5. Divinyl monomer 2.4 could be prepared from glycol containing diiodide 2.6 which itself can be prepared from hydroquinone 2.7.

Diiodide monomer 2.5 could be prepared from the deprotection of disilylether 2.9 which itself could also be prepared from hydroquinone 2.7.
PPEOH 2.3 can similarly be broken down to two monomers dialkyne 2.10 and diiodobenzene monomer 2.5, the same monomer used in synthesis of PPVOH 2.2. Dialkyne monomer 2.10 could be prepared using Sonogashira reaction from diiodide monomer 2.6, which would be used in the synthesis of PPVOH 2.2.
An alternative monomer 2.11, which already contains radical initiator functionality could be prepared from dialcohol monomer 2.5.

Scheme 2.2. Retrosynthesis pathway of PPEOH 2.3.
2.2 Discussion

The synthesis of first monomer which contains a triglycol group (2.4 and 2.10) was achieved by tosylation of 2-(2-(2-methoxyethoxy)ethoxy)ethan-1-ol alcohol 2.8 using tosyl chloride 2.12 and sodium hydroxide as a base in THF Scheme 2.3.327,328

![Scheme 2.3. Synthesis of 2-(2-(2-methoxyethoxy)ethoxy)ethyl 4-methylbenzenesulfonate 2.13.](image)

After purification the desired tosylate 2.13 was obtained in 96 % yield and the NMR data of the product matched the literature.327,328 In the 1H NMR the addition of four new aromatic signals between 7.27 ppm to 7.81 ppm and the tosyl methyl at 2.44 ppm proved the successful tosylation.

Following this the alkylation of hydroquinone 2.7 using tosylated 2-(2-(2-methoxyethoxy)ethoxy)ethan-1-ol 2.13 was achieved using potassium tert-butoxide as the strong base in EtOH, Scheme 2.4.329,330

![Scheme 2.4. Synthesis of 1,4-bis(2-(methoxymethoxy)ethoxy)benzene 2.14.](image)
After purification the desired alkylated 1,4-bis(2-(methoxymethoxy)ethoxy)benzene \(2.14\) was obtained in 77% yield and the NMR data matched the literature.\(^{329,330}\) In the \(^1\)H NMR the addition of a new singlet integrating to two protons at 6.83 ppm, as well as two terminal methyl groups at 3.37 ppm integrating for six protons showed the successful alkylation reaction.

The next step in the synthesis was the iodination of 1,4-bis(2-(methoxymethoxy)ethoxy)benzene \(2.14\) which was achieved using iodine and mercury acetate in CH\(_2\)Cl\(_2\) (Scheme 2.5).\(^{329}\)

![Scheme 2.5: Synthesis of 1,4-diiodo-2,5-bis(2-(methoxymethoxy)ethoxy)benzene 2.6.](image)

After purification the desired 1,4-diiodo-2,5-bis(2-(methoxymethoxy)ethoxy)benzene \(2.6\) was obtained in 95% yield with the NMR data again matching literature values.\(^{329}\) In the \(^1\)H NMR the appearance of a new two protons singlet at 7.23 ppm and the terminal methoxy groups at 3.38 ppm with the integral of six showed the successful iodination reaction.\(^{329}\)

The iodination of diallylated benzene took place using iodine and mercury acetate.\(^{331}\) The iodination rate is increased in the presence of the mercury salt as two reagents combine to form an iodine-mercury \(2.15\) salt and an iodoacetate \(2.16\) which, is a source of I\(^+\) in the form of IOAc \(2.16\). The iodination occurs to give the \textit{para} disubstituted product due to the steric hindrance that would be observed with a \textit{meta-para} disubstituted pattern of two iodine. Also after the first iodination the added iodine further actuates the \textit{para} position (Scheme 2.6).
The final step in the synthesis of 1,4-bis(2-(methoxymethoxy)ethoxy)-2,5-divinylbenzene 2.4 was achieved through the Stille reaction using 1,4-diiodo-2,5-bis(2-(methoxymethoxy)ethoxy)benzene 2.6, vinyl tributyltin 2.17 and catalytic tetrakis(triphenylphosphine)palladium (0) in DMF (Scheme 2.7).54

After purification the desired 1,4-bis(2-(methoxymethoxy)ethoxy)-2,5-divinylbenzene 2.4 was obtained in 56 % yield and the NMR data of the product matched literature values.54 In the $^1$H NMR the addition of three new multiplets at 5.22-5.25 ppm, 5.69-5.79 ppm and 6.99-7.06 ppm, relating to the vinyl formation, showed the successful Stille reaction. FT-IR of the product also confirmed the formation of the desired compound with the appearance of C=C absorption at 1622 cm$^{-1}$. 
In the Stille reaction the mechanism begins with a catalytic cycle which involves an oxidative addition of an aryl halide 2.6 to a palladium catalyst 2.18. Followed by transmetalation of palladium ligand complex 2.19 with organotin 2.20. Reductive elimination of \textit{trans}-palladium ligand complex 2.21 resulted in the coupled product as well as regeneration of the palladium catalyst 2.18 (Scheme 2.8).

![Scheme 2.8. Stille reaction mechanism.](image)

Similarly, the synthesis of \(((2,5\text{-}\text{bis}(2\text{-}\text{methoxyethoxy})\text{-}1,4\text{-}\text{phenylene})\text{bis}(\text{ethyne}-2,1\text{-}d\text{iy})\text{bis}(\text{trimethylsilane})\) 2.22 was achieved through the Sonogashira reaction using 1,4-diiodo-2,5-bis(2-(methoxymethoxy)ethoxy)benzene 2.6 and tri-methylsilyl acetylene 2.23 in THF (Scheme 2.9).
Scheme 2.9. Synthesis of \((2,5\text{-bis(2-methoxyethoxy)-1,4-phenylene})\text{bis(ethyne-2,1-diyl))bis(trimethylsilane)}\ 2.22.

After purification the desired \(2\text{-5-bis(2-(methoxymethoxy)ethoxy)-1,4-phenylene})\text{bis(ethyne-2,1-diyl))bis(trimethylsilane)}\ 2.22\ was obtained in 63 % yield with the NMR data of the product matching literature values.\(^{330,332}\) In the \(^1\)H NMR the appearance of an 18 proton singlet peak at 0.22 ppm belonging to the two trimethyl silyl groups showed the successful reaction.\(^{330,332}\) FT-IR also confirmed the formation of the desired compound with the appearance of new \(\text{C}≡\text{C}\) and Si-C absorptions at 1622 cm\(^{-1}\) and 1247 cm\(^{-1}\).

The Sonogashira reaction mechanism is depicted in Scheme 2.10. It is inferred from the reaction mechanism that it begins after the activation of \(\text{Pd}^{\text{II}}\) \(2.24\), being reduced to \(\text{Pd}^{0}\) \(2.25\). The activated palladium is further reacted with \(2.6\) to form the \(\text{Pd}^{\text{II}}\) complex \(2.26\) as an intermediate. The transmetallation reaction of the intermediate complex \(2.26\) with copper acetylene \(2.27\), which is produced in the cycle B, results in the formation of another \(\text{Pd}^{\text{II}}\) complex \(2.28\) containing 1,4-bis(3-((tert-butyldimethylsilyl)oxy)propoxy)benzene as well as the regeneration of the copper iodide \(2.29\) in Cycle B. This step is followed by trans-cis isomerisation of the groups around palladium. Finally, reductive elimination of the cis complex \(2.30\) results in the formation of \(2\text{-5-bis(2-(methoxymethoxy)ethoxy)-1,4-phenylene})\text{bis(ethyne-2,1-diyl))bis(trimethylsilane)}\ 2.22\ and regeneration of the \(\text{Pd}^{0}\) catalyst. In the Cycle B the presence of \(\text{Et}_3\text{N}\) results in the formation of the \(\pi\text{-alkyne complex} \ 2.31\), which assists in the deprotection of the acidic terminal proton on the ethynyltrimethylsilane \(2.23\), resulting in the formation of the copper acetylene compound \(2.27\). The copper acetylene compound \(2.27\) continues to form trans- \(\text{Pd}^{\text{II}}\) complex \(2.28\), while regenerating the copper iodide \(2.29\).\(^{19,131–133}\)
Scheme 2.10. Sonogashira reaction mechanism.
To obtain the required 1,4-diethynyl-2,5-bis(2-(methoxymethoxy)ethoxy)benzene 2.10, deprotection of (2,5-bis(2-(methoxymethoxy)ethoxy)-1,4-phenylene)bis(ethyne-2,1-diy)bis(trimethylsilane) 2.22 was performed using potassium fluoride in MeOH (Scheme 2.11).330,333,334

![Scheme 2.11. Synthesis of 1,4-diethynyl-2,5-bis(2-(methoxymethoxy)ethoxy)benzene 2.10.](image)

After purification the desired 1,4-diethynyl-2,5-bis(2-(methoxymethoxy)ethoxy)benzene 2.10 was obtained in 87 % yield.330,333,334 In the 1H NMR the appearance of a two proton singlet at 2.32 ppm resulting from the newly formed terminal acetylene showed the successful reaction.330,333,334 The NMR data matched the literature values.330,333,334

The synthesis of the second group of monomers began with the alcohol protection of 3-bromo-1-propanol 2.32 using tert-butyl-dimethylsilyl chloride (TBDMSCl) and imidazole in DMF (Scheme 2.12).

![Scheme 2.12. Synthesis of 3-bromopropoxy)(tert-butyl)dimethylsilane 2.33.](image)
After purification the desired (2-bromopropoxy)(tert-butyldimethyl)silane 2.33 was obtained in 97 % yield and the NMR data matched the literature.\textsuperscript{335,336} In the \textsuperscript{1}H NMR addition of nine protons at 0.83 ppm belonging to tert-butyldimethylsilyl and six proton at 0.06 ppm belonging to the two methyl groups showed the successful protection.\textsuperscript{335,336}

Alkylation of hydroquinone 2.7 with 3-(bromopropoxy)(tert-butyldimethyl)silane 2.33 using potassium carbonate as a base in DMF gave the desired product 1,4-bis(3-((tert-butyldimethyl)silyl)oxy)propoxy)benzene 2.34 in 63 % yield (Scheme 2.13).\textsuperscript{336}

In the \textsuperscript{1}H NMR of the product showed the addition of four aromatic protons at 6.77 ppm as well as the 18 and 12 protons referring to tert-butyldimethylsilyl and methyl groups, respectively, at 0.85 ppm and 0.05 ppm, proving the reaction was successful.\textsuperscript{336}

The iodination of the 1,4-bis(3-((tert-butyldimethyl)silyl)oxy)propoxy)benzene 2.34 was then achieved using iodine and mercury acetate in CH\textsubscript{2}Cl\textsubscript{2} in similar manner as used for the iodination of 2.14 (Scheme 2.14).\textsuperscript{329}
Scheme 2.14. Synthesis of ((((2,5-diiodo-1,4-phenylene)bis(oxy))bis(propane-3,1-diyl))bis(oxy))bis(tert-butyldimethylsilane) 2.9.

After purification the desired ((((2,5-diiodo-1,4-phenylene)bis(oxy))bis(propane-3,1-diyl))bis(oxy))bis(tert-butyldimethylsilane) 2.9 was obtained in 90 % yield. In the 1H NMR a two proton singlet at 7.13 ppm and the consistency of the tert-butyl and methyl groups at 0.85 ppm and 0.06 ppm showed the successful iodination reaction.

Removal of the tert-butyltrimethylsilane TBDMS groups to give hydroxyl functionalised monomer 3,3'-(2,5-diiodo-1,4-phenylene)bis(oxy))bis(propan-1-ol) 2.5 was achieved using methanolic solution of hydrochloric acid, which was prepared using acetyl chloride in methanol, and ((((2,5-diiodo-1,4-phenylene)bis(oxy))bis(propane-3,1-diyl))bis(oxy))bis(tert-butyldimethylsilane) 2.9 (Scheme 2.15).336

Scheme 2.15. Synthesis of 3,3'-(2,5-diiodo-1,4-phenylene)bis(oxy))bis(propan-1-ol) 2.5.

After 2 h reaction, purification gave the desired 3,3'-(2,5-diiodo-1,4-phenylene)bis(oxy))bis(propan-1-ol) 2.5 in 97 % yield. In the 1H NMR the loss of the signals from the TBDMS groups and appearance of two protons of hydroxyl groups at 4.53 ppm showed the successful deprotection reaction. FT-IR data also confirmed the formation of hydroxyl functionalised monomer 2.5 through the strong absorbance at 3350 cm\(^{-1}\) of hydroxyl group.
Lastly, bromoester functionalised monomer 2,5-diiodo-1,4-phenylenebis(oxy)bis(propane-3,1-diyl) bis(2-bromo-2-methylpropanoate) 2.11 was prepared using 3,3’-((2,5-diiodo-1,4-phenylene)bis(oxy))bis(propan-1-ol) 2.5 and α-bromoisobutyryl bromide 2.35, in the presence of catalytic 4-dimethylaminopyridine (DMAP) and trimethylamine as the base, which gave the and gave desired product 2.11 in 75 % yield (Scheme 2.16).337,338

![Scheme 2.16. Synthesis of 2,5-diiodo-1,4-phenylenebis(oxy)bis(propane-3,1-diyl) bis(2-bromo-2-methylpropanoate) 2.11.](image)

In the 1H NMR the appearance of a 12 proton singlet of the two bromoester groups at 1.94 ppm and the disappearance of the hydroxyl protons showed the successful esterification reaction. FT-IR spectra also confirms the formation of bromoester functionalised monomer with the strong absorbance at 1729 cm⁻¹ of the newly introduced carboxyl groups.

The first trials for the esterification were performed without the use of DMAP and were not successful. When DMAP was added the reactions proceeded well and gave ester 2.11 in good yield. DMAP assists the esterification reaction by forming an activated acyl species 2.36 which is very reactive due to its charged nature. Reaction with the alcohol forms the ester and regenerates DMAP, free to assist further reactions (Scheme 2.17).


**2.3 Summary**

Four functionalised monomers (2.4, 2.10, 2.5 and 2.11) were successfully synthesised for the further preparation of PPV and PPE derivatives (Scheme 2.18).

Iodinated monomer 2.6 and 2.9 were easily obtained in high yields from commercial starting materials 2.7 and 2.32 respectively. Monomer 2.6 was then utilised in a Stille reaction to give monomer 2.4 in an overall yield of 41 % over three steps. Alternatively, using monomer 2.6 in a Sonogashira reaction, followed by silyl deprotection gave monomer 2.10 in an overall yield of 40 % over four steps.

Similarly, monomer 2.11 was successfully synthesised from from commercial starting material 2.7 in an overall yield of 38 % over four steps. It was found that the final step in the synthesis, the esterification of 2.5, required the presence of DMAP in order to successfully obtain monomer 2.11.

Overall, the four desired functionalised monomers (2.4, 2.10, 2.5 and 2.11) were successfully obtained in pleasing yields to be utilised in proceeding polymerisation reactions to afford the desired PPVOH 2.2 and PPEOH 2.3 CPs.
Scheme 2.18. Summarised synthesis pathway of the functionalised monomers.
2.4 Experimental Procedures

2.4.1 Synthesis of Functionalised Monomers

2-(2-(2-Methoxyethoxy)ethoxy)ethyl 4-methylbenzenesulfonate 2.13

To the solution of tosyl chloride 2.12 (5.70 g, 45.62 mmol) in THF (8 mL) was added a solution of 2-(2-(2-methoxyethoxy)ethoxy)ethanol 2.8 (4.00 g, 24.50 mmol) in sodium hydroxide (6 M, 7.5 mL), dropwise under an atmosphere of nitrogen at 0 °C. The reaction mixture was stirred and allowed to warm to the room temperature over 2 h. The organic layer was then extracted with diethyl ether (25 mL) and washed with aqueous sodium hydroxide (10 mL) and water (10 mL) and dried over sodium sulphate. The solvent was removed under vacuum to provide 2-(2-(2-methoxyethoxy)ethoxy)ethyl 4-methylbenzenesulfonate 2.13 as a colourless liquid (7.48 g, 96% yield).

δ_H (400 MHz; CDCl3) 2.44 (3H, s, CH3), 3.37 (3H, s, OCH3), 3.51-3.54 (2H, m, CH2-OCH3), 3.62-3.69 (6H, m, OCH2), 4.14-4.17 (2H, t, J = 4.9 Hz, CH2O), 7.34 (2H, d, J = 8.4 Hz, Ar-H), 7.78-7.81 (2H, d, J = 8.4 Hz, Ar-H). δ_C (400 MHz; CDCl3) 21.5 (CH3, C-12), 55.8 (CH3, C-11), 68.5 (O-CH2, C-10), 69.3 (CH2-O, C-9), 70.4 (O-CH2, C-8), 70.5 (CH2-O, C-7), 70.6 (O-CH2, C-6), 71.8 (CH2OSO2, C-5), 127.8 (C-CH3, C-4), 129.8 (CH, C-3), 132.9 (CH, C-2), 144.8 (C, C-1). IR: ν max (film) / cm⁻¹; 1488 (C=C aromatic), 1161 (S=O), 1303, 1230 and 1046 (C-O), 922, 825 and 744 (aromatic ring). All ^1H NMR and ^13C NMR data matched the literature values.327,328
1,4-Bis(2-(methoxymethoxy)ethoxy)benzene 2.14

To a solution of hydroquinone 2.7 (0.43 g, 3.90 mmol) in ethanol (20 mL), was added potassium tert-butoide (1.1 g, 9.80 mmol) and 2-(2-(2-methoxyethoxy)ethoxy)ethyl 4-methylbenzenesulfonate 2.13 (3.07 g, 9.64 mmol) at room temperature. The reaction mixture was heated at refluxed, under an atmosphere of nitrogen for 48 h, and then diluted with water (20 mL). The organic layer was extracted with CH$_2$Cl$_2$ (35 mL), washed with sodium hydroxide (2.5 M, 20 mL) and dried over sodium sulphate. The solvent was removed under vacuum to give the crude product which, was purified using flash chromatography (Et$_2$O-MeOH, 19:1) to give the title compound 2.14 as a bright yellow oil (2.98 g, 77% yield).

$\delta$$_H$(400 MHz; CDCl$_3$): 3.37 (6H, s, OCH$_3$), 3.53 (4H, t, $J = 4.5$ Hz, OCH$_2$), 3.64-3.69 (8H, m, OCH$_2$), 3.72-3.74 (4H, m, OCH$_2$), 3.82 (4H, t, $J = 5.0$ Hz, OCH$_2$), 4.07 (4H, t, $J = 5.0$ Hz, OCH$_2$), 6.83 (4H, s, Ar-H). $\delta$$_C$(400 MHz; CDCl$_3$): 58.9 (OCH$_3$, C-11), 68.0 (OCH$_2$, C-10), 69.8 (OCH$_2$, C-9), 70.5 (OCH$_2$, C-8), 70.6 (OCH$_2$, C-7), 70.7 (OCH$_2$, C-6), 71.9 (OCH$_2$, C-5), 115.5 (CH, C-2, C-3), 153.0 (C, C-1, C-4). IR: $\nu_{\text{max}}$(film) / cm$^{-1}$; 2879 (C-H stretching of CH$_3$), 1967 (aromatic ring overtones), 1484 (aromatic ring), 1267 (C-O), 1062 (C-C), 931 and 833 (aromatic ring). All $^1$H NMR and $^{13}$C NMR data matched the literature values.\textsuperscript{329,330}
1,4-Diiodo-2,5-bis(2-(methoxymethoxy)ethoxy)benzene 2.6

1,4-Bis(2-(methoxymethoxy)ethoxy)benzene 2.14 (0.88 g, 2.19 mmol) was added dropwise to a solution of mercury(II) acetate (2.80 g, 8.78 mmol) and iodine (2.21 g, 17.41 mmol) in CH₂Cl₂ (31 mL) and the reaction mixture stirred for 4 h, under an atmosphere of nitrogen. The slurry was filtered through celite and the filtrate was sequentially washed with sodium thiosulphate (15 mL), sodium hydrogen carbonate (15 mL), water (15 mL) and brine (15 mL) then dried over sodium sulphate. The solvent was removed under vacuum and the crude mixture purified using flash chromatography (DCM–MeOH, 100:5) to give the title compound 2.6 as a bright yellow solid (1.4 g, 95% yield).

**MP**: 28-30 °C. δH (400 MHz; CDCl₃) 3.38 (6H, s, OCH₃), 3.54-3.56 (4H, m, OCH₂), 3.64-3.70 (8H, m, OCH₂), 3.77-3.79 (4H, m, OCH₂), 3.87 (4H, t, J = 5.0 Hz, OCH₂), 4.10 (4H, t, J = 5.0 Hz, OCH₂), 7.23 (2H, s, Ar-H). δC (400 MHz; CDCl₃) 29.7 (OCH₃, C-13), 59.1 (OCH₂, C-12), 70.3 (OCH₂, C-11), 70.6 (OCH₂, C-10), 70.8 (OCH₂, C-9), 71.2 (OCH₂, C-8), 72.0 (OCH₂, C-7), 86.4 (C, C-1, C-4), 123.5 (CH, C-3, C-6), 153.1 (C, C-2, C-5). IR: νmax(film) / cm⁻¹; 2879, 1967, 1484, 1267 (C-O), 1062 (C-C), 931 and 833 (aromatic ring). All ¹H NMR and ¹³C NMR data matched the literature values.³²⁹
(3-Bromopropoxy)(tert-butyl)dimethylsilane 2.33

To the solution of tert-butylchlorodimethylsilane TBDMSCl (2.49 g, 16.52 mmol) and imidazole (1.23 g, 18.06 mmol) in DMF (10 mL) was added 3-bromo 1-propanol 2.32 (2.07 g, 13.73 mmol) at 0 °C, under an atmosphere of nitrogen, and the mixture stirred for 1 h. The reaction was then warmed to room temperature and stirred for 24 h then diluted with diethyl ether (20 mL). The organic layer was separated and washed with sodium hydrogen carbonate (2 × 20 mL) and 3M HCl (2 × 20 mL) and dried over sodium sulphate. The solvent was then removed under vacuum and the crude mixture was purified using flash chromatography (n-hexanes-EtOAc, 14:1) to give the title product 2.33 as a colourless liquid (2.80 g, 97% yield).

δH (400 MHz; CDCl3) 0.06 (6H, s, CH3Si), 0.83 (9H, s, C4H9Si), 1.99-2.09 (2H, m, CH2), 3.51 (2H, t, J = 6.5 Hz, CH2Br), 3.73 (2H, t, J = 5.6 Hz, CH2O). δC (400 MHz; CDCl3): -5.4 (SiC, C-5), -5.3 (SiCH3, C-4, C-6), 35.4 (CH2Br, C-3), 35.6 (CH2, C-2), 60.4 (OCH2, C-1). IR: νmax(film) / cm⁻¹; 1104 (C-O), 845 (O-Si-CH3), 745 (C-Br). All ¹H NMR and ¹³C NMR data matched the literature values.³³⁵,³³⁶
1,4-Bis(3-((tert-butyldimethylsilyl)oxy)propoxy)benzene 2.34

A solution of (3-bromopropoxy)(tert-butyl)dimethylsilane 2.33 (3.16 g, 12.50 mmol) in DMF (2.50 mL) was added dropwise to a solution of hydroquinone 2.7 (0.55 g, 5.00 mmol) and potassium carbonate (1.72 g, 12.44 mmol) in DMF (2.82 mL) at room temperature. The mixture was then stirred at 100 °C for 48 h. The mixture was then cooled and diluted with CH2Cl2 (35 mL). The mixture was washed sequentially with water (15 mL) and brine (15 mL) and dried over sodium sulphate. The solvent was removed under vacuum and the mixture was purified using flash chromatography with (n-hexanes-Et2O, 19:1) to give the title product 2.34 as a white solid (2.87 g, 63% yield).

MP: 40-43 °C. δH (400 MHz; CDCl3): 0.006 (6H, s, CH3Si), 0.85 (18H, s, C4H9Si), 1.95-1.99 (4H, m, CH2), 3.74 (4H, t, J = 6.0 Hz, OCH2), 3.96 (4H, t, J = 6.5, OCH2), 6.77 (4H, s, Ar-H). δC (400 MHz; CDCl3): -5.3 (CH3Si, C-10), 18.3 (OCH2, C-9), 25.9 (CH2, C-8), 32.5 (CH3, C-12), 59.6 (C, C-11), 65.1 (OCH2, C-7), 115.3 (CH, C-2, C-3, C-4, C-5), 153.1 (C, C-1, C-2).

IR: νmax(film) / cm⁻¹; 2953 (C-H, stretching), 2929 (C-H), 2857 (C-H), 1868, 1510, 1253 (C-O), 1224 (Si-O), 1041 (C-C), 970, 770 and 731. HRMS (ESI⁺) Found (MH⁺): 455.2990; C24H47O4Si2 requires 455.3007.
1,4-Bis(3-(tert-butyldimethylsilyl)oxy)propoxy)benzene 2.34 (1.42 g, 2.63 mmol) was added drop-wise to the solution of mercury(II) acetate (3.01 g, 9.44 mmol) and Iodine (2.17 g, 17.1 mmol) in CH$_2$Cl$_2$ (20 mL) and the mixture was stirred for 4 h, under an atmosphere of nitrogen. The slurry was then filtered through Celite and the filtrate was sequentially washed with sodium thiosulphate (15 mL), sodium hydrogen carbonate (15 mL), water (15 mL) and brine (15 mL) then dried over sodium sulphate. The solvent was removed under vacuum and the mixture was purified using flash chromatography (n-hexanes-CH$_2$Cl$_2$, 1:1) to give the titled product 2.9 as a white solid (1.87 g, 90% yield).

**MP:** 125-127 °C. **$\delta_H$** (400 MHz; CDCl$_3$): 0.05 (12H, s, CH$_3$Si), 0.85 (18H, s, C$_4$H$_{18}$Si), 1.89-1.92 (4H, q, $J = 6.0$ Hz, CH$_2$), 3.85 (4H, t, $J = 6.0$ Hz, OCH$_2$), 4.03 (4H, t, $J = 6.0$ Hz, OCH$_2$), 7.13 (2H, s, Ar-H). **$\delta_C$** (400 MHz; CDCl$_3$) -5.3 (CH$_3$Si, C-10), 18.4 (CH$_3$, C-12), 26.0 (C-Si, C-11), 32.4 (CH$_2$, C-8), 59.5 (OCH$_2$, C-9), 66.7 (OCH$_2$, C-7), 81.2 (C, C-2, C-5), 122.6 (CH, C-3, C-6), 152.7 (C, C-1, C-4). **IR:** $\nu$$_{max}$(film) / cm$^{-1}$: 2949 (C-H), 2927 (C-H), 2853 (C-H), 14590 (C-C), 1249 (C-O), 1218 (Si-O), 1046 (C-C), 952, 866 and 776. **HRMS** (ESI$^+$) Found (MNa$^+$): 729.0771; C$_{24}$H$_{44}$I$_2$NaO$_4$Si$_2$ requires 729.0760.
A methanolic solution of HCl (0.41 mL, 1.25 M) was added dropwise to an ice cold solution of 1,4-di-iodo 2,5-bis[3-(tert-butyldimethylsilyloxy)propoxy]benzene 2.9 (0.34 g, 0.43 mmol) in anhydrous methanol (3 mL) dropwise. The mixture was warmed to room temperature and stirred for 2 h. The mixture was then diluted with ethyl acetate (20 mL), washed with water (15 mL) and brine (15 mL) and dried over sodium sulphate. The solvent was then removed under vacuum to give the title product 2.5 as a white powder (0.2 g, 97% yield).

**MP**: 127-130 °C. δ\(_\text{H}\) (400 MHz; d\(_6\) - DMSO) 1.84 (4H, q, J = 6.0 Hz, CH\(_2\)), 3.59-3.61 (4H, m, OCH\(_2\)), 4.03 (4H, t, J = 6.0 Hz, OCH\(_2\)), 5.53 (2H, t, J = 5.5 Hz, OH), 7.34 (2H, s, Ar-H). δ\(_\text{C}\) (400 MHz; d\(_6\) - DMSO): 32.1 (CH\(_2\), C-8), 57.3 (CH\(_2\)OH, C-9), 66.7 (OCH\(_2\), C-7), 88.9 (Cl, C-2, C-5), 122.3 (CH, C-3, C-6), 152.3 (C, C-1, C-4). **IR**: \(\nu_{\text{max}}\) (film) / cm\(^{-1}\); 3350 (OH), 3272, 2937 (C-H), 2887 (C-H), 2042 and 1718, 1487, 1266 (C-O), 1054 (C-C), 954, 846 and 759 (C-H ring). **HRMS** (ESI\(^+\)) Found (MNa\(^+\)): 500.9038; C\(_{12}\)H\(_{16}\)I\(_2\)NaO\(_4\) requires 500.9030.
To a solution of 3,3’-((2,5-diiodo-1,4-phenylene)bis(oxy))bis(propan-1-ol) \textbf{2.5} (200 mg, 0.42 mmol) in dry DMF (4 mL) and triethylamine (200 \, \mu \text{L}) was added DMAP (28 mg, 0.23 mmol) followed by \(\alpha\)-bromoisobutyryl bromide (140 \, \mu \text{L}, 1.13 mmol) dropwise. The mixture was stirred at 0 \, ^\circ\text{C}, and allowed to warm to room temperature over 48 h. The mixture was filtered, washed with water (15 mL), NH\(_4\)Cl (15 mL), NaHCO\(_3\) (15 mL) and brine (15 mL) and then dried over sodium sulphate. The solvent was removed under vacuum and the mixture was purified using flash chromatography (\(n\)-hexanes-EtOAc, 9:1) to give the title product \textbf{2.11} as a white solid (0.134 g, 75\% yield).

**MP**: 80-83 \, ^\circ\text{C}. \(\delta\)\(_H\) (400 MHz; d\(_6\) - DMSO) 1.94 (12H, s, CH\(_3\)), 2.18-2.21 (4H, q, \(J = 6.0\) Hz, CH\(_2\)), 4.06 (4H, t, \(J = 6.0\) Hz, OCH\(_2\)), 4.44 (4H, t, \(J = 6.0\) Hz, OCH\(_2\)), 7.20 (2H, s, Ar-H). \(\delta\)\(_C\) (400 MHz; d\(_6\) - DMSO) 28.4 (CH\(_2\), C-8), 30.78 (CH\(_3\), C-12), 55.8 (C, C-11), 62.6 (OCH\(_2\), C-9), 66.5 (OCH\(_2\), C-7), 86.5 (Cl, C-2, C-5), 123.1 (CH, C-3, C-6), 152.83 (C, C-1, C-4), 171.6 (C=O, C-10). **IR**: \(\nu_{\text{max}}(\text{film}) / \text{cm}^{-1}\); 2931 (C-H), 2886 (C-H), 2031, 1977, 1729 (C=O), 1488, 1055 (C-C), 953, 846 and 762 (C-H). **HRMS** (ESI\(^+\)) Found (MNa\(^+\)): 796.8108; C\(_{20}\)H\(_{26}\)Br\(_2\)I\(_2\)NaO\(_6\) requires 796.8078.
Tetrakis(triphenylphosphine)palladium(0) (21 mg, 0.02 mmol) was added to a solution mixture of 1,4-diodo-2,5-bis(2-(methoxymethoxy)ethoxy)benzene \( \text{2.6} \) (0.11 g, 0.17 mmol) in DMF (5 mL) under an atmosphere of nitrogen. After 15 min, vinyl tri-butyl tin (0.163 g, 0.51 mmol) was added and the mixture stirred at 100 °C for 5 h. The mixture was cooled to room temperature, diluted with water (15 mL), extracted with CH\(_2\)Cl\(_2\) (25 mL). The organic extracts were then dried over magnesium sulphate and the solvent removed under vacuum. The crude mixture was purified using flash chromatography (EtOAc-\( n \)-hexane, 2:1) to afford the title product \( \text{2.4} \) as a yellow oil (0.04 g, 56% yield).

δ\(_H\) (400 MHz; CDCl\(_3\)): 3.38 (6H, s, CH\(_3\)), 3.54-3.55 (4H, m, OCH\(_2\)), 3.63-3.70 (8H, m, OCH\(_2\)), 3.72-3.75 (4H, m, OCH\(_2\)), 3.85 (4H, t, \( J = 5.0 \) Hz, CH\(_2\)), 413 (4H, t, \( J = 4.6 \) Hz, CH\(_2\)), 5.22 (2H, d, \( J = 1.5 \) Hz, C=CH\(_2\)), 5.25 (1H, d, \( J = 1.5 \) Hz, C=CH\(_2\)), 5.69 (1H, d, \( J = 1.5 \) Hz, C=CH\(_2\)), 5.73 (1H, d, \( J = 1.5 \) Hz, C=CH\(_2\)), 6.99-7.06 (2H, m, CH). δ\(_C\) (400 MHz; CDCl\(_3\)): 59.0 (OCH\(_3\), C-13), 69.1 (OCH\(_2\), C-7), 69.9 (OCH\(_2\), C-8), 70.6 (OCH\(_2\), C-9), 70.7 (OCH\(_2\), C-10), 70.9 (OCH\(_2\), C-11), 71.9 (OCH\(_2\), C-12), 111.2 (C, C-2, C-5), 114.3 (CH\(_2\), C-2'), 127.6 (CH, C-3, C-6), 131.4 (CH, C-1'), 150.7 (C, C-1). IR: \( \nu_{\max}(\text{film}) / \text{cm}^{-1} \): 2873, 2173, 1625 (C=C), 1498, 1245 (C-O), 1060 (C-C), 942. The \(^1\)H NMR and \(^{13}\)C NMR data matched literature values.\(^{54}\)
To a solution 1,4-diiodo-2,5-bis(2-(methoxymethoxy)ethoxy)benzene 2.6 (1 g, 1.50 mmol), palladium dichloride bis(tri-phenyl phosphine) (44 mg, 0.06 mmol) and copper iodide (24 mg, 0.12 mmol) in THF (4 mL) and trimethylamine (2 mL) was added Tri-methylsilyl acetylene (1.5 g, 15.27 mmol). The mixture was stirred at room temperature for 48 h under an atmosphere of nitrogen. The mixture was then diluted with water (15 mL) and extracted with chloroform (25 mL). The organic extract was dried over sodium sulphate and the solvent removed under vacuum. The mixture was purified using flash chromatography (n-hexanes-EtOAc, 4:1) to afford the title product 2.22 a light brown powder (0.60 g, 63% yield).

**MP**: 133-135 °C. δH (400 MHz; CDCl3): 0.24 (18H, s, SiCH3), 3.37 (6H, s, OCH3), 3.53-3.56 (4H, m, OCH2), 3.64-3.68 (8H, m, OCH2), 3.77-3.80 (4H, m, OCH2), 3.86 (4H, t, $J = 5.0$ Hz, OCH2), 4.11 (4H, t, $J = 5.0$ Hz, OCH2), 6.91 (2H, s, Ar-H). δC (400 MHz; CDCl3): 0.0 (SiCH3, C-14), 59.1 (OCH3, C-13), 69.9 (OCH2, C-12), 67.7 (OCH2, C-11), 70.6 (OCH2, C-10), 70.8 (OCH2, C-9), 71.2 (OCH2, C-8), 72.0 (OCH2, C-7), 100.4 (C, C-2'), 100.9 (C, C-1'), 114.3 (C, C-2, C-5), 117.9 (CH, C-3, C-6), 153.9 (C, C-1, C-4). IR: $ν_{max}$(film) / cm⁻¹; 2958 and 2821 (CH3), 2150 (C≡C), 1499, 1248 (C-Si), 1058 (C-C), 938 and 757. All ¹H NMR and ¹³C NMR data matched literature values.330,332
1,4-Diethynyl-2,5-bis(2-(methoxymethoxy)ethoxy)benzene 2.10

To a solution of ((2,5-bis(2-(methoxymethoxy)ethoxy)-1,4-phenylene)bis(ethyne-2,1-diyl))bis(trimethylsilane) 2.22 (0.68 g, 1.14 mmol) in methanol (7 mL) was added potassium fluoride (0.44 g, 5.75 mmol). The reaction was left for 24 h at room temperature, then diluted with water (15 mL), extracted with chloroform (25 mL). The organic extract was dried over sodium sulphate and the solvent was then removed under vacuum. The mixture was purified using flash chromatography (CH2Cl2-MeOH, 24:1) to afford the title product 2.10 as a dark brown solid (0.45 g, 87% yield).

**MP**: 121-123 °C. \( \delta_H \) (400 MHz; CDCl3): 3.32 (2H, s, C=CH), 3.37 (6H, s, CH3), 3.53-3.56 (4H, m, OCH2), 3.64-3.68 (4H, m, OCH2), 3.75-3.78 (4H, m, OCH2), 3.86 (4H, t, \( J = 5.0 \), OCH2), 4.14 (4H, t, \( J = 5.0 \), OCH2), 6.99 (2H, s, Ar-H). \( \delta_C \) (400 MHz; CDCl3): 59.0 (OCH3, C-13), 69.5 (OCH2, C-12), 69.6 (OCH2, C-11), 70.6 (OCH2, C-10), 70.7 (OCH2, C-10), 71.1 (OCH2, C-8), 71.9 (OCH2, C-7), 79.6 (CH, C-2'), 82.8 (C, C-2'), 113.6 (C, C-1, C-4), 118.3 (CH, C-3, C-6), 154.11 (C, C-2, C-5). **IR**: \( \nu_{\text{max}} \) (film) / cm\(^{-1}\): 2958, 2855, 2162 (C≡C), 1463 and 10508 (C-C), 938 and 749 (aromatic ring). All the \(^1\)H NMR and \(^13\)C NMR data matched literature values.\(^{330,333,334}\)
Chapter 3: Synthesis of Functionalised Poly(para-phenylene vinylene) PPV and Poly(para-phenylene ethynylene) PPE Backbones
3.1 Introduction

With the successful synthesis of the monomer units completed in Chapter 2 the next task was to use these monomers to prepare the desired PPEs and PPVs. The hydroxyl functionalised polymers could then be converted to active acylbromides suitable for further modifications, Fig 3.1.

![Molecular structures of PPVOH 2.2, PPEOH 2.3, PPVMI 3.1 and PPEMI 3.2.](image)

Fig 3.1. Molecular structures of PPVOH 2.2, PPEOH 2.3, PPVMI 3.1 and PPEMI 3.2.
An efficient and versatile synthetic pathway was sought to prepare poly(3-(5-((E)-2,5-bis(2-(methoxymethoxy)ethoxy)-4-((E)-prop-1-en-1-yl)styryl)-4-(2-hydroxyethoxy)-2-((E)-prop-1-en-1-yl)phenoxy)propan-1-ol) abbreviated as PPVOH 2.2. While several synthetic pathways were possible to achieve the desired PPVs; including Wittig-Horner, Gilch, sulfinyl and Wessling polymerisations however, considering the importance of purity and the trans configuration of the final product, the Heck polymerisation was chosen for the synthesis of PPVOH 2.2.54,339–341

For the synthesis of poly(3,3'-(2-((2,5-bis(2-(methoxymethoxy)ethoxy)-4-(prop-1-yn-1-yl)phenyl)ethynyl)-5-(prop-1-yn-1-yl)-1,4-phenylene)bis(oxy))bis(propan-1-ol)) PPEOH 2.3, the yield of the reaction, a high molecular weight and purity of the polymer were of particular importance. Taking into consideration these factors, from the several synthetic pathways available for PPEs the Sonogashiro polymerisation was chosen.130,142,342

3.2 Synthesis of Poly 3-(5-((E)-2,5-bis(2-(methoxymethoxy)ethoxy)-4-((E)-prop-1-en-1-yl)styryl)-4-(2-hydroxyethoxy)-2-((E)-prop-1-en-1-yl)phenoxy)propan-1-ol, PPVOH 2.2

A number of Heck polymerisation reactions have been reported54,339,341 for the synthesis of different functionalised PPVs as shown in Fig 3.2. However, the conditions used by Anupama Rao et al.54 to obtain 3.4 were considered most relevant due to the similarity of the desired polymers.
Therefore a mixture of monomer 2.5 and divinyl monomer 2.4 were combined with palladium acetate in the presence of tri-O-tolylphosphine and tributylamine. After 24 hour reaction the polymer was precipitated using diethylether and dried to give a red solid in 67 % yield (Scheme 3.1).
Fig 3.3. $^1$H NMR spectra of monomer 2.5 (A), 2.4 (B) and PPVOH 2.2 (C).
The $^1$H NMR data confirmed the formation of PPVOH 2.2 through the appearance of the new peaks when comparing with monomers 2.4 and 2.5, as well as through integration. In the $^1$H NMR spectra, the peaks at 7.21, 7.41 and 7.51 ppm represent the aromatic rings as well as the *trans* vinyl groups present. Also, the methylene peaks of the tri-glycol groups in monomer 2.4 and those in propyl group on monomer 2.5 appear at 4.27 and 3.45 ppm as broad peaks. The six protons of the triglycol methoxy groups appear at 3.34 ppm as a singlet (Fig 3.3).

In the FT-IR spectrum of PPVOH 2.2, the hydroxyl absorption is apparent at 3398 cm$^{-1}$ and the absorption resulting from the *trans*-vinyl groups are apparent in the areas of 951 and 964 cm$^{-1}$ respectively (Fig 3.4).$^{54}$

Considering the spectroscopic results, it was confirmed that the Heck polymerisation was successfully conducted, with an expected mechanism of reaction depicted in Scheme 3.2.
3.3 Synthesis of poly 3,3'-(2-((2,5-bis(2-(methoxymethoxy)ethoxy)-4-(prop-1-yn-1-yl)phenyl)ethynyl)-5-(prop-1-yn-1-yl)-1,4-phenylene)bis(oxy))bis(propan-1-ol) (PPEOH 2.3) and the direct synthesis of poly ((2-((2,5-bis(2-(methoxymethoxy)ethoxy)-4-(prop-1-yn-1-yl)phenyl)ethynyl)-5-(prop-1-yn-1-yl)-1,4-phenylene)bis(oxy))bis(propane-3,1-diyl) bis(2-bromo-2-methylpropanoate) (PPEMI 3.2.2)

Sonogashira coupling polymerisation is the most common reaction for the synthesis of PPE derivatives (Fig 3.5). The conditions reported by Wosnick et al. and Kuroda and Swager (for synthesis of 3.5 and 3.6) were considered most relevant due to their similarity with the desired polymers.
Therefore a mixture of monomer 2.5 and diacetylene monomer 2.10 were combined with tetrakis(triphenylphosphine)palladium (0) and copper iodide. After 24 hour reaction the polymer was precipitated using n-hexanes and dried to give a red solid in 62% yield (Scheme 3.3).

The $^1$H NMR data of PPEOH 2.3 compared to its monomers, 2.5 and 2.10 confirmed the formation of the polymer backbone. In the $^1$H NMR data of the PPEOH 2.3 showed broad peaks at 7.13 ppm and 7.04 ppm; for the aromatic hydrogens. Also, the methylene peaks of either monomers 2.5 and 2.10 appear as broad peaks between 7.42 ppm and 7.51 ppm. The six protons of triglycol methoxy groups appear at 3.35 ppm as a singlet (Fig 3.6).
Fig 3.6. $^1$H NMR spectra of monomers 2.5 (A), 2.10 (B) and PPEOH 2.3 (C).
In the FT-IR spectrum of PPEOH 2.3, the hydroxyl absorption is apparent at 3371 cm$^{-1}$ (Fig 3.7).

![FT-IR spectra of PPEOH 2.3.](image)

Considering the spectroscopic results, it is clear that the Sonogashira polymerisation was successfully conducted, with an expected mechanism of reaction depicted in Scheme 3.4.

In this polymerisation method, copper and palladium catalysts were used for the coupling of the terminal acetylene monomer 2.10 to aryl iodide monomers 2.5 and 2.11. As is presented in the reaction mechanism, the first step of the reaction within Cycle A starts with tetrakis(triphenylphospine) palladium(0) and the either monomers 2.5 or 2.11, which resulted in the insertion of the Pd(0) into the arylhalide 2.26 bond via oxidative addition. This step is followed by the transmetallation of the monomer 2.10 with Cu(I) catalyst 3.7 in the presence of the di-isopropyl amine. Finally, the reductive elimination step of 3.8 results in the formation of the PPE products (2.3 or 3.2.2) as well as the regeneration of the palladium catalyst. The reaction procedure was started with several freeze-thaw steps and followed with a continuous flow of nitrogen to prevent the presence of oxygen in the reaction which could result in the formation of the inactive form of the palladium complex.
3.4 Synthesis of PPVMI 3.1 and PPEMI 3.2.1

After the successful synthesis of PPVOH 2.2 and PPEOH 2.3 the next task was to convert the bromides into macroinitiators PPVMI 3.1 and PPEMI 3.2 respectively. This was to be done by the esterification of the alcohols with α-bromo isobutyrylbromide (BIBB) 2.35. The resulting terminals should have suitable reactivity in future radical polymerisation grafting Scheme 3.5.
The esterification reaction was achieved through the nucleophilic reaction between the hydroxyl groups of the polymers and the BIBB in the presence of dimethylaminopyridine (DMAP) and trimethylamine.

Post polymerisation esterification reaction was conducted on both PPV and PPE hydroxyl functionalised polymers (2.2 and 2.3). PPEMI 3.2.1 was obtained in lower yields (20 %) compared to PPVMI 3.1 (55 %) (Scheme 3.6).
Due to the poor yield of post polymerisation PPEMI 3.2.1, the direct synthesis of PPEMI (3.2.2) was attempted. Direct synthesis of PPEMI (3.2.2) was successfully conducted within the same procedure used for the synthesis of PPEOH 2.3 and resulted in higher overall yield of PPEMI 3.2.2 (Scheme 3.7).

Comparing the $^1$H NMR data of the PPVOH 2.2 with the PPVMI 3.1 as is presented in Fig 3.8, shows the appearance of the sharp singlet peak at 1.92 ppm belonging to dimethyl bromo ester groups. Also compared to the PPVOH 2.2, the appearance of the broad peak at the 4.51 ppm indicated the presence of a methylene adjacent to the ester functionalised group in PPVMI 3.1. The remaining peaks in PPVOH 2.2 are similarly found in PPVMI 3.1, showing no degradation of the polymer backbone (Fig 3.8).
The FT-IR spectrum of the PPVMI 3.1 shows strong absorption from 1731 cm\(^{-1}\) relating to ester carbonyl group (Fig 3.9).\(^{222,344,345}\)
The $^1$H NMR data of PPEMI 3.2 compared to PPEOH 2.3 shows the addition of a sharp singlet peak at 1.91 ppm resulting for the dimethylbromo esters$^{222,344,345}$ and additionally shifting of the methylene group adjacent to the ester groups at the area of 4.51 ppm in PPEMI (3.2.1 and 3.2.2). Again the methylene peaks of the monomers as well as the aromatic hydrogen remain similar to PPEOH 2.3 showing no degradation of the polymer (Fig 3.10).
Fig 3.10. $^1$H NMR spectra of PPEOH 2.3 (A), PPEMI 3.2.1 (B) and directly synthesised PPEMI 3.2.2 (C).
The FT-IR spectrum of PPEMI (3.2.1 and 3.2.2) also confirm the addition of the ester carboxyl group at 1729 cm$^{-1}$ (Fig 3.11).222,344,345

![Fig 3.11. FT-IR spectrum of directly synthesised PPEMI 3.2.1 and 3.2.1.](image)

### 3.5 Photophysical characteristics of the polymer backbones and the initiators

To investigate the photoluminescent properties of the synthesised CPs, UV-Vis absorption and the fluorescence intensity of the polymers and macroinitiators were compared to identify the effect of the esterification reaction on the conjugated backbone.

To investigate the UV-Vis properties of PPVOH 2.2 and PPVMI 3.1 samples were prepared at 2 mg mL$^{-1}$ and run between 300 nm to 700 nm. UV-Vis studies of PPVOH 2.2 and PPVMI 3.1 indicate that the maximum absorption of the polymers are at 458 nm and 451 nm, respectively, which is in agreement with previously reported PPVs photoluminescence properties (Fig 3.12).54,222
Fig 3.12. UV-Vis spectra of 2 mg mL⁻¹ of PPVOH 2.2 and PPVMI 3.1.

The UV-Vis spectrum of the PPEOH 2.3 and PPEMI (3.2.1) and direct synthesised PPEMI (3.2.2), in Fig 3.13, indicates the maximum absorption of these polymers to be at 435 nm, 428 nm and 433 nm, respectively which is also in agreement with the previously prepared PPEs.³⁴₄,³⁴₅

![UV-Vis spectra of 2 mg mL⁻¹ of PPEOH 2.3, PPEMI 3.2.1 and direct synthesised PPEMI 3.2.2.](image)

Fig 3.13. UV-Vis spectra of 2 mg mL⁻¹ of PPEOH 2.3, PPEMI 3.2.1 and direct synthesised PPEMI 3.2.2.

Comparing the spectral shift of PPVMI 3.1 and PPEMI 3.2.1 with both PPVOH 2.2 and PPEOH 2.3 shows a spectral blue shift of 7 nm for both polymers. This shift is related to the loss of conjugation most likely through slightly acidic degradation during the reaction with 2-
bromoisobutyryl bromide in the esterification reaction. Although triethylamine was used in the esterification reaction to keep the reaction condition neutral, both of the polymer backbones have been affected by the conditions. Also, observing that the $\lambda_{\text{max, abs}}$, which appears at 433 nm, in comparison for the direct synthesised PPEMI, no blue shift is observed when compared to PPEOH 2.3. The loss of conjugation, when comparing PPVOH 2.2 with PPVMI 3.1 and PPEOH 2.3 with PPEMI 3.2.1, has also been identified through the optical band gap calculation using the UV-Vis data using the following **Equation 3.1**.

$$E_{(\text{opt})} = \frac{h \cdot c}{\lambda_m}$$

**Equation 3.1.** Optical band gap measurements.

Where in the equation $h$, $c$ and $\lambda$ are Planck’s constant, velocity of light and the cut-off wave length respectively and $E$ represents the optical band gap energy. Band gap calculations in **Equation 3.1** indicate the optical band gap for PPVOH 2.2 and PPVMI 3.1 to be 2.25 eV and 2.30 eV and for PPEOH 2.3 and PPEMI 3.2.1, 2.55 eV and 2.58 eV, respectively. Analysing the band gap results, showed the loss of conjugation after formation of the esters by an increase in optical band gap energy of around 50 meV in PPVMI 3.1 and 30 meV in PPEMI 3.2.1. Also, band gap calculation for the direct synthesised PPEMI 3.2.2 shows 2.20 eV optical band gap energy, which is in concordance with the observed optical band gap of the PPEOH 2.3.

Next the fluorescence spectra of PPVOH 2.2, PPEOH 2.3, PPVMI 3.1, PPEMI 3.2.1 and direct synthesised PPEMI 3.2.2 were measured between 450 nm to 700 nm using 100 µg mL$^{-1}$ of polymer solutions. It was observed, that the $\lambda_{\text{max, em}}$ in PPVOH 2.2 and PPVMI 3.1 appears at 550 nm and 545 nm (**Fig 3.14**).
Looking at the fluorescent spectrum of the PPEOH 2.3, PPEMI 3.2.1 and direct synthesised PPEMI 3.2.2, shows the maximum emission for the polymers at 477 nm, 471 nm and 473 nm respectively (Fig 3.15).

The fluorescent spectra of both the PPV and PPE backbones after the esterification reaction shows a blue shift of almost 5 nm for PPVMI 3.1 and 6 nm for the indirect synthesised PPEMI 3.2.1. As with the blue shift of the polymer macroinitiators in the UV-Vis spectra, in the
fluorescent spectra the blue shift is related to the conjugation band loss after esterification reaction.

The effect of conjugation band loss in polymer macroinitiators was also studied through the quantum yield measurements of the polymer backbones and macroinitiators, calculating the quantum yield using Equation 3.2.\(^\text{54,349–351}\)

\[
\phi = \phi_R \times \left( \frac{I}{I_R} \right) \times \left( \frac{A}{A_R} \right) \times \left( \frac{n^2}{n_R^2} \right)
\]

Equation 3.2. Quantum yield calculation.

Where \(\phi\) is the quantum yield, \(I\) the measured integrated emission intensity, \(A\) the optical density and \(n\) the refractive index of the solvents. The subscript \(R\) refers to the reference. Quantum yield calculations using the abovementioned equation gave the fluorescence intensity of the polymers in DMF as 0.72 and 0.64 for PPVOH 2.2 and PPVMI 3.1, respectively. DMF was used in measuring the quantum yield because it was found to be a good solvent for both of the polymers. The measured quantum yield of the polymers indicates it is decreased for PPVMI 3.1. Such quantum yield reduction is also in concordance with the optical band gap calculation, which is attributed to the loss of conjugation in the polymer backbone.

Quantum yield measurements were also recorded for PPEOH 2.3, PPEMI 3.2.1 and direct synthesised PPEMI 3.2.2. The results showed the quantum yield of PPEOH 2.3, PPEMI 3.2.1 and the direct PPEMI 3.2.2 to be 0.32, 0.25 and 0.67, respectively. It can be concluded that the ester groups result in more favourable PPE backbone configuration in solvent. With no conjugation loss in the directly synthesised PPEMI 3.2.2, the calculated quantum yield is higher compared to the PPEOH 2.3. All the detailed photophysical properties of the polymer backbones and the macroinitiators are summarised in Table 3.1.
<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{max,abs}}$ (cm$^{-1}$)</th>
<th>$\lambda_{\text{max,em}}$ (cm$^{-1}$)</th>
<th>Optical Band-Gap (eV)</th>
<th>Quantum Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPVOH 2.2</td>
<td>458</td>
<td>550</td>
<td>2.25</td>
<td>0.53</td>
</tr>
<tr>
<td>PPEOH 2.3</td>
<td>435</td>
<td>477</td>
<td>2.55</td>
<td>0.32</td>
</tr>
<tr>
<td>PPVM 3.1</td>
<td>451</td>
<td>545</td>
<td>2.30</td>
<td>0.64</td>
</tr>
<tr>
<td>PPEMI 3.2.1</td>
<td>428</td>
<td>471</td>
<td>2.58</td>
<td>0.25</td>
</tr>
<tr>
<td>Direct Synthesised</td>
<td>433</td>
<td>473</td>
<td>2.20</td>
<td>0.67</td>
</tr>
<tr>
<td>PPEMI 3.2.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.1. Photophysical properties of the polymer backbones and the macro initiators.

### 3.6 Molecular Weight Characterisations

The molecular weight of the prepared polymers and macroinitiators was determined using gel permeation chromatography (GPC). The polymer’s number-average molecular weight ($M_n$), average molecular weight ($M_w$) and the typical dispersity were measured using DMF as an eluent. Polystyrene standards were used for calibration and mass determination.

GPC analysis for PPVOH 2.2 and PPVM 3.1 indicated that the average molecular weight of the polymers were 37390 g mol$^{-1}$ and 22656 g mol$^{-1}$, respectively. Also the polydispersity was measured to be 1.6 for PPVOH 2.2 and 1.5 for PPVM 3.1. Considering GPC results “n” is calculated of 55 and 23 repeating units for PPVOH 2.2 and PPVM 3.1, respectively.

The GPC molecular weight result of PPVM 3.1 was also compared to the theoretical predefined molecular weight of the polymer while using the initiation ratio of the polymer backbone calculated by Equation 3.3.

$$I_r = \left( \frac{W_2 - W_1}{W_2} \right) \times 100$$

Equation 3.3. Initiation ratio calculation.
Where in Equation 3.3, \( W_2 \) (g) is the dry weight of PPVMI 3.1 and \( W_1 \) (g) is the dry weight of PPVOH 2.2 and the \( I_r \) represents the initiation ratio of the esterification reaction. Estimating the theoretical molecular weight using the above mentioned equation, resulted in a molecular weight of 22434 gmol\(^{-1}\), which is very close to that which was found using GPC.

The molecular weight of PPEOH 2.3 and PPEMI 3.2.1 and the direct synthesised PPEMI 3.2.2 was also measured. GPC results indicate molecular weight of 28705 gmol\(^{-1}\), 18582 gmol\(^{-1}\) and 22308 gmol\(^{-1}\) for PPEOH 2.3, PPEMI 3.2.1 and directly synthesised PPEMI 3.2.2, respectively. GPC results of the calculated molecular weights also indicates \( n = 42, 19 \) and 23 for PPEOH 2.3, PPEMI 3.2.1 and PPEMI 3.2.2. The polydispersity was measured to be 1.32, 1.73 and 1.86 for PPEOH 2.3 PPEMI 3.2.1 and the directly synthesised PPEMI 3.2.2 (Table 3.2).

As it was previously described, the esterification procedure used to prepare PPVMI 3.1 was not ideal for PPEMI 3.2.1 in respect to the lower reaction yield, a result which is also confirmed when comparing the molecular weight. This was also the case in that the molecular weight of the directly synthesised PPEMI 3.2.2 was lower than PPEOH 2.3. Although the molecular weight of the direct synthesised PPEMI 3.2.2 was lower than the PPEOH 2.3, this smaller value was attributed to the reaction yield, not due to the lack of functionalised initiated groups. Therefore, such an initiated PPE could be preferably useful for further grafting polymerisations.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( M_n )</th>
<th>( M_w )</th>
<th>( M_w / M_n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPVOH 2.2</td>
<td>23122</td>
<td>37390</td>
<td>1.62</td>
</tr>
<tr>
<td>PPVMI 3.1</td>
<td>15356</td>
<td>22656</td>
<td>1.47</td>
</tr>
<tr>
<td>PPEOH 2.3</td>
<td>21669</td>
<td>28705</td>
<td>1.32</td>
</tr>
<tr>
<td>PPEMI 3.2.1</td>
<td>10689</td>
<td>18582</td>
<td>1.74</td>
</tr>
<tr>
<td>Direct Synthesised</td>
<td>11964</td>
<td>22308</td>
<td>1.86</td>
</tr>
</tbody>
</table>

Table 3.2. Molecular weight characteristics of polymer backbones and macroinitiators.
3.7 Summary

The synthesis of PPV and PPE conjugated backbones as well as initiators has been achieved. The presented PPVs and PPEs contain lateral triglycol in each sequence which is aimed at improving the polymer backbone’s solubility and processability in organic solvents. Moreover, the polymer backbones also contain hydroxyl functional groups which enabled the esterification of the polymer backbones. The esterification reactions were successfully performed through a post polymerisation reaction on PPVOH 2.2, which unfortunately was not very successful for PPEOH 2.3. Accordingly, a direct PPEMI synthesis pathway was designed using monomers 2.10 and 2.11 to achieve the PPE macroinitiator. The successful synthesis of the macroinitiators was confirmed by 1H NMR as well as through FT-IR. The appearance of a sharp signal at around 1.91 nm for methyl groups and a broad signal at 4.76 nm, belonging to methylene protons adjacent to the ester groups, in 1H NMR, as well as the sharp absorbance at 1731cm⁻¹ in FT-IR, belonging to carbonyl groups, indicates the formation of the macroinitiators.

In studying the photophysical properties of the polymer backbones and macroinitiators indicate that although in PPVMI 3.1 the conjugation loss causes a spectral blue shift, in general the esterification reaction improved the polymers physical properties when looking at the quantum yield of the polymer backbones and its initiators. Such an improvement in photophysical properties of the polymers might be related to its increased solubility as well as changes conformation favouring less polymer backbone aggregation.

The molecular weight analysis of the polymer backbones indicate appropriate molecular weight compared to the reported PPV54 (where n was calculated for 63, 38 and 19) and PPE345 (where n was calculated for 52) derivatives.

Therefore, it may be generally concluded that the combination of the added functionalised groups and enhanced photophysical properties of the PPVMI 3.1 and PPEMI 3.2.2 will prove the usefulness of the mentioned macroinitiators in the following chapters for atom transfer radical polymerisation (ATRP) reactions in the synthesis of a wide range of non-ionic and ionic grafted molecular brushes for the purpose of different applications.
3.8 Experimental Procedures

$^1\text{H}$ NMR spectra were recorded on 400 MHz Bruker instrument using either deuterated chloroform or DMSO. The chemical shift data for each signal are given in units of (ppm) relative to tetramethylsilane (TMS) where four methyl groups of TMS were calibrated to 0. FT-IR spectra were collected with a Perkin Elmer Fourier transform-infrared (FT-IR) spectrometer, with a wavenumber range from 4000 to 400 cm$^{-1}$. UV-Visible absorption spectra were measured with a Pharmaspec UV-1700, Shimadzu UV-Visible spectrophotometer. Fluorescence spectra were measured with a Perkin Elmer LS 55 spectrophotometer with a 3-Q-10 mm rectangular quartz cell. Solution state quantum yields were determined relative to Coumarin 314 in DMF ($\phi = 0.63$). The molecular weights of polymers were determined by (GPC) running with DMF as the eluent versus polystyrene standards (PolySciences) using Viscotek TDAmx from Malvern Instruments equipped with a Plgel 5 mm Mixed-C (300 x 7.5 mm) column. Reagents were purified and dried using standard techniques. All air and water-sensitive synthetic manipulations were performed under nitrogen atmosphere. All other chemicals were of reagent grade and used as received.
Poly 3-(5-((E)-2,5-bis(2-(methoxymethoxy)ethoxy)-4-((E)-prop-1-en-1-yl)styryl)-4-(2-hydroxyethoxy)-2-((E)-prop-1-en-1-yl)phenoxy)propan-1-ol (PPVOH 2.2)

A two-neck flask was charged with monomers 2.5 (0.21 g, 0.44 mmol) and 2.4 (0.2 g, 0.44 mmol), palladium acetate (20 mg, 0.09 mmol) and tri-o-tolylphosphine (44 mg, 0.136 mmol) in a mixture of tri-n-butylamine (350 μL) and DMF (6 mL). The flask was then degassed and back-filled with nitrogen five times. The mixture was stirred at 90 ºC for 24 h. The resulting mixture was then cooled to r.t, diluted with CH₂Cl₂ (20 mL), filtered, the filtrate was then washed with water (2 × 20 mL). The polymer was then precipitated by the addition of diethyl ether (35 mL) and collected using centrifuge (40 rpm, 15 min). The precipitate was dried under vacuum at 40 ºC to afford the polymer PPVOH 2.2, to yield the title product as a dark red solid (0.31 g, 67 % yield).

δ_H (400 MHz; CDCl₃; Me₄Si): 2.13-2.14 (4H, m, CH₂), 3.33 (6H, s, CH₃), 3.45-4.32 (34H, m, CH₂), 7.17-7.20 (2H, m, ArH), 7.24-7.26 (2H, d, J = 14.0 Hz, CH=CH). IR: ν_max(neat)/cm⁻¹; 3398 (OH), 2924 (CH), 2869 (CH), 1197 (CH), 1054 (C-O), 951 (C=C, trans vinyl). GPC: M_w: 3.7×10⁴ gmol⁻¹, M_n: 3.7×10⁴ gmol⁻¹, M_w/M_n: 1.62. UV (2 mgmL⁻¹, DMF) λ_max,abs = 458 nm. PL (100 µgmL⁻¹, DMF) λ_max,em = 550 nm.
Poly 3,3'-(2-(2,5-bis(2-(methoxymethoxy)ethoxy)-4-(prop-1-yn-1-yl)phenyl)ethynyl)-5-(prop-1-yn-1-yl)-1,4-phenylene)bis(oxy))bis(propan-1-ol) (PPEOH 2.3)

A two-neck flask was charged with monomers 2.10 (100 mg, 0.22 mmol) and 2.5 (110 mg, 0.22 mmol), tetrakis(triphenylphosphine)palladium (0) (24 mg, 0.021 mmol) and copper iodide (21 mg, 0.11 mmol) in a mixture of THF (8 mL) and diisopropylamine (4 mL). The flask was then degassed and back-filled with nitrogen five times and left at 65 ºC for 24 h. The resulting mixture was then cooled to r.t, diluted with chloroform (25 mL), filtered, washed with NH₄OH (2 × 20 mL), water (3× 25 mL) and brine (30 mL) and dried (Na₂SO₄). The polymer was then precipitated by the addition of n-hexanes (35 mL) and collected via centrifuge (40 rpm, 15 min) to give the product which was and dried under vacuum at 40 ºC to yield PPEOH 2.3 product as a light brown solid (0.30 g, 62% yield).

δH (400 MHz; (CD₃)₂SO): 1.79-1.96 (4H, m, CH₂), 3.20 (6H, s, CH₃), 3.36-3.84 (32H, m, CH₂), 4.47-4.56 (2H, s, OH), 7.11-7.19 (2H, m, ArH), 7.59-7.67 (2H, m, ArH). IR: νmax(neat)/cm⁻¹; 3371 (OH), 2867 (C≡C), 1210 (CH), 1093 (CH), 1051 (C-O). GPC: Mw: 2.9×10⁴ gmol⁻¹, Mn: 2.2×10⁴ gmol⁻¹, Mw/Mn: 1.32. UV (2 mgmL⁻¹, DMF) λmax,abs = 435 nm. PL (100 µgmL⁻¹, DMF) λmax,em = 477 nm.
Poly (2-(\(E\))-2,5-bis(2-(methoxymethoxy)ethoxy)-4-(\(E\))-prop-1-en-1-yl)styryl)-5-(\(E\))-prop-1-en-1-yl)-1,4-phenylene)bis(oxy))bis(propane-3,1-diyl)bis(2-bromo-2-methylpropanoate) (PPVMI 3.1)

A two neck flask was loaded with hydroxyl functionalised polymer PPVOH 2.2 (40 mg, 0.60 mmol), triethylamine (1 mL, 7.17 mmol) and 4-dimethylaminopyridine (DMAP) (48 mg, 336 mmol) in CH₂Cl₂ (4 mL). The flask was then degassed and back filled with nitrogen three times. The mixture was cooled to 0 °C and 2-bromoisobutyryl bromide (BIBB) (97 mg, 0.4 mmol) was added dropwise. The mixture was stirred at r.t for 24 h and the resulting mixture was then diluted with CH₂Cl₂ (25 mL), filtered, washed with NH₄OH (20 mL) and water (3 × 20 mL). The polymer was then precipitated by the addition of hexanes (35 mL), centrifuged (40 rpm, 15 min) to collect the precipitate and dried under vacuum at 40 ºC to yield the PPVMI 3.1 as a light red solid (100 mg, 55 % yield).

\[ \delta_H (400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si}): 1.92 \text{ (12H, s, CBr(CH}_3\text{)}_2\text{)}, 2.67-2.78 \text{ (2H, m, CH}_2\text{)}, 3.35 \text{ (6H, s, CH}_3\text{)}, 3.50-3.78 \text{ (28H, m, CH}_2\text{)}, 3.89-3.99 \text{ (4H, m, CH}_2\text{)}, 4.16-4.33 \text{ (4H, m, CH}_2\text{)}, 4.35-4.55 \text{ (2H, m, OCH}_2\text{)}, 7.10-7.16 \text{ (2H, s, CH=CH)}, 7.42-7.46 \text{ (4H, s, Ar-H)}. \]

\[ \text{IR: } \nu_{\text{max(neat)}}/\text{cm}^{-1}; 2925 \text{ (CH), 2873 (CH), 1198 (CH), 1731 (C=O), 1054 (C-O), 964 (C=C, \text{ trans vinyl})}. \]

\[ \text{GPC: } M_w: \text{g} \text{ mol}^{-1} 2.3 \times 10^4 \text{ g} \text{ mol}^{-1}, M_n: 1.5 \times 10^4 \text{ g} \text{ mol}^{-1}, M_w/M_n: 1.47. \]

\[ \text{UV (2 mg mL}^{-1}, \text{ DMF) } \lambda_{\text{max,abs}} = 451 \text{ nm. PL (100 } \mu\text{g mL}^{-1}, \text{ DMF) } \lambda_{\text{max,em}} = 545 \text{ nm.} \]
Poly \((2-(2,5\text{-}(2\text{-methoxyethoxy})\text{ethoxy})\text{-}4\text{-}(\text{prop-1-yn-1-yl})\text{phenyl})\text{ethynyl})\text{-}5\text{-}(\text{prop-1-yn-1-yl})\text{-}1,4\text{-}\text{phenylene})\text{bis(oxy))bis(propane-3,1-diyl) bis(2-bromo-2-methylpropanoate)}\) (PPEMI 3.2.1)

A two-necked flask was loaded with hydroxyl functionalised polymer PPEOH 2.3 (40 mg, 0.64 mmol), triethylamine (1 mL) and DMAP (48 mg, 336 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (4 mL). The flask was then degassed and back filled over nitrogen three times, left in an ice bath and BIBB (97 mg, 0.4 mmol) as an initiator was added dropwise. The reaction mixture was left at r.t for 24 h and the resulting mixture was then diluted with CH\textsubscript{2}Cl\textsubscript{2} (20 mL), filtered and washed with NH\textsubscript{4}OH (2 \times 15 mL), and water (3 \times 15 mL). The mixture was then precipitated by the addition of hexanes (3 \times 35 mL), centrifuged (40 rpm, 15 min) to collect the precipitate and dried over the vacuum at 40 °C to afford the polymer PPEMI 3.2.1 as a dark brown solid.

\[\delta^H (400 \text{ MHz}; \text{(CD}3)\text{SO}): 1.90 (10H, s, C\text{Br} (\text{CH}_3)_2), 3.21 (6H, s, CH\text{}_3), 3.45-3.56 (11H, m, CH\text{}_2), 3.61-3.71 (6H, m, CH\text{}_2), 3.76-3.86 (4H, m, CH\text{}_2), 4.11-4.29 (8H, m, CH\text{}_2), 4.35-4.46 (4H, m, CH\text{}_2), 7.13-7.26 (4H, m, ArH). GPC: M\text{w}: 1.8 \times 10^4 \text{ g mol}^{-1}, M\text{n}: 1.1 \times 10^4 \text{ g mol}^{-1}, M\text{w/Mn}: 1.74. UV (2 mg mL\textsuperscript{-1}, DMF) \lambda_{\text{max,abs}} = 428 \text{ nm. PL (100 \mu g mL}^{-1}, \text{DMF) } \lambda_{\text{max,em}} = 471 \text{ nm.}\]
Poly \((2-(2,5\text{-bis(2-(methoxymethoxy)ethoxy})-4-\text{(prop-1-yn-1-yl)phenyl}ethynyl)-5-\text{(prop-1-yn-1-yl)-1,4-phenylene)bis(oxy)})\text{bis(propane-3,1-diyl) bis(2-bromo-2-methylpropanoate)}\) (PPEMI 3.2.2)

A two neck flask was loaded with monomers \(2.10\) (110 mg, 0.142 mmol) and \(2.11\) (172 mg, 0.627 mmol), tetrakis(triphenylphosphine)palladium (0) (24 mg, 0.021 mmol) and copper iodide (20 mg, 0.11 mmol) in a mixture of diisopropyl amine (5 mL), toluene (2 mL) and tetrahydrofuran (8 mL). The flask was then degased and back-filled over the nitrogen for the five consecutive times and the mixture was left for 48 h over nitrogen at 67 ºC. The resulting mixture then became cooled-down into the r.t and filter within filter paper with CH₂Cl₂. After evaporating the excess amount of CH₂Cl₂ the mixture was precipitated into the \(n\)-hexane (3 × 20 mL), collected over the centrifuge and dried over vacuum to afford the polymer PPEMI 3.2.2 as a dark brown solid (0.2 g, 75% yield).

\[\delta_H (400 \text{ MHz}; (CD_3)_2SO): 1.89 (12H, s, CBr(CH_3)_2), 3.20 (6H, s, CH_3), 3.43-3.57 (12H, m, CH_2), 3.60-3.70 (4H, m, CH_2), 3.75-3.89 (4H, m, CH_2), 4.13-4.29 (6H, m, CH_2), 4.33-4.48 (4H, m, CH_2), 7.12-7.25 (4H, m, ArH). \]

\[\text{IR: } \nu_{\text{max(neat)}}/\text{cm}^{-1}; 2870 (\text{C}≡\text{C}), 1729 (\text{C}=\text{O}), 1160 (\text{C}-\text{O}), 849 (\text{phenyl ring}). \]

\[\text{GPC: } M_w: 2.2\times10^4 \text{ gmol}^{-1}, M_n: 1.2\times10^4 \text{ gmol}^{-1}, M_w/M_n: 1.8. \]

\[\text{UV (2 mgmL}^{-1}, \text{DMF) } \lambda_{\text{max,abs}} = 433 \text{ nm. PL (100}\mu \text{ mgmL}^{-1}, \text{ DMF) } \lambda_{\text{max,abs}} = 473 \text{ nm.} \]
Chapter 4: Synthesis of Neutral Grafted Poly(\textit{para}-phenylene vinylene) and Poly(\textit{para}-phenylene ethynylene)
4.1 Introduction

Due to the photoluminescent properties of conjugated polymers (CPs), they find extensive range of applications in optical and optoelectrical devices. As such work has gone into investigating maintenance and optimisation of optical properties in CPs.

In this chapter, the modification via grafting of PPVMI 3.1 and PPEMI 3.2.2 with the aim of achieving photophysical properties comparable or greater than the macroinitiators or core backbones themselves. The α-bromo ester functionality of macroinitiators 3.1 and 3.2.2 would hopefully allow polymer modifications using atom transfer radical polymerisation ATRP.

As described in the previous chapter, both PPVOH 2.2 and PPVMI 3.1 as well as PPEOH 2.3 PPEMI (3.2.1 and 3.2.2) systems showed photoluminescent properties which suffered from aggregation in solution, resulting in small quantum yields. Reducing this deficiency while improving the fluorescent intensity in both solution and solid state was desired. It is known that grafting of brush-like structures can result in a polymer where the fluorescent backbones are separated by brush molecules, and results in an amplified photoluminescent efficiency. As well as improving the fluorescence of the new grafted polymers, the processability of the polymers in various solvents was also of importance. As such, the choice of monomer to be used in the grafting was important as its physical properties should dominate those of the core CP.

The overall approach was to functionalise the CPs using ATRP, such that the grafted polymers have a range of applications and that the brush polymers still exhibit the photoactive properties of the CP. Enhancement of processability in CPs using non-ionic grafted brushes has been studied using polymethacrylate, polycrylate and polystyrene which determined that the dispersion of the overall polymer matrix reduces π-stacking interactions in the CP which results in improvement of photoluminescent properties. It was also observed that grafting polymerisation using ATRP is a synthetic procedure with exceptional control over the molecular weight and dispersity, compared to other grafting methods.

It was therefore decided to use butyl acrylate as a monomer in the ATRP grafting of PPVMI 3.1 and PPEMI 3.2.2. The aim was to determine the effect of adding polybutyl acrylate brushes on the prepared CPs. It was desired for the new graft copolymers to have the physical properties
(such as elasticity and rubbery like shape) of polybutyl acrylate whilst still maintaining, or in fact improving, the photophysical properties of the CP backbone.

4.2 Preparation of PPV-g-nBA and PPE-g-nBA using ATRP

ATRP has been shown to be an effective method for grafting various polymers from macroinitiators in a number of different morphologies \(^{370}\) brushes, \(^{201,355}\) block copolymers, \(^{371–374}\) from surfaces, \(^{375–377}\) crosslinks \(^{378,379}\) etc., conventional ATRP was therefore used for the grafting polymerisation from both PPVMI 3.1 and PPEMI 3.2.2 (Fig 4.1).

In the first attempt at grafting, conventional ATRP was used where both butyl acrylate and the macroinitiators 3.1 or 3.2.2 were dissolved in DMF and anisole was added, as an internal standard, for the kinetic study measurements.

Cu(I)Cl was added as a catalyst for the reaction and the reaction mixture was de-gassed to remove oxygen using five consecutive freeze-thaw cycles. Finally PMDETA ligand was added to the reaction. For these reactions 500 equivalents of butyl acrylate was used (Scheme 4.1 and 4.2).
**Fig 4.1.** Molecular structure of PPV-g-PnBA 4.1 and PPE-g-PnBA 4.2.

**Scheme 4.1.** Synthesis of PPV-g-PnBA 4.1 using conventional ATRP.
Unfortunately grafting polymerisation using conventional ATRP for both PPVMI 3.1 and PPEMI 3.2.2 provided PPV-g-PnBA 4.1 and PPE-g-PnBA 4.2 in low yields of around 10%. In the $^1$H NMR of the precipitated products residual butyl acrylate was observed with the vinyl protons of the monomer observed around 6.4 ppm. These signals were obvious compared to the desired signals from the newly formed polyacrylate at 0.9 and 1.4 ppm. The kinetic study evaluations indicated a low monomer conversion rate for both PPVMI 3.1 and PPEMI 3.2.2 macroinitiators, at 6.57% and 6.67% respectively (Graph 4.1). The kinetic measurements were recorded by removing a small sample of the reaction mixture at time points (0, 15, 30, 60, 120, 240, 360 and 480 min) and analysing the conversion via NMR.
ATRP reactions start with radical initiation. This relatively fast activation process is also accelerated by copper catalyst oxidation. However exposure to oxygen, may result in radical accumulation as well as the formation of the dormant species. Therefore if oxygen is present then the deactivation process may reach a point where the concentration of the deactivated species (higher oxidative ligand-catalyst) becomes equal to the concentration of the activated one and the reaction rate can dramatically slow and finally stop. The propagation rate becomes very small and consequently results in low molecular weight grafted polymers.\textsuperscript{380} Despite attempting to ensure all oxygen was removed from the reaction it was considered that its presence could have been the reason for the low yield of the grafted polymers.

Considering the drawback of conventional ATRP with regard to its sensitivity to oxygen and complex reaction conditions, Activators ReGenerated by Electron Transfer ARGET ATRP was chosen as an alternative. The decision to use ARGET ATRP would not only keep the reaction conditions more straightforward but hopefully improve the polymerisation yield.\textsuperscript{279} This idea arose from the fact that in ARGET ATRP, the Cu(II) complex is directly inserted to the reaction, which is not so sensitive to oxygen, and the reaction is started with Cu(I) while an added reducing agent continuously regenerates it.\textsuperscript{277–279,285}

For the synthesis of both PPV-g-nBA \textbf{4.1} and PPE-g-nBA \textbf{4.2} via ARGET ATRP, the macroinitiators were dissolved in butylacrylate and a minimum amount of DMF. Anisole, as an internal standard, was again added for the kinetic study. Whilst in conventional ATRP, the catalyst system is extremely sensitive to oxygen and thus the solutions were rigorously degassed to remove oxygen in ARGET ATRP this limitation is overcome by continuously regenerating the deactivated oxidised catalyst using the reducing agent tin (II).
ethylhexanoate.\textsuperscript{277,279} Although the reaction is stirred under nitrogen for ARGET ATRP procedures, it is unnecessary to degas the solution. In the case of ligand, both PMDETA and TPMA were used and it was determined that TPMA was the better ligand choice for grafting polymerisation via ARGET ATRP for both PPVMI \textbf{3.1} and PPEMI \textbf{3.2}.\textsuperscript{267,286}

Examining the kinetic results it was found that the initial kinetic relationship of monomer consumption was much higher with a conversion rate of 63.5 \% in PPV-g-nBA \textbf{4.1}, and 65.6 \% in PPE-g-nBA \textbf{4.2} both higher when compared to the conventional ATRP (\textbf{Graph 4.2}).

\textbf{Graph 4.2}. ARGET ATRP kinetick study of PPV-g-nBA \textbf{4.1} and PPE-g-nBA \textbf{4.2}.

The kinetic plots reveal that conversion is linear up to around two hour after which a decrease is seen. This is presumably due to the large brush-like structure forming which could reduce rates of reaction.

Characterising both PPV-g-PnBA \textbf{4.1} and PPE-g-PnBA \textbf{4.2} using \textsuperscript{1}H NMR indicated the formation of a poly acrylate in the grafted polymers by the absence of the vinyl signals and appearance of new multiples at about 1.8 and 2.3 ppm. Also the formation of the grafted polymers was tracked at specific times by quenching the reaction and characterising through \textsuperscript{1}H NMR. As is shown in \textbf{Fig 4.2} the \textsuperscript{1}H NMR of the grafted polymer shows only signals from the polyacrylate grafts and the PPV backbone is not seen.
Fig. 4.2. $^1$H NMR spectra of PPVOH 2.1 (A), nBA (B) and PPV-g-PnBA 4.1 (C).
Both of the grafted polymers 4.1 and 4.2 adopted physical properties (such as fluorescent properties) of polybutyl acrylate and showed a rubbery characteristic rather than the solid properties of either PPVMI 3.1 or PPEMI 3.2.2, (Fig 4.2).

Such physical properties arise from the 63.5% and 65.6% resulted yields of the synthesised PPV-g-PnBA 4.1 and PPE-g-PnBA 4.2. Considering the kinetic study results and the conversion rates they are expected to have 495 and 430 number of acrylate units in the grafted molecular brushes of 4.1 and 4.2, respectively.

![Image of PPE-g-PnBa 4.2 (a) and PPEMI 3.2.2 (b) in normal light (A) and under UV light (B).](image)

**4.3 Molecular Weight Characterisations**

GPC was used to assess the molecular weight of the grafted PPV 4.1 and PPE 4.2. Using polystyrene standards and THF as an eluent, the number-average molecular weight (Mn), average molecular weight (Mw) and the typical dispersity of the grafted PPV and PPE were analysed.

GPC analyses of samples of PPV-g-PnBA 4.1 and PPE-g-PnBA 4.2 after 24 hours of grafting indicate the average molecular weight of the grafted polymers to be 90000 g mol⁻¹ and 74000 g mol⁻¹, respectively. GPC experimental molecular weight results also suggest the approximate growing of 702 and 500 nBA molecular brushes after 24 h onto PPVMI 3.1 and PPEMI 3.2.2 respectively, which is actually higher than what it was actually used for the grafting
polymerisation. Also, the typical polydispersity was measured to be 1.4 in PPV-g-PnBA 4.1 and 1.3 in PPE-g-PnBA 4.2.

The experimental molecular weight results of the grafted PPV 4.1 and PPE 4.2 with specific grafting polymerisation times, were compared to the theoretical results based on the kinetic study plots which the results are summarized in Table 4.1.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Theoretical $M_w$</th>
<th>$M_w$</th>
<th>$M_n$</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPVM 3.1</td>
<td>-</td>
<td>22656</td>
<td>15356</td>
<td>1.47</td>
</tr>
<tr>
<td>PPEMI 3.2.2</td>
<td>-</td>
<td>22308</td>
<td>11964</td>
<td>1.86</td>
</tr>
<tr>
<td>PPV-g-PnBA 4.1 (4h)</td>
<td>32042</td>
<td>28705</td>
<td>21669</td>
<td>1.30</td>
</tr>
<tr>
<td>PPV-g-PnBA 4.1 (8h)</td>
<td>40373</td>
<td>39528</td>
<td>19472</td>
<td>2.03</td>
</tr>
<tr>
<td>PPV-g-PnBA 4.1 (24h)</td>
<td>64085</td>
<td>89927</td>
<td>63551</td>
<td>1.41</td>
</tr>
<tr>
<td>PPE-g-PnBA 4.2 (4h)</td>
<td>30760</td>
<td>29112</td>
<td>22598</td>
<td>1.28</td>
</tr>
<tr>
<td>PPE-g-PnBA 4.2 (8h)</td>
<td>42296</td>
<td>71964</td>
<td>41355</td>
<td>1.74</td>
</tr>
<tr>
<td>PPE-g-PnBA 4.2 (24h)</td>
<td>64085</td>
<td>74337</td>
<td>55089</td>
<td>1.35</td>
</tr>
</tbody>
</table>

Table 4.1. GPC results of the fractioned PPV-g-PnBA 4.1 and PPE-g-PnBA 4.2 comparing to its theoretical ones.

Looking at the $M_w$ results for both PPV-g-PnBA 4.1 and PPE-g-PnBA 4.2, there are time points which are consistent with calculated theoretical values, which are determined using NMR. However, there also inconsistency at other time points especially at the larger density (after 24 h). This result may be due to the relative determination of molecular weights with polystyrene standards, which does not effectively represent the actual molecular weight. GPC results are based on the size of overall polymer relative to the standards used. In this case the grafted polymers may not adopt similar size and shape to the polystyrene standards. Das et al have reported similar varieties in GPC versus NMR calculated $M_w$ when working with grafted polythiophene.\textsuperscript{381}

However, analysing the GPC results with regard to polymer dispersity in both the grafted PPV 4.1 and PPE 4.2, it can be concluded that grafting polymerisation has followed a roughly linear relationship.

For the polydispersity results; although the best results, in both grafted PPV 4.1 and PPE 4.2, are observed in the lower molecular weight polymers (after 4 h), the highest molecular weight polymers (after 24 h) still represent a narrow polydispersity.
4.4 Photophysical characteristics of the Grafted Polymers

With samples of PPV-g-nBA 4.1 and PPE-g-nBA 4.2 prepared we wished to examine the polymer’s photophysical properties, to determine the effect of adding the grafted brushes.

4.4.1 Photophysical Properties of the PPV-g-nBA

To investigate the photoluminecent efficiency resulting from the core PPV backbone, the absorption of PPV-g-nBA 4.1 was investigated using UV-Vis measurements. Also, to evaluate the effect of the grafting polymerisation on the conjugated backbone, the maximum absorption of the grafted PPV 4.1 was compared to ungrafted polymers PPVOH 2.2 and PPVMi 3.1 (Fig. 4.3).

![UV-Vis spectra of PPV backbones (2.2 and 3.1) and PPV-g-nBA 4.1.](image)

As it is shown in Fig 4.3 the maximum absorption of the PPV-g-PnBA 4.1 was at 378 nm. Compared to PPVMi 3.1, this is a spectral blue shift of around 73 nm. It is proposed that this spectral blue shift is related to a decrease in conjugation in the PPV backbone. This is due to the breaking of vinyl double bonds presumably due to free radicals during ATRP. Further evidence for the loss of conjugation and breaking up of the PPV backbone is the creation of paraylene segments, which could be observed for PPV-g-PnBA 4.1, at 300 nm in the UV spectra.382
The loss of conjugation in the PPV backbone within the grafted PPV was also noted by calculating the optical band-gap using the Equation 4.1, which was described in Chapter 3.\textsuperscript{346–348}

\[
E_{(joules)} = \frac{h \cdot c}{\lambda_m}
\]

Equation 4.1. Optical band gap measurements.

Band gap measurements within the above mentioned equation indicate that the optical band gap of PPV-g-P\textsubscript{n}BA 4.1 was approximately 2.44 eV. Comparing the optical band gap of PPV-g-P\textsubscript{n}BA with PPVMI 3.1, shows a 140 meV increase in optical band gap energy which also confirms the shortening of the conjugation after grafting polymerisation.

The maximum emission wavelength and the maximum fluorescent intensity of the grafted PPV 4.1 was measured and compared to PPVMI 3.1, presented in Fig 4.4. It is apparent that grafted PPV 4.1 shows a significant spectral shift compared to the PPV core.

As can be seen in Fig 4.4, the $\lambda_{\text{max em}}$ of PPV-g-P\textsubscript{n}BA 4.1 after a 24 hour reaction time was at 502 nm. Comparing the $\lambda_{\text{max em}}$ of the PPV-g-P\textsubscript{n}BA 4.1 with the PPVMI, a spectral blue shift of around 43 nm is apparent, which can be attributed to the loss of conjugation after the grafting polymerisation. Further, comparing the fluorescent intensity of the PPV grafted polymer with the PPVMI 2.2 shows an increasing for almost 1.3 times after 24 h grafting. This increase can be attributed to extension of the CP backbone and less interchain interactions after grafting.
Also, in evaluating the effect of the grafted brush length on the photoluminescent properties of PPV-g-PnBA 4.1, the fluorescent intensity of the grafted polymers was measured on samples where the grafting polymerisation was run for 4, 8 and 24 hours (Fig 4.5).

When comparing the fluorescent intensity of the PPV-g-PnBA 4.1 after 4 h, 8 h and 24 h grafting, which the fluorescent intensity is seen to increase with increased grafting time, presumably due to longer molecular brushes. However, when the $\lambda_{\text{max}}$ values of the grafted
PPVs at 4, 8 and 24 h are compared it is seen that the spectral blue shift is reduced while increasing the reaction time.

To study the effect of the brush growth on the photoluminescent characteristics of PPV-g-PnBA 4.1, quantum yield measurements were taken for all the above mentioned grafted PPVs which were compared to PPVMI 3.1 (results are summarised in Table 4.2).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\lambda_{\text{max em}}$ (nm)</th>
<th>$\phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPVMI 3.1</td>
<td>545</td>
<td>0.59</td>
</tr>
<tr>
<td>PPV-g-PnBA 4.1 (4h)</td>
<td>489</td>
<td>0.30</td>
</tr>
<tr>
<td>PPV-g-PnBA 4.1 (8h)</td>
<td>497</td>
<td>0.71</td>
</tr>
<tr>
<td>PPV-g-PnBA 4.1 (24h)</td>
<td>501</td>
<td>0.86</td>
</tr>
</tbody>
</table>

Table 4.2: Photoluminescent characteristics of the grafted PPVs 4.1 compared to PPVMI 3.1.

Looking at the results, it can be concluded that the lowest spectral blue shift is observed when the grafting polymerisation is after 24 hours, which also had the highest quantum yield. Therefore, it can be concluded that the increased brush growth results in better fluorescent intensity of the grafted polymer. The quantum yield improvement is most obviously apparent when comparing the grafted polymer quantum yields for the 8 and 24 hour grafting polymerisation reaches, which represents a jump of 1.2 in the quantum yield. Such an increase in quantum yield of the grafted PPVs, while increasing the brush density, may be attributed to the prevention of interchain interactions between PPV backbones.345,357,360,361 The introduction of larger grafted brushes may reduce interchain interactions which are responsible for the self-quenching of CP through non-radiative decay of excitons.383

The non-radiative decay of excitons is responsible for lower quantum yields in solution and the lack of fluorescence in the solid state.383 It is clear that the prevention of the interchain interactions through the introduction of polymer brush side chains results in a higher quantum yield in the solution phase.

To further investigate interchain interactions, the solid state fluorescence was measured using PPVOH 2.2, PPVMI 3.1 and PPV-g-PnBA 4.1. The solid state quantum yield results, compared to the solution quantum yields are shown in Table 4.3.
Reduction of interchain interactions results in the solid state fluorescence of PPV-g-nBA 4.1, whereas this fluorescent property is not observed in both of the ungrafted polymers PPVOH 2.2 and PPVMI 3.1.\textsuperscript{345,357,360,383} It is therefore clear that addition of brushes to the PPV core has allowed fluorescence in the solid state even if the values are lower than in solution state.

### 4.4.2 Photophysical Properties of the PPE-g-nBA

After completing the study on PPV-g-PnBA 4.1, PPE-g-PnBA 4.2 was then investigated. To study the photoluminescent efficiency of the PPE backbone, the UV-Vis spectra for PPE-g-nBA was recorded. Also, to evaluate the effect of the grafting on the conjugated backbone the maximum absorption of the grafted PPE 4.2 was compared to PPEOH 2.3 and PPEMI 3.2.2 (Fig 4.6).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\Phi_{\text{solution}}$ (%)</th>
<th>$\Phi_{\text{solid state}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPVOH 2.2</td>
<td>53</td>
<td>0</td>
</tr>
<tr>
<td>PPVMI 3.1</td>
<td>59</td>
<td>0</td>
</tr>
<tr>
<td>PPV-g-nBA 4.1</td>
<td>86</td>
<td>15 ± 2</td>
</tr>
</tbody>
</table>

Table 4.3. Solid state quantum yield results of PPVOH 2.1, PPVMI 3.1 and PPV-g-PnBA 4.1 comparing to the solution quantum yields results.
As is shown in **Fig 4.6**, the maximum absorption of PPE-g-PnBA 4.2 was observed at 422 nm. Comparing the grafted PPE 4.2 absorption with the PPEMI 3.2.2, the spectral blue shift of approximately 11 nm was observed. This spectral blue shift is again most likely related to the loss of conjugation band due to breaking of the alkyne groups during radical polymerisation, however the shift is considerably less than the 73 nm see in PPV-g-PnBA 4.1.

To evaluate the effect of grafting on the conjugation, the optical band gap of PPE-g-PnBA 4.2 was measured, and compared to PPEMI 3.2.2. An optical band gap measurement, using the previously mentioned equation, indicates the optical band gap of PPE-g-nBA to be 2.58 eV. Comparing the optical band gap of PPE-g-PnBA 4.2 with PPEMI 3.2.2 shows a 10 meV increase in the optical band gap energy which is also confirms some loss of conjugation band after grafting polymerisation.

Comparing the increased optical band gap energy after grafting polymerisation in both PPV-g-PnBA 4.1 and PPE-g-PnBA 4.2 shows less conjugation loss in in the PPE, which is most likely attributed to the more resistant PPE backbone in radical polymerisation compared to PPVs.

To further examine the photoluminescence properties, the fluorescence of PPE-g-PnBA 4.2 was recorded and compared to non-grafted PPEs (**Fig 4.7**).

As is presented in **Fig 4.7**, the maximum emission wave length of PPE-g-PnBA 4.2 is 473 nm. While comparing the $\lambda_{\text{max em}}$ of the grafted PPE 4.2 with its initiated backbone 3.2.2, no particular spectral shift was observed. Also no significant fluorescent intensity changes compared to the PPEMI 3.2.2 are observed.
Further, to observe the effect of grafting length on the spectral changes and on the fluorescent intensity of the PPE grafted polymer, the fluorescent spectra of the PPE-g-PnBA 4.2 were measured on samples that had underwent grafting polymerisation for 8 and 24 hours (Fig 4.8).

It was observed that the $\lambda_{\text{max em}}$ of the PPE-g-PnBA 4.2 with 24 hours of grafting polymerisation showed the least spectral blue shift of the grafted PPE 4.2. Although fluorescent intensity of the PPE-g-PnBA 4.2 shows no particular changes compared to PPEMI 3.2.2, increasing fluorescent intensity while increasing grafting time and grafting length is apparent. This increase in fluorescence is similar to what it was observed in PPV-g-PnBAs, which is presumably due to the more interchain interaction preventions in longer grafted molecular brushes. It is possible that even larger grafts could further increase fluorescence intensity above that of PPEMI 3.2.2. Quantum yield calculations were performed on all the grafted PPEs and compared to the PPEMI 3.2.2 (results are summarised in Table 4.4).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\lambda_{\text{max em}}$ (nm)</th>
<th>$\phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPEMI 3.2.2</td>
<td>473</td>
<td>0.87</td>
</tr>
<tr>
<td>PPE-g-nBA 4.2 (8h)</td>
<td>468</td>
<td>0.71</td>
</tr>
<tr>
<td>PPE-g-nBA 4.2 (24h)</td>
<td>473</td>
<td>0.90</td>
</tr>
</tbody>
</table>

Table 4.4. Photoluminescent Characteristics of the grafted PPEs 4.2 Compared to PPEMI 3.2.2.
From these results, it is concluded that the lowest spectral blue shift was observed when doing the grafting polymerisation for 24 hours, in which the grafted PPE 4.2 possessed the highest quantum yield. Therefore, as what was observed with the grafted PPV 4.1 polymers, it might be concluded that a greater length of brush on the polymer backbone results in better fluorescent intensity of the grafted polymer. Therefore it might be concluded that, as similarly seen with the grafted PPVs, increase in quantum yield in the PPEs is driven by reduction in interchain interactions as the brush length and density increases.345,357,360,361

The solid state fluorescence of PPE-g-PnBA 4.2 was measured and the solid state quantum yield results compared with both PPEOH 2.3 PPEMI 3.2.2 in both solution and solid state and the quantum yields are shown in Table 4.5.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Φ_{solution} (%)</th>
<th>Φ_{solid state} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPEOH 2.3</td>
<td>32</td>
<td>0</td>
</tr>
<tr>
<td>PPEMI 3.2.2</td>
<td>87</td>
<td>0</td>
</tr>
<tr>
<td>PPE-g-nBA 4.2</td>
<td>90</td>
<td>21 ± 2</td>
</tr>
</tbody>
</table>

Table 4.5. Solid state quantum yield results of PPEOH 2.3, PPEMI 3.2.2 and PPE-g-PnBA 4.2 comparing to the solution results.

Similar to what was observed with PPV-g-PnBA 4.1, PPE-g-PnBA 4.2 also exhibited solid state fluorescence whilst ungrafted polymers did not. Again this shows grafting reduces interchain interactions and allows solid state fluorescence.383

It is assumed that the increased fluorescent activity of both grafted polymers 4.1 and 4.2 results from separation of the CPs due to the addition of grafts. The grafts reduce interchain interactions, reducing non-radiative relaxation (Fig 4.9).
4.5 Summary

The synthesis of PPV-g-PnBA \textbf{4.1} and PPE-g-PnBA \textbf{4.2} using ARGET ATRP has been achieved and resulted in good yields and $M_w$ for both grafted PPV and PPE. Using ARGET ATRP allowed good controllability of the grafting as shown in kinetic results on both polymers.

It was hoped that the grafted polymers would have improved photoluminescent properties compared to macrorinitiators by reduced interchain interactions. The UV-Vis results of both the grafted PPV and PPE show spectral blue shifting was prominent when compared to the macrorinitiators. This spectral blue shift was significantly larger for PPV when compared to PPE. The difference in $\lambda_{\text{max abs}}$ suggests that the PPE CP is more resistance towards radical grafting, which may be expected when taking into account the PPE’s greater rigidity comparing to PPV. The optical band gap energy was also almost 14 times less in the more rigid PPE-g-PnBA \textbf{4.2} compared to PPV-g-PnBA \textbf{4.1}.

The impact of grafting on the photoluminescent properties of the PPV and PPE backbone was also investigated through fluorescence spectroscopy. A spectral blue shift was also observed similar to that observed for the UV-Vis. The spectral blue shift was also more apparent in the grafted PPV \textbf{4.1} compared to the grafted PPE \textbf{4.2}. The effect of the molecular brush growth was studied by analysing the results of grafting polymerisation after 4, 8 and 24 hours. With increasing time and brush density, an increase in the fluorescent intensity and quantum yield of the both PPV and PPE grafted polymers (\textbf{4.1} and \textbf{4.2}) was observed. The blue shift in the UV-Vis and the fluorescence spectra, as well as the optical band gap energy increase is most likely resulting from loss of conjugation which may have occurred during the radical grafting.
polymerisation. The increasing quantum yield over time is directly associated to the reduction in interchain interactions, which are responsible for the self-quenching.

The polydispersity of the grafted polymers and the GPC data, show a linear relationship result for grafting polymerisation, which is also in accordance with the $^1$H NMR kinetic study of both the PPV and PPE grafted polymers.

It may be concluded that a suitable ARGET ATRP method was developed for the successful synthesis of PPV-g-P$\text{nBA}$ 4.1 and PPE-g-P$n$BA 4.2 with the good photoluminescent properties. The results also confirm the success of the proposed synthetic pathway, which resulted in grafted polymers with low polydispersity. The ARGET ATRP method would hopefully allow for the addition of the other brushes with different physical properties to that of butyl acrylate.

### 4.6 Experimental Procedures

$^1$H NMR spectra for PPV-g-$$n$BA 4.1 and PPE-g-$$n$BA 4.2 were recorded on a 400 MHz Bruker instrument using deuterated chloroform as reference or internal deuterium lock. The chemical shift data for each signal are given in units of (ppm) relative to tetramethylsilane (TMS) where the four methyl groups of TMS were calibrated to zero. UV-visible absorption spectra were measured with a Pharmaspec UV-1700, Shimadzu UV-Visible spectrophotometer. Fluorescence spectra were measured with a Perkin Elmer LS 55 spectrophotometer with a 3-Q-10 mm rectangular quartz cell. Solution state quantum yields were determined using either PPV or PPE grafted polymer samples in toluene relative to Anthracene 314 in ethanol ($\varphi = 0.27$). Solid state samples were prepared by drop casting the relevant polymer solution (5 mg mL$^{-1}$ in toluene) onto a quartz slide and solvent annealed with toluene. The quantum yield was then determined using an integrating sphere, exciting at 360 nm. The molecular weights of the grafted polymers were determined by Gel Permeation Chromatography (GPC) using THF as the eluent versus polystyrene standards (PolySciences) using Viscotek TDAmx from Malvern Instruments equipped with a Plgel 5 mm Mixed-C (300 x 7.5 mm) column. Chemicals were purified and dried by standard technique. All air and water-sensitive synthetic manipulations were performed under nitrogen atmosphere using standard techniques. All other chemicals were of reagent grade and used as received.
To evaluate the controllability of either the conventional ATRP or ARGET ATRP, 100 μL samples were taken from the reaction at specific times. The monomer consumption rate was then calculated using 1H NMR, preparing the samples in CDCl3. The calculation was performed through comparing the reduction of the triplet at 4.04 nm, resulting from the monomers, being compared with the integrated anisole peak at 3.81 nm. The relationship of the monomer conversion over time was used to determine the controllability of the grafting polymerisation reactions.

**Synthesis of PPV-g-nBA 4.1 via conventional ATRP**

A two neckflask was loaded with a solution of PPV-MI 3.1 (270 mg, 0.02 mmol), anisole (250 μL), N,N,N′,N′,N′′-pentamethyldiethylenetriamine (PMDETA) (600 μL, 0.28 mmol) and n-butyl acrylate (nBA) (1.76 mL, 12.3 mmol) in DMF (4 mL) under an atmosphere of nitrogen at r.t. The mixture was then degassed using freeze-thaw and back filled with nitrogen five times. To the frozen solution, under nitrogen, was added Cu(I)Br (30 mg, 21 mmol). The reaction was then stirred at 80 ºC for 8h. The polymerisation was quenched through the exposure of the mixture to air and quickly cooled with liquid nitrogen. The mixture was then diluted with CH2Cl2 (30 mL), filtered, washed with water (3 × 20 mL), precipitation by the
addition of methanol (3 × 35 mL), centrifuged (40 rpm, 15 min) to collect the precipitate, which was dried under vacuum to give PPV-g-n-BA 4.1 as a bright yellow viscous oil (0.58 g, 10%).

δ_H (400 MHz; CDCl₃; Me₄Si): 0.91-0.95 (3H, m, CH₃), 1.34-1.39 (2H, m, CH₂), 1.57-1.60 (2H, m, CH₂), 1.76 (1H, m, CH), 1.9-2.27 (2H, m, CH₂), 4.01-4.04 (2H, m, CH₂). **GPC**: M_w: 2.9×10⁵ gmol⁻¹, M_n: 1.8×10⁵ gmol⁻¹, M_w/M_n: 1.5.

**Synthesis of PPE-g-nBA 4.2 via conventional ATRP**

A two-neck flask was loaded with a solution of PPE-MI 3.2.2 (220 mg, 0.02 mmol), anisole (250 μL), N,N,N′,N′,N′′-pentamethyldiethylenetriamine (PMDETA) (600 μL, 0.28 mmol) and n-butyl acrylate (nBA) (1.76 mL, 12.3 mmol) in DMF (4 mL) under an atmosphere of nitrogen at r.t. The mixture was then degassed using freeze-thaw and back filled with nitrogen five times. To the frozen solution, under nitrogen, was added Cu(I)Br (30 mg, 21 mmol). The reaction was then stirred at 80 °C for 8 h. The polymerisation was quenched through the exposure of the mixture to air and quickly cooled with liquid nitrogen. The mixture was then diluted with CH₂Cl₂ (30 mL), filtered, washed with water (3 × 20 mL), precipitation by the
addition of methanol (3 × 35 mL), centrifuged (40 rpm, 15 min) to collect the precipitate, which was dried under vacuum to give PPV-g-PnBA 4.2 as a bright yellow viscous oil (0.023 g, 7%).

\[ \delta_H \ (400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si}): \ 0.93-0.98 \ (3\text{H, m, CH}_3), 1.38-1.43 \ (2\text{H, m, CH}_2), 1.63-1.67 \ (2\text{H, m, CH}_2), 1.81 \ (1\text{H, m, CH}), 2.02-2.31 \ (2\text{H, m, CH}_2), 4.05-4.10 \ (2\text{H, m, CH}_2). \]

**GPC:** \( M_w: 2.3 \times 10^4 \text{ g/mol}^{-1}, M_n: 1.4 \times 10^4 \text{ g/mol}^{-1}, M_w/M_n: 1.64. \)

### Synthesis of PPV-g-nBA 4.1 via ARGET ATRP

A two-neck flask was loaded with the mixture of PPV-MI 3.1 (270 mg, 0.02 mmol), anisole (250 \( \mu \text{L} \)), \( n \)-BA (1.76 mL, 12.27 mmol) in DMF (10 mL) under an atmosphere of nitrogen at r.t. The mixture was then degassed and backfilled using freeze-thaw with nitrogen twice. A solution of Cu(II) complex tri(2-pyridylmethyl)amine (TPMA) (6.5 mg, 0.022 mmol) in DMF (1 mL), was prepared at 45 °C for 3 h and then added to the mixture. The reaction was then stirred at 65 °C. Tin(II) ethylhexanoate (0.3 mL, 0.93 mmol) was then added and the mixture stirred for 24 h at 65 °C, under an atmosphere of nitrogen. The solution was allowed to cool to room temperature and then dissolved in CH\(_2\)Cl\(_2\), reduced via vacuum, precipitated by the addition of methanol (100 mL) and centrifuged (40 rpm, 15 min) to collect the precipitate. The
precipitate was dialysed with dialysis bag (Sigma dialysis tubing 10 mm) using methanol. The precipitate in the dialysis bag was then collected and dried under vacuum to afford the desired PPV-g-nBA 4.1 as a bright yellow gum (0.8 g, 60%).

δH (400 MHz; CDCl3; Me4Si): 0.92-0.95 (3H, m, CH3), 1.34-1.40 (2H, m, CH2), 1.58-1.63 (2H, m, CH2), 1.75 (1H, m, CH), 1.91-2.30 (2H, m, CH2), 4.08-4.11 (2H, m, CH2). GPC: Mw: 8.9×10^4 gmol⁻¹, Mn: 6.3×10^4 gmol⁻¹, Mw/Mn: 1.41. UV (4 mgmL⁻¹, DMF) λmax abs = 378 nm. PL (350 µgmL⁻¹, DMF) λmax em = 501 nm.

**Synthesis of PPE-g-nBA 4.2 via ARGET ATRP**

A two neckflask was loaded with the a mixture of PPE-MI 3.2.2 (220 mg, 0.02 mmol), anisole (250 µL), nBA (1.76 mL, 12.27 mmol) in DMF (10 mL) under an atmosphere of nitrogen at r.t. The mixture was then degassed and backfilled using freeze-thaw with nitrogen twice. A solution of Cu(II) complex tri(2-pyridylmethyl)amine (TPMA) (6.5 mg, 0.0224 mmol) in DMF (1 mL), was prepared at 45 °C for 3 h and then added to the mixture. The reaction was then stirred at 65 °C. Tin(II) ethylhexanoate (0.3 mL, 0.93 mmol) was then added and the mixture stirred for 24 h at 65 °C, under an atmosphere of nitrogen. The solution was allowed to cool to
room temperature and then dissolved in CH$_2$Cl$_2$, reduced via vacuum, precipitated by the addition of methanol (100 mL) and centrifuged (40 rpm, 15 min) to collect the precipitate. The precipitate was dialysed with dialysis bag (Sigma dialysis tubing 10 mm) over methanol. The precipitate in the dialysis bag was then collected and dried under vacuum to afford the desired PPE-g-PnBA 4.2 as a bright yellow gum (0.9 g, 62%).

$\delta$H (400 MHz; CDCl$_3$; Me$_4$Si): 0.91-0.97 (3H, m, CH$_3$), 1.36-1.41 (2H, m, CH$_2$), 1.59-1.63 (2H, m, CH$_2$), 1.78 (1H, m, CH), 2.02-2.31 (2H, m, CH$_2$), 4.10-4.14 (2H, m, CH$_2$). **GPC:** $M_w$: 7.4×10$^4$ g mol$^{-1}$, $M_n$: 5.5×10$^4$ g mol$^{-1}$, $M_w/M_n$: 1.35. **UV** (4 mg mL$^{-1}$, DMF) $\lambda_{\text{max abs}}$ = 422 nm. **PL** (350 µg mL$^{-1}$, DMF) $\lambda_{\text{max em}}$ = 473 nm.
Chapter 5: Synthesis of Cationic Grafted Poly(*para*-phenylene vinylene) and Poly(*para*-phenylene ethynylene)
5.1 Introduction

Cationic polymers are interesting materials, serving in a wide range of applications.\textsuperscript{197,386} Owing to their water solubility, they have been extensively used in biological applications, particularly as materials in non-viral gene delivery.\textsuperscript{387–392} Although a variety of cationic compounds with ionic sidechains have been reported (with several promising applications),\textsuperscript{390,393–398} they still show limitations, in particular with respect to their selectivity and specificity. To tackle these limitations, recent studies have focused on amplifying the responsive sites in cationic polymers. To achieve this goal, grafted cationic brushes have attracted much attention.\textsuperscript{197,399,400} Several grafted cationic polymers have been reported, some of which (5.1-5.5) are summarised in Fig 5.1.

![Fig 5.1. Reported cationic grafted molecular brushes.](image)

In this chapter the modification of PPVMI 3.1 and PPEMI 3.2.2, aiming to achieve water soluble PPVs and PPEs with exceptional hydroscopic properties will be discussed. As was successfully determined in the previous chapter, the bromoester functionality of PPVMI 3.1 and PPEMI 3.2.2 allows polymer modifications using either ATRP or ARGET ATRP.\textsuperscript{387} As described in chapter four, both PPV-g-PnBA 4.1 and PPE-g-PnBA 4.2 showed improved photophysical properties, compared to their ungrafted CPs, in organic solvents, most likely due
to reduced interchain interactions. It also shown that both grafted polymers adapted the physical properties of the grafted molecular brushes and were sticky liquids rather than solids.

Improved processability of CPs using ionic grafted brushes in water has been studied using dimethylamino)ethyl methacrylate (DMAEMA), poly(butylmethacrylate) grafted with poly(Boc-aminoethyl methacrylate) and N-[3-(dimethylamino)propyl]methacrylamide. These results showed water compatibility of the resultant grafted polymers. It was shown that grafting polymerisation using ATRP can be achieved in an aqueous media with an appropriate controllability over both molecular weight and dispersity.

What was initially required was the development of a method for the synthesis of grafted quaternary ammonium molecular brushes. To achieve this goal, N,N,N-trimethylaminoethylmethacrylate (TMAEMA) was used as a monomer in the grafting from both PPVMI and PPEMI using both conventional and ARGET ATRP methods, in order to determine the best synthetic route. The aim was to determine the effect of adding cationic brushes on the prepared CPs. It was hoped that for the new graft copolymers would have the physical properties of poly N,N,N-trimethylaminoethylmethacrylate (PTMAEMA) whilst still maintaining the photophysical properties of the CP backbone.

In Chapter four it was shown that grafting of butyl acrylate on to PPV or PPE cores resulted in improved processability of the resulting grafted polymers in organic solvents and also improved photophysical properties. Therefore the aim was to explore whether grafting charged sidechains onto the PPV and PPE core would result in grafted copolymers which have water solubility but still retain, or improve, their photoluminescence properties.

5.2 Preparing the Cationic Grafted Polymers

In order to synthesise N,N,N-trimethylaminoethylmethacrylate molecular brushes, two synthetic routes, based on atom transfer radical polymerisation (ATRP) and activator regenerated by electron transfer ATRP (ARGET ATRP) were studied to evaluate and optimise the most appropriate pathway.

Firstly the traditional ATRP was performed, using Cu(I)Br (0.022 eq.) and N,N,N',N'-pentamethyldiethylenetriamine (PMDETA) (0.024 eq.) as a ligand in DMSO. Grafting polymerisation was first conducted on to the initiated monomer 2.11 in order to optimise
reaction conditions and then using PPVMI 3.1 and PPEMI 3.2.2, in all three case 500 equivalents of TMAEMA was used.

Similar to that seen with butyl acrylate (Chapter four) grafting using conventional ATRP on the abovementioned species (2.11, 3.1 and 3.2.2) gave the products in low yields, in all cases. The low yields indicates a low monomer conversion rate, which was clear when analysing kinetic study results.

Furthermore, $^1$H NMR characterisation of the resulting polymers showed that even after work-up and re-precipitation of the grafted polymers into acetone, residual monomer was still present. This could be observed in the $^1$H NMR spectra through signals in the area of 5.6–6.3 ppm. This result was similar to that reported in chapter four, where conventional ATRP gave poor yields. It was therefore decided to investigate the use of ARGET ATRP.\textsuperscript{370,403}

To successfully conduct ARGET ATRP, the choice of ligand and reducing agent needed to be optimised. In literature, examples using ARGET ATRP grafted polymers,\textsuperscript{274,280–284} ligands tris(2-pyridylmethyl)amine (TPMA), $N,N,N',N''$-pentamethyldiethylenetriamine (PMDETA), were used along with either tin(II) 2-ethylhexanoate or ascorbic acid as reducing agents.

Investigating the controllability of ARGET ATRP reaction conditions suggested that PMDETA was the best ligand rather than the TPMA for the synthesis of the indicated grafted cationic polymers. The optimal ligands for grafting of TMAEMA was found not to be the same as what was used for grafting polymerisation of the nBA in chapter four and the previously studied polystyrene grafting polymerisation.\textsuperscript{277,283,284,404,405} The ammonium characteristics of the monomer TMAEMA may interact with the ligand-catalyst complex altering their reaction. In this case the less stable tridentate ligand PMDETA was found to be more effective for grafting.\textsuperscript{232,256,262,264,406}

The reducing agent was also studied and optimised of TMAEMA grafting with both tin(II) 2-ethylhexanoate and ascorbic acid used.\textsuperscript{277,279} It was realised that both reducing agents were compatible for this ARGET ATRP reaction. However, it was also observed that the use of ascorbic acid was more beneficial because it could be more easily removed in the purification process via dialysis with water. Also by varying the temperature of the reaction from 50 °C to 65 °C, it was discovered reactions at 65 °C produced optimal results.
For the synthesis of IIB-g-PTMAEMA 5.6, PPV-g-PTMAEMA (5.7 and 5.8) and PPE-g-PTMAEMA (5.9 and 5.10) via ARGET ATRP the macroinitiators were dissolved in TMAEMA, which is supplied as 30 % solution in water, and DMSO. Anisole was added as an internal standard for the kinetic study using ^1H NMR in order to calculate monomer conversion (Scheme 5.1, 5.2 and 5.3). Although the reaction is firmly sealed in ARGET ATRP, it is unnecessary to degas the solution.277–279,285

After optimising the polymerisation conditions, grafting was conducted on the PPVMI 3.1 and PPEMI 3.2.2 using two sets of conditions to achieve high and low molecular weight copolymers. For both initiated backbones PPVMI 3.1 and PPEMI 3.2.2 two monomer ratios were used, 250 : 1 and 500 : 1 which gave low and high molecular weight CP based grafted copolymers, respectively.

Scheme 5.1. Synthesis of IIB-g-PTMAEMA via ARGET ATRP.
Scheme 5.2. Synthesis of PPV-g-PTMAEMA via ARGET ATRP.
Characterisation of the grafted polymers (5.6 to 5.10) was performed using $^1$H NMR. Comparison of the $^1$H NMR spectra of the initiators (3.1 and 3.2.2) and the grafted polymers revealed that the CP backbone signals are not visible, owing to the low proton concentration of the CP backbone compared to those of the grafted brushes. Therefore using $^1$H NMR to show the presence of the polymer backbone after grafting is not sufficient. However, comparing the $^1$H NMR spectra of the TMAEMA monomer to the grafted polymers indicates the disappearance of the (CH$_2$=CH) signals at of 5.6-6.3 ppm while the shifting of signals to 1.07-2.0 ppm for the copolymers. Additionally all the other monomer signals broadened. These $^1$H NMR observations indicate the formation of a methacrylate polymer, which would only occur after initial addition to the bromo-ester functionalised groups of 3.1 or 3.2.2 (Fig 5.2).
Fig 5.2. $^1$H NMR spectra of PPVMI 3.1 (in CDCl$_3$) (A), TMAEMA (B) and PPV-g-PTMAEMA (HMw 5.8) (in D$_2$O) (C).
The ARGET ATRP procedure was also examined using a kinetic study via $^1$H NMR spectroscopy during the grafting polymerisation on both PPEMI 3.2.2 and PPVMI 3.1. Kinetic study results are interpreted as monomer conversion percentage (results are presented in Fig 5.3).

![Fig 5.3. ARGET ATRP kinetic study of PPV-g-PTMAEMA (HMw) 5.7 and PPE-g-PTMAEMA (HMw) 5.10.](image)

Comparing the kinetic study results of the grafted PPV 5.7 and PPE 5.10 indicates a lower overall linear relationship while conducting grafting polymerisation onto PPVMI 3.1. To try and understand the nonlinearity, the polymerisation reactions for both PPVMI 3.1 and PPEMI 3.2.2 were visually monitored. It was observed that although the conditions were consistent for both PPV and PPE initiated backbones, grafting polymerisation onto PPVMI 3.1 shows some inhomogeneity during the grafting process. Therefore, it is assumed that the nonlinear kinetic behaviour in PPV grafting polymerisation may be related to the inhomogeneous reaction mixture which forms over time.$^{407,408}$ However, although the reaction media is not optimal for the recording of kinetic measurements of grafting polymerisation, in the case of PPVMI 3.1 it still shows a linear correlation up to 100 mins.

### 5.3 Molecular Weight Determination

Gel permeation chromatography (GPC) was used to assess the molecular weight of the grafted monomer 5.6, PPV (5.7 and 5.8), and PPE (5.9 and 5.10). Using dextran standards (considering to the organic/aqueous compatibility of dextran standard) in water (0.02% NaN$_3$) a calibration
curve was determined and the number-average molecular weight ($M_n$), average molecular weight ($M_w$) and the typical dispersity of the grafted polymers was obtained. GPC analyses of the grafted monomer 5.6 determined the average molecular weight to be 6416 with a typical polydispersity of 1.28.

Further molecular weight experiments were also conducted to evaluate high and low molecular weights of PPV-g-PTMAEMA (5.8 and 5.7), based on the same above mentioned procedure with average molecular weights of 22867 and 77496 being measured, respectively. Experimental calculated molecular weights also suggest grafting of TMAEMA onto PPVMI 3.1 added 374 and 110 TMAEMA acrylate units for high and low molecular weights PPV-g-PTMAEMA respectively (5.8 and 5.7). Further typical polydispersity was also measured for the low (1.36) and high (1.67) molecular weight grafted PPVs (5.7 and 5.8).

Molecular weight measurements were also conducted using the same procedures to determine values for the high 5.10 and low 5.9 molecular weight PPE-g-PTMAEMA. The average molecular weight of 21969 and 78079 were determined for the low and high molecular weight PPE-g-PTMAEMA (5.9 and 5.10) respectively, with polydispersities of 1.35 and 1.7 respectively. Here also experimental calculated molecular weights also suggest grafting of TMAEMA onto PPEMI 3.2.2 added 377 and 106 TMAEMA acrylate units for high and low molecular weights PPE-g-PTMAEMA respectively (5.10 and 5.9).

These results show controllability has been achieved in the synthesis of both grafted PPVs (5.7 and 5.8) and PPEs (5.9 and 5.10). The theoretical molecular weight of the each grafted polymers was calculated using the monomer ratio as well as the observed conversion ratio observed using the $^1$H NMR kinetic study. The comparison of the theoretical molecular weight and the experimentally determined values based on kinetic results of high molecular weight grafting polymerisations shows that in both high molecular weight grafted PPV 5.8 and PPE 5.10 actual and theoretical molecular weights are in close concordance. However, while considering the low molecular weight grafted polymers (5.7 and 5.9) such adaptability reduces by around 50 %, which suggests that the kinetic models of the high molecular weight grafted polymers do not match the low molecular weight ones. Therefore kinetic behaviours of both the low molecular weight grafted PPV 5.7 and PPE 5.9 were studied and compared to their high molecular weight polymers (5.8 and 5.10) (Fig 5.4).
Comparing kinetic behaviour of high and low molecular weight PPV-g-PTMAEMA (5.7 and 5.8) and PPE-g-PTMAEMA (5.9 and 5.10).

Considering this it is understood that in low molecular weight grating polymerisation maximum grafting reached to almost 45 %. Using the proper kinetic models, the actual and theoretical molecular weights were compared both in high and low molecular weight grafted polymers, which the results are summarised in Table 5.1.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Theoretical M&lt;sub&gt;w&lt;/sub&gt;</th>
<th>Actual M&lt;sub&gt;w&lt;/sub&gt;</th>
<th>M&lt;sub&gt;n&lt;/sub&gt;</th>
<th>M&lt;sub&gt;w&lt;/sub&gt;/M&lt;sub&gt;n&lt;/sub&gt;</th>
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<tbody>
<tr>
<td>PPV-g-PTMAEMA</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>(LMw) 5.7</td>
<td>21793.5</td>
<td>22867</td>
<td>16721</td>
<td>1.37</td>
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<tr>
<td>PPV-g-PTMAEMA</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(HMw) 5.8</td>
<td>75328.94</td>
<td>77496</td>
<td>46192</td>
<td>1.67</td>
</tr>
<tr>
<td>PPE-g-PTMAEMA</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(LMw) 5.9</td>
<td>22035.65</td>
<td>21969</td>
<td>16201</td>
<td>1.35</td>
</tr>
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<td>PPE-g-PTMAEMA</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(HMw) 5.10</td>
<td>78172.05</td>
<td>78079</td>
<td>45889</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Table 5.1. Comparison of grafted PPVs and PPEs molecular weight results based on GPC experiments with its theoretical value.
It is inferred from Table 5.1 that in both high and low molecular weight grafted PPV and PPE actual and theoretical molecular weights are in close concordance. Further it is also realized that although the kinetic behaviour of the grafting polymerisation is not initially linear but the molecular weight is still controllable within the presented grafting kinetic models.

5.4 Photophysical Measurements of the Cationic Grafted Polymers

With samples of PPV-g-PTMAEMA (5.7 and 5.8) and PPE-g-PTMAEMA (5.9 and 5.10) prepared using ARGET ATRP we wished to examine their photophysical properties to determine the effect of adding the cationic grafted brushes.

5.4.1 Photophysical Properties of PPV-g-PTMAEMA

To study the photoluminescent efficiency of the PPV backbone after grafting polymerisation, the UV absorption of PPV-g-PTMAEMA 5.7 was recorded and compared with non-grafted backbones PPVOH 2.2 and PPVMI 3.1 (Fig 5.5).

![Fig 5.5. UV-Vis spectra of PPVOH 2.2, PPVMI 3.1 and PPV-g-PTMAEMA 5.7.](image-url)
As it is shown in Fig 5.5 the maximum absorption of a PPV-g-PTMAEMA 5.7 solution in water appeared at 435 nm. Compared with PPVMI, the spectral blue shift of around 15 nm for the grafted PPV is observed. Considering the structure of the grafted polymer, although water is an appropriate solvent for the grafted molecular brushes, it is not the best solvent for the CP backbone, due to its mostly organic characteristics. Therefore, such a spectral blue shift may not be only attributed to the conjugation loss after grafting polymerisation but could also be due to change of the polymer conformation in water. Comparing spectral blue shift of PPV-g-PTMAEMA 5.7 with PPV-g-nBA 4.1 shows almost 60 nm more spectral blue shift in PPV-g-nBA, which might be attributed to the greater loss of conjugation while performing nBA grafting polymerisation comparing to TMAEMA.

The effect of grafting polymerisation on the conjugated PPV backbone was also studied through calculating optical band gap energy of PPV-g-PTMAEMA 5.7 Optical band gap measurements for PPV-g-PTMAEMA 5.7 were calculated using the same procedure as that used for the PPV-g-PnBA 4.1, based on polymer UV-Vis absorption. A 2.37 eV optical band gap energy was calculated for PPV-g-PTMAEMA 5.7 which shows an almost 70 meV increase in optical band gap compared to PPVMI 3.1. Such an increase in optical band gap energy illustrates loss of conjugation in the PPV during grafting, which is almost two times less than that was observed for PPV-g-PnBA 4.1.

The photoluminescence properties of the grafted PPV 5.7, the maximum emission wavelength and the maximum fluorescent intensity, was also measured and compared to PPVMI 3.1 (results are presented in Fig 5.6).
It was observed that the maximum emission intensity was approximately 10 nm blue shifted compared to the PPVMI 3.1. It is also seen that, after grafting polymerisation, the fluorescent intensity was 2.5 times lower than the PPV backbones (2.2 and 3.1), which may be attributed to the lower solvent compatibility of the PPV backbone in the aqueous solution.

The effect of solvent on the photophysical properties of the CP was studied with a series of experiments on PPV-g-PTMAEMA 5.7 (3 mg mL⁻¹) using water : methanol solvent systems, and comparing the maximum fluorescent intensity and the maximum emission wavelength. Different ratios of water to methanol were used and the effect on fluorescence measured (Fig 5.7).³¹–³¹⁴
As can be seen, solvent polarity can affect both the fluorescence intensity and the maximum emission wavelength of the grafted PPV polymer (Fig 5.8). This is most clearly seen as the solvent mixture changes from (2:1, water : methanol) to (1:2, water : methanol). The changes, however, are not very large but would indicate that changes in conformation occur in the variously polar solvents.
To further explore solvent effects on grafted PPVs, neutral PPV-g-\(n\text{BA} \, 4.1\) was also studied in a similar experiment, this time using varying ratios of THF-EtOAc (Fig 5.9). THF and EtOAc were used because PPV-g-P\(n\text{BA} \, 4.1\) is completely soluble in both solvents.

![Fig 5.9. Solvent polarity effect on PPV-g-\(n\text{BA} \, 4.1\) spectral shift.](image)

In this case there is very little change in the wavelength of maximum emission and only 10% deviation in intensity occurs across the range of solvents used while varying the solvent mixture (Fig 5.10). Therefore, it can be concluded that solvent effects do not particularly change the photophysical properties of PPV-g-PTMAEMA 5.7 which was shown through changing solvent polarity and concluding that little spectral shift is observed when increasing solvent polarity.
Furthermore, it can also be noted that PPV polymer backbone behaviour after grafting polymerisation might be attributed to PPV flexibility and its free rotation which reduce polymer aggregation in polar solvents as well as aqueous medium, which might help to somehow keep PPV backbone extension after grafting even in water. Such polymer backbone extension maintenance would be able to be explored through a spectral blue shift both in $\lambda_{\text{max abs}}$ and $\lambda_{\text{max em}}$.

The effect of grafting length and brush density on the photoluminescent properties of PPV-g-PTMAEMA was also studied. The $\lambda_{\text{max em}}$ and the fluorescent intensity were measured for high 5.8 and low 5.7 molecular weights of PPV-g-PTMAEMA (Fig 5.11).
The $\lambda_{\text{max em}}$ of high molecular weight PPV-g-PTMAEMA 5.8 appears at 537 nm with low molecular weight grafted PPV 5.7 red shifted by only 2 nm. High molecular weight grafted PPV 5.8 showed a decrease in fluorescent intensity. Such a decrease in fluorescent intensity may be attributed to the lower solubility of the much larger HMw grafted PPV 5.8 compared to the LMw grafted PPV 5.7. The decrease in intensity may also be a result of increased aggregation of the CP core within the much larger hydrophilic grafted brushes. Increased aggregation would result in increased inter-chain interactions and decrease in photoluminescent intensity.

To identify the effect of molecular weight on the photoluminescent characteristic of PPV-g-PTMAEMA, quantum yield measurements of the grafted PPVs (5.7 and 5.8) were calculated and compared to PPVMI 3.1 (Table 5.2).
<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\lambda_{\text{max em}}$ (nm)</th>
<th>$\phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPVMI 3.1</td>
<td>545</td>
<td>0.94</td>
</tr>
<tr>
<td>PPV-g-PTMAEMA(LMw) 5.7</td>
<td>535</td>
<td>0.58</td>
</tr>
<tr>
<td>PPV-g-PTMAEMA(HMw) 5.8</td>
<td>537</td>
<td>0.32</td>
</tr>
</tbody>
</table>

Table 5.2. Photoluminescent characteristics of the grafted PPVs compared to PPVMI.

It can be seen that the quantum yield decreases after grafting water soluble molecular brushes onto the PPV backbone. Such a decrease in quantum yield is larger with increased grafting. This shows that despite the addition of hydrophilic molecular brushes the grafted polymer does not result in a structure with efficient photoluminescence. It is proposed that the PPV-g-PTMAEMA (5.7 and 5.8) could adopt a micelle-like structure (Fig 5.12) where the chains are in close contact to water. Considering the micelle structure of the grafted PPV in water it is understood that there could be increased interchain interactions of the PPV backbone, the reverse of that observed in PPV-g-PnBA 4.1. The folded structure is not assumed to have formed for PPV-g-PnBA 4.1 where the grafting results in a linear brush-like structure (Fig 5.12) where the CP cores are held linear and far apart, resulting in increased quantum yield.

This hypothesis is best understood while comparing the quantum yield of the low molecular weight and high molecular weight grafted PPVs (5.7 and 5.8). Increased aggregation of the HMw grafted PPV 5.8 results in increased interchain interactions, which reduces quantum yield efficiency approximately 1.80 times compared to the low molecular weight grafted PPV 5.7 (Table 5.2).
Such photophysical observations are in concordance with what it was previously observed with Xu et al. They studied conformational changes of poly[2,5-bis(diethylaminetetraethylene glycol)phenylene vinylene] (DEATG-PPV) in various solvents and proposed micelle-like configuration for DEATG-PPV in water (Fig 5.13).
5.4.2 Photophysical Properties of PPE-g-PTMAEMA

To study the photoluminescent efficiency of PPE-g-PTMAEMA 5.9, its optical properties after grafting polymerisation were measured and compared with ungrafted PPEs PPEOH 2.3 and PPEMI 3.2.2 (Fig 5.14). Considering the organic characteristic of the PPE backbone, photophysical studies could not be conducted in the same solvent therefore grafted polymers measurements were conducted in water and PPE backbones measurements in DMF same as what it was performed previously (Chapter four).
As is shown in Fig 5.14, the maximum absorption of PPE-g-PTMAEMA solution in water is at 428 nm. Compared to PPEMI 3.2.2, the spectral blue shift of around 7 nm for the grafted PPE was observed. Considering the polymer structure, although water is a good solvent for grafted molecular brushes, it is a poor solvent for the PPE CP; similar to that observed for grafted PPV. As such, such a spectral blue shift may not be only attributed to the conjugation loss of the PPE backbone after grafting polymerisation, which was also observed in PPV-g-PTMAEMA 5.7. Comparing this result to PPV-g-PTMAEMA 5.7 it is inferred that grafting polymerisation is less influential on the PPE conjugated backbone relating to the more rigid structure of the PPE backbone, same as what it was previously observed in chapter four while comparing PPE-g-PnBA 4.2 to PPV-g-PnBA 4.1. It is clear that PPEMI 3.2.2 is therefore more resistant to radicals formed in grafting polymerisation compared to PPVMI 3.1.

Looking further at the photophysical properties of PPE-g-PTMAEMA 5.9, the fluorescent efficiency of the grafted PPE was studied and compared to its non-grafted backbone (Fig 5.15). The grafted polymer was measured in water and compared with non-grafted polymers 2.3 and 3.2.2 whose results in DMF are shown in Fig 5.15.
The effect of grafting polymerisation on the conjugated PPE backbone was also studied by calculating the optical band gap energy of PPE-g-PTMAEMA 5.9. Optical band gap calculations for PPE-g-PTMAEMA 5.9 were performed using the same procedure used for the PPE-g-PnBA 4.2, based on polymer UV-Vis absorption. An optical band gap energy of 2.56 eV was calculated for PPE-g-PTMAEMA 5.9 which shows an almost 20 meV increase in optical band gap comparing to PPEMI 3.2.2. Such an increase in optical band gap energy illustrates loss of conjugation during the grafting polymerisation.

The maximum emission intensity of PPE-g-PTMAEMA 5.9 is at 493 nm (Fig 5.15). Interestingly the grafted PPE shows spectral red shift after grafting polymerisation of approximately 22 nm compared to PPEMI 3.2.2. This different to the spectral blue shift observed in the UV-Vis results and a different result as seen on the PPV-g-PTMAEMA 5.9. To further understand these spectral shifts a series of experiments were performed using water-methanol solvent systems varying polarity using different ratios (Fig 5.16). It was hoped that changes in solvent and polarity could reveal greater information.

Fig 5.15. Fluorescent spectra of PPEOH 2.3, PPEMI 3.2.2 and PPE-g-PTMAEMA 5.9.
It was observed that there was a significant spectral blue shift with an increasing amount of methanol. It could also be seen in mixtures containing greater amounts of water, that maximum wavelength and intensity were fairly constant at approximately 480 nm and intensity of 500. In comparison, in mixtures higher in methanol the wavelength blue shifted to around 420 nm with a decrease in intensity of around 40% of the majority solvent mixtures (Fig 5.17).

Fig 5.16. Solvent polarity effect on PPE-g-PTMAEMA spectral shift.

Fig 5.17. Fluorescent intensity and λ_{max em} variations of PPE-g-PTMAEMA versus solvent polarity changes.
The addition of methanol solvent resulted in the maximum emission wavelength of the grafted polymer to be approximately the same value as the ungrafted PPE 3.2.2. Also an unusual increase in emission intensity was observed at exactly (1:1, water:methanol), which did not correspond to measurements of other solvent ratios. Such increase in emission intensity might be attributed to the adaptability of the PPE CP with methanol addition to an appropriate solubility of the grafted molecular brushes in 1:1 (water:methanol) solvent system, which resulted in an interchain interaction prevention and more expanded PPE backbone.

Solvent polarity effects on the conjugated PPE backbone was then studied on PPE-g-PnBA 4.2, using THF and EtOAc same as used on PPV-g-PnBA 4.1 (Fig 5.18).

In this case there was a difference in behaviour between PPE-g-PnBA 4.2 and PPV-g-PnBA 4.1 when varying the solvent polarity. To better study the solvent polarity effect, the spectral shift as well as the maximum fluorescent intensity versus solvent system was plotted (Fig 5.19).
As can be seen, with increasing solvent polarity through increasing the relative amount of ethyl acetate, an obvious red shift is observed, which reaches almost 20 nm between varying solvent from solely THF to THF-EtOAc (1:20). The spectral red shift also accompanied by a decrease in fluorescent intensity to one third of the maximum value.

For PPE-g-PTMAEMA 5.9 it was noted that reducing solvent polarity favours photoluminescence efficiency of the grafted PPE as long as it is not exceeding a methanol to water ratio of (1:1). This result can be simply understood by considering that the water-methanol (1:1) solvent system is good for both grafted molecular brushes and the conjugated PPE backbone.
It is also inferred, related to the rigid structure of the conjugated PPE backbone, in the presence of water although the grafted molecular brushes are fully soluble, the polymer backbone does not have the flexibility which might result in more folding of the polymer backbone, which shows photoluminescence properties more similar to the aggregated form.\(^{306,308}\) Therefore, such activity may reduce photoluminescence efficiency of the grafted PPEs in the presence of hydrosopic solvents and more specifically in water. PPE-g-PTMAEMA 5.9 behaviour in respect to solvent variation is in concordance with what was previously observed by Swager et al.\(^ {306,308}\) They have studied PPEs photophysical attitudes while using methanol, water-methanol and solely water, which they speculated more aggregation-like configuration for the PPE backbone in more polar solvent system more specifically in water.

The effect of increased molecular weight and grafting on the photoluminescent characteristics of PPE-g-PTMAEMA was then studied, looking at the photoluminescence properties and quantum yield measurements of both high 5.10 and low 5.9 molecular weight grafted PPEs (Fig 5.21).
Comparing the fluorescence results of high 5.10 and low 5.9 molecular weight grafted PPEs shows a decrease in fluorescent intensity in the high molecular weight grafted PPE 5.10, which is also accompanied by small spectral red shift. Although the spectral shift is not large the fluorescent intensity decreased by almost 1.5 times. This reduction can be attributed to the lower solubility of the high molecular weight grafted PPE 5.10 compared to the low molecular weight grafted PPE 5.9.\(^\text{409,410}\)

The effect of graft length and molecular weight on the photoluminescence properties was also compared with the core PPEMI 3.2.2 using quantum yield measurements, the results are summarised in Table 5.3.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>(\lambda_{\text{max em}}) (nm)</th>
<th>(\phi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPEMI 3.2.2</td>
<td>471</td>
<td>0.87</td>
</tr>
<tr>
<td>PPE-g-PTMAEMA(LM(_w)) 5.9</td>
<td>493</td>
<td>0.49</td>
</tr>
<tr>
<td>PPE-g-PTMAEMA(HM(_w)) 5.10</td>
<td>497</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Table 5.3. Photoluminescent characteristics of the grafted PPEs (5.9 and 5.10) compared to PPEMI 3.2.2.
These results show that the quantum yield efficiency decreases after grafting water soluble molecular brushes onto the PPE backbone, the same as was observed in PPV grafted polymers (5.7 and 5.8). There is a larger decrease in quantum yield in the grafted PPEs (5.9 and 5.10) with higher molecular weight. Therefore, it can be understood that although the PPE backbone is still be able to show its inherent photophysical properties even in polar and aqueous medium, grafting hydrophilic molecular brushes affects its photoluminescence efficiency and reduces quantum yield.

Such effects can be explained by the hydrophilic nature of the grafted molecular brushes, which contrasts with the hydrophobic nature of the PPE conjugated backbone. Therefore, despite addition of large hydrophilic side chains, the grafted polymers appear to adopt conformations that result in increased interchain interactions. The result of this is reduced quantum efficiency compared to the core CP alone.

5.5 Summary

A synthetic route, based on ARGET ATRP, was developed for the synthesis of IIB-g-PTMAEMA 5.6, PPV-g-PTMAEMA (5.7 and 5.8) and PPE-g-PTMAEMA (5.9 and 5.10). The resulting grafted polymers were produced in high yields and expected molecular weights when compared to the same polymers produced with conventional ATRP. The compatibility of the solvents with all reagents and ligands also made ARGET ATRP a good method for the synthesis of grafted polymers. PMDETA ligand showed better efficiency compared to TPMA, and ascorbic acid was the preferred reducing agent.

The molecular weights of the grafted monomer 5.6, PPVs (5.7 and 5.8) and PPEs (5.9 and 5.10) were further analysed, and the experimental molecular weights of polymer 5.7, 5.8, 5.9 and 5.10 were in agreement with theoretically calculated values but required kinetic analysis of each grafting to correctly determine the theoretical mass.

To study the photoluminescence properties of the grafted PPVs and PPEs, photophysical studies were conducted and then compared to their respective backbones. Spectral blue shifts of 15 nm and 7 nm were observed in the UV spectra in grafted PPV 5.7 and PPE 5.9, respectively. After measuring the fluorescence spectra, a spectral blue shift in PPV-g-
PTMAEMA 5.7 and, interestingly, a spectral red shift in PPE-g-PTMAEMA 5.9 was observed. In order to further explore the photoluminescence behaviour of both grafted PPV 5.7 and PPE 5.9, fluorescence was monitored while changing solvent polarity. Solvent effect studies were conducted also on both PPV-g-PnBA 4.1 and PPE-g-PnBA 4.2 to fully understand the effect of solvent on the behaviour of the grafted molecular brushes.

Both PPV-g-PTMAEMA 5.7 and PPV-g-PnBA 4.1 showed little spectral changes when varying solvent polarity. This is despite the proposal that PPV-g-PnBA 4.1 adopts a highly linear conformation in organic solvents whilst the charged grafted PPV forms micelle-like structures. Although the overall photoluminescent efficiency of PPV-g-PTMAEMA 5.7 is lower than the ungrafted core PPVMI 3.1 it should be noted that measurements are undertaken in different solvents. The grafting has resulted in a water soluble fluorescent polymers whereas PPVMI 3.1 had no water solubility at all.

For the conjugated PPE backbone, obvious spectral shifts were observed when changing solvent polarity, both in PPE-g-PTMAEMA 5.9 and PPE-g-PnBA 4.2. It was further observed that a spectral red shift is seen with increasing solvent polarity and the blue shift is observed with reducing solvent polarity. Therefore, it was surmised that owing to the rigid structure of the PPE conjugated in polar medium it would be folded rather than rotating. Accordingly, even after grafting polymerisation, lower extension in the polymer backbone might be observed in conjugated PPE backbone in polar solvents. Such an observation is also in accordance when comparing the UV-Vis spectral blue shift of PPE-g-PTMAEMA 5.9 with PPV-g-PTMAEMA 5.7, which is almost two times more.

The observed results of the structural effect for both PPV and PPE backbones are in concordance with what it previously observed with Xu et al. and Swager et al. 306,308,311,312

5.6 Experimental Procedures

$^1$H NMR spectra for IIB-g-PTMAEMA 5.6, PPV-g-PTMAEMA (5.7 and 5.8) and PPE-g-PTMAEMA (5.9 and 5.10) were recorded on a 400 MHz Bruker instrument using deuterium oxide as reference or internal deuterium lock. The chemical shifts for each signal are given in units of (ppm). UV-Visible absorption spectra were measured with a Pharmaspec UV-1700, Shimadzu UV-Visible spectrophotometer. Fluorescence spectra were measured with a Perkin
Elmer LS 55 spectrophotometer with a 3-Q-10 mm rectangular quartz cell. Solution state quantum yields were determined using either PPV or PPE grafted polymer samples in water relative to Anthracene 314 in ethanol ($\phi = 0.27$). The molecular weights of the grafted polymers were determined by Gel Permeation Chromatography (GPC) running with filtered water through 0.02 µm Nylon membrane filter (Grace) containing 0.02 % NaN₃ as the eluent versus dextran standards (Sigma-Aldrich) using Viscotek TDAmx from Malvern Instruments equipped with the 2 x A5000 (300 mm x 8 mm each) Viscotech columns and A7Guard (50 mm x 8 mm) Guard column. Chemicals were purified and dried using standard techniques. Also all air and water-sensitive synthetic manipulations were performed under a nitrogen atmosphere using standard techniques. All commercial chemicals were of reagent grade and used as received. Also $N,N,N$-trimethylaminoethylmethacrylate (TMAEMA) was used as 30 % solution in water.

As the grafting polymerisation was determined to be successful using ARGET ATRP, the kinetics of reaction was studied using $^1$H NMR. At specific interval times, 100 µL samples were taken out of the reaction flask. The monomer conversion was tracked by comparing the integration to the anisole signal, as an internal standard, at 4.7 ppm in D₂O.

**Synthesis of IIB-g-PTMAEMa via conventional ATRP 5.6**

A solution of monomer **1.11** (15 mg, 0.02mmol) in DMSO (5 mL) was added to a stirring solution of the $N,N,N$-trimethylaminoethylmethacrylate (1.88 mL, 10 mmol) in DMSO (5 mL) and water (300 µL). After achieving a clear solution Cu(I)Cl (22 mg, 0.22 mmol) was added.
The reaction was then degassed and the mixture placed under an atmosphere of nitrogen. The mixture was heated to 60 °C and \( N,N,N',N',N'' \)-pentamethyldiethylenetriamine PMDETA (50 µL, 0.24 mmol) was added slowly and the mixture left for 24 h. The reaction was quenched by cooling the mixture with liquid nitrogen and exposing the mixture to air. The greenish precipitate was filtered, collected and then dissolved in water. The product was re-precipitated using acetone (100 mL) and collected using centrifuge. The bluish solid was purified using dialysis with KCl (2 M) solution and then water to achieve a white solid polymer 5.6 (10.8 mg, 5 %).

\[ \delta_H \text{ (400 MHz; D}_2\text{O): 1.08-1.21 (2H, m, CH}_2\text{), 2.01-2.08 (1H, m, CH), 3.30 (9H, br s, CH}_3\text{), 3.82-3.87 (2H, m, CH}_2\text{), 4.50-4.54 (2H, m, CH}_2\text{). GPC: M}_w\text{: 1.08} \times 10^3 \text{ gmol}^{-1}, M_n\text{: 0.98} \times 10^3 \text{ gmol}^{-1}, M_w/M_n\text{: 1.10.} \]

**Synthesis of high molecular weight PPV-g-PTMAEMA via conventional ATRP 5.8**

![Diagram](image)

A solution of PPVMI 3.1 (270 mg, 0.01 mmol) in DMSO (5 mL) was added to a stirring solution of the \( N,N,N \)-trimethylaminoethylmethacrylate (1.88 mL, 10 mmol) in DMSO (10
mL) and water (600 µL). After achieving a clear solution Cu(I)Cl (22 mg, 0.22 mmol) was added. The reaction was then degassed and the mixture placed under an atmosphere of nitrogen. The mixture was heated to the 60 °C and N,N,N′,N′,N′′-pentamethyldiethylenetriamine PMDETA (50 µL, 0.24 mmol) was added slowly and the mixture left for 24 h. The reaction was quenched by cooling the mixture with liquid nitrogen and exposing the mixture to air. The dark orange precipitate was filtered, collected and then dissolved in water. The product was re-precipitated using acetone (100 mL) and collected using centrifuge. The bluish-orange solid was purified using dialysis with KCl (2 M) solution and then water to achieve an orange precipitate 5.8 (10 mg, 2 %).

δH (400 MHz; D2O): 1.11-1.21 (2H, m, CH2), 2.05-2.10 (1H, m, CH), 3.27 (9H, br s, CH3), 3.80-3.87 (2H, m, CH2), 4.53-4.56 (2H, m, CH2). GPC: Mw: 4.4×10³ gmol⁻¹, Mn: 4.3×10³ gmol⁻¹, Mw/Mn: 1.03.

**Synthesis of high molecular weight PPE-g-PTMAEMA via conventional ATRP 5.10**
A solution of PPEMI 3.2.2 (220 mg, 0.01 mmol) in DMSO (5 mL) was added to a stirring solution of the N,N,N-trimethylaminoethylmethacrylate (1.88 mL, 10 mmol) in DMSO (10 mL) and water (600 µL). After achieving a clear solution Cu(I)Cl (22 mg, 0.22 mmol) was added. The reaction was then degassed and the mixture placed under an atmosphere of nitrogen. The mixture was heated to 60 °C and N,N,N′,N′,N′′-pentamethyldiethylenetriamine PMDETA (50 µL, 0.24 mmol) was added slowly and left for 24 h. The reaction was quenched by cooling the mixture with liquid nitrogen and exposing the mixture to air. The dark yellow precipitate was filtered, collected and then dissolved in water. The product was re-precipitated using acetone (100 mL) and collected using centrifuge. The bluish-yellow solid was purified using dialysis with KCl (2 M) solution and then water to achieve a bright yellow precipitate 5.10 (37 mg, 5 %).

δH (400 MHz; D2O): 1.05-1.17 (2H, m, CH2), 1.98-2.05 (1H, m, CH), 3.32 (9H, br s, CH3), 3.83-3.87 (2H, m, CH2), 4.52-4.56 (2H, m, CH2). GPC: Mw: 5.2×103 gmol⁻¹, Mn: 4.94×103 gmol⁻¹, Mw/Mn: 1.05.

**Synthesis of IIB-g-PTMAEMA via ARGET ATRP 5.6**

![Synthesis of IIB-g-PTMAEMA via ARGET ATRP 5.6](image)

A solution of monomer 1.11 (15 mg, 0.02 mmol) in DMSO (5 mL) was added to a stirring solution of the N,N,N-trimethylaminoethylmethacrylate (1.88 mL, 10 mmol) in DMSO (5 mL) and water (600 µL) to achieve a colourless solution. Separately the ligand-catalyst complex was prepared by adding PMDETA (7.5 mg, 0.041 mmol) into a mixture of Cu(II)Cl (2 mg, 0.0148 mmol) and anisole (1 mL) at 67 °C for 3 h. This complex was added to the reaction mixture at 60 °C. Then a solution of ascorbic acid (980 mg, 5.56 mmol) in anisole (1 mL) and
water (300 µL) was added slowly to the reaction and left for 24 h under an atmosphere of nitrogen at 60 °C. The reaction was quenched by cooling the mixture with liquid nitrogen and exposing the mixture to air. The white precipitate was collected and then dissolved in water. The product was re-precipitated using acetone (100 mL) and collected using centrifuge to achieve polymer **5.6** as a white solid (78 mg, 42 %).

δ_H (400 MHz; D_2O): 1.01-1.12 (2H, m, CH₂), 1.97-2.03 (1H, m, CH), 3.27 (9H, br s, CH₃), 3.78-3.83 (2H, m, CH₂), 4.48-4.52 (2H, m, CH₂). **GPC:** M_w: 6.41×10³ g mol⁻¹, M_n: 4.98×10³ g mol⁻¹, M_w/M_n: 1.288.

**Synthesis of high 5.8 and low 5.7 molecular weight PPV-g-PTMAEMA via ARGET ATRP**

A solution of PPVMI **3.1** (270 mg, 0.01 mmol) in DMSO (5 mL) was added to a stirring solution of the N,N,N-trimethylaminoethylmethacrylate (1.88 mL, 10 mmol) in DMSO (5 mL) and water (600 µL) to achieve a colourless solution. Separately the ligand-catalyst complex was prepared by adding PMDETA (7.5 mg, 0.041 mmol) into a mixture of Cu(II)Cl (2 mg,
0.0148 mmol) mixture in anisole (1 mL) at 67 °C for 3 h. This complex was added to the reaction mixture at 60 °C. Then a solution of ascorbic acid (980 mg, 5.56 mmol) in anisole (1 mL) and water (300 µL) was added slowly to the reaction and left for 24 h under an atmosphere of nitrogen at 60 °C. The reaction was quenched by cooling the mixture with liquid nitrogen and exposing the mixture to air. The orange precipitate was collected and then dissolved in water. The product was re-precipitated using acetone (100 mL) and collected using centrifuge to give polymer 5.8 as a bright orange solid (850 mg, 55 %).

δH (400 MHz; D2O): 1.01-1.10 (2H, m, CH2), 1.95-2.01 (1H, m, CH), 3.25 (9H, br s, CH3), 3.75-3.82 (2H, m, CH2), 4.45-4.50 (2H, m, CH2). GPC: Mw: 77.49×10³ g mol⁻¹, Mn: 46.19×10³ g mol⁻¹, Mw/Mn: 1.67. UV (2 mg mL⁻¹, water) λmax abs = 435 nm. PL (125 µg mL⁻¹, water) λmax em = 535 nm.

The same procedure was used to achieve the low molecular weight PPV-g-PTMAEMA 5.7, except using N,N,N-trimethylaminoethylmethacrylate (950 µL, 5 mmol) in DMSO (5 mL) and water (300 µL) and ascorbic acid (600 mg, 3.40 mmol) in anisole (1 mL) and water (150 µL) to give polymer 5.7 as a bright orange solid (180 mg, 40 %).

δH (400 MHz; D2O): 1.01-1.10 (2H, m, CH2), 1.92-2.03 (1H, m, CH), 3.28 (9H, br s, CH3), 3.77-3.85 (2H, m, CH2), 4.43-4.48 (2H, m, CH2). GPC: Mw: 22.86×10³ g mol⁻¹, Mn: 16.72×10³ g mol⁻¹, Mw/Mn: 1.36. UV (2 mg mL⁻¹, water) λmax abs = 435 nm. PL (125 µg mL⁻¹, water) λmax em = 537 nm.
Synthesis of high 5.10 and low 5.9 molecular weight PPE-g-PTMAEMA via ARGET ATRP

A solution of PPEMI 3.2.2 (220 mg, 0.02 mmol) in DMSO (5 mL) was added to a stirring solution of the N,N,N-trimethylaminoethylmethacrylate (1.88 mL, 10 mmol) in DMSO (5 mL) and water (600 µL) to achieve a colourless solution. Separately the ligand-catalyst complex was prepared by adding PMDETA (7.5 mg, 0.041 mmol) into a mixture of Cu(II)Cl (2 mg, 0.0148 mmol) in anisole (1 mL) at 67 °C for 3 h. This complex was added to the reaction mixture at 60 °C. Then a solution of ascorbic acid (980 mg, 5.56 mmol) in anisole (1 mL) and water (300 µL) was added slowly to the reaction and left for 24 h under an atmosphere of nitrogen at 60 °C. The reaction was quenched by cooling the mixture with liquid nitrogen and exposing the mixture to air. The orange precipitate was collected and then dissolved in water. The product was re-precipitated using acetone (100 mL) and collected using centrifuge to give polymer 5.10 as a bright orange solid (870 mg, 63 %).
$\delta_H$ (400 MHz; D$_2$O): 1.02-1.11 (2H, m, CH$_2$), 1.97-2.03 (1H, m, CH), 3.26 (9H, br s, CH$_3$), 3.77-3.82 (2H, m, CH$_2$), 4.47-4.51 (2H, m, CH$_2$). **GPC**: $M_w$: 77.48$\times 10^3$ g mol$^{-1}$, $M_n$: 46.02$\times 10^3$ g mol$^{-1}$, $M_w/M_n$: 1.68. **UV** (5 mg mL$^{-1}$, water) $\lambda_{\text{max abs}}$ = 428 nm. **PL** (5 mg mL$^{-1}$, water) $\lambda_{\text{max em}}$ = 493 nm.

The same procedure was used to achieve the low molecular weight PPE-g-PTMAEMA **5.9**, except using $N,N,N$-trimethylaminoethylmethacrylate (950 µL, 5 mmol) in DMSO (5 mL) and water (300 µL) and a solution of ascorbic acid (600 mg, 3.40 mmol) in anisole (1 mL) and water (150 µL) to give polymer **5.9** as a bright orange solid (190 mg, 43 %).

$\delta_H$ (400 MHz; D$_2$O): 1.04-1.13 (2H, m, CH$_2$), 1.95-2.01 (1H, m, CH), 3.24 (9H, br s, CH$_3$), 3.78-3.83 (2H, m, CH$_2$), 4.45-4.47 (2H, m, CH$_2$). **GPC**: $M_w$: 22.43$\times 10^3$ g mol$^{-1}$, $M_n$: 16.38$\times 10^3$ g mol$^{-1}$, $M_w/M_n$: 1.37. **UV** (2 mg mL$^{-1}$, water) $\lambda_{\text{max abs}}$ = 428 nm. **PL** (125 µg mL$^{-1}$, water) $\lambda_{\text{max em}}$ = 497 nm.
Chapter 6: Synthesis of Anionic Grafted Poly(\textit{para}-phenylene vinylene) and Poly(\textit{para}-phenylene ethynylene)
6.1 Introduction

Anionic polymers are often as water soluble compounds that can serve several applications owing to their structural properties. One of the most important uses of anionic polymers is their ability to act as surfactants. Such a capability makes anionic polymers suitable components to make detergents and hygiene products.

Based on the structural functionality of all anionic polymers, anionic conjugated polymers have attracted much attention because of the discovery of their suitability for optical and biological applications. As a result of the water solubility of anionic conjugated polymers, several biological applications have been identified through careful design of the polymer’s functional groups. Anionic conjugated polymers have recently been used as a new class of highly sensitive and rapidly responsive chemical and biological sensors where the fluorescence response of these materials can change even with very small amount of the sensed analyte molecules.

Anionic conjugated polymers show an ability to bind with the surface of protein molecules surface through multivalent interactions, which then varies the optical properties of these polymers. The utilisation of anionic conjugated polymers as viable protein sensors has been reported; some of the chemical structures of these compounds are shown in Fig 6.1.

Furthermore, fluorescence quenching of anionic CPs with either neutral or cationic species allows for sensitive and sometimes selective sensing of specific compounds. Specifically designed anionic CPs have therefore been used for metal ion sensing; some of these metal ion sensors are represented in Fig 6.2.
In this chapter, the modification of PPVMI 3.1 and PPEMI 3.2.2 aiming to forms anionic grafted molecular brushes is reported. The aim being to introduce the physical characteristics of the anionic grafted molecular brushes on fluorescence CPs.
As described in the previous chapter, both PPV-g-PTMAEMA (5.7 and 5.8) and PPE-g-PTMAEMA (5.9 and 5.10) were successfully synthesised using ARGET ATRP. Both PPV and PPE cationic grafted polymers show physical properties of the cationic grafted molecular brushes, which made them water soluble. It was also observed that although some degree of solvent polarity could affect the photophysical properties of the grafted PPEs, but the resulted polymers still preserved photoluminescence properties of their core backbones.

The overall approach is to functionalise the CPs using either ATRP or ARGET ATRP such that to achieve anionic grafted polymers having a range of application and that the brush polymers still exhibit the CPs properties. Improvement in the processability in nonorganic solvents of CPs using ionic grafted brushes has been studied using, poly(butylmethacrylate) grafted with poly(Boc-aminoethyl methacrylate)424 and sulfopropyl methacrylate (SPMA).425,426 These studies determined that controlability of grafting polymerisation can achieve. It was observed that the grafting polymerisation using ATRP could be used in aqueous media with an appropriate controllability over both molecular weight and dispersity.370

ATRP as a grafting polymerisation has been successfully reported in the synthesis of well-defined anionic grafted polymers.427 The ATRP method, however, has some associated limitation, specifically when using this polymerisation route with a combination of hydrophilic anionic monomers and a hydrophobic, initiated, polymer backbone.428,429 Such limitations not only arise from solubility issues but also reflects ATRP sensitivity towards ionic reaction conditions. To sidestep these issues, several ATRP based grafting polymerisations have been reported using protected ionic monomers.427,430,431 Although these ATRP methods with a protected monomer successfully produce grafted charged polymers, they often have difficulty with regard to the deprotection step and this can result in decreased molecular weight of the final polymers.427,430–432 Phase transfer complexations have been reported to reduce these solubility issues.433–437

In this chapter we focussed on the development of a method for the direct synthesis of grafted anionic sulfonate molecular brushes. To achieve this goal, 3-(acyrloyloxy)propane-1-sulfonate (SPA) was used as a monomer in the grafting of PPVMI 3.1 and PPEMI 3.2.2 using ARGET ATRP method. Convectional ATRP was considered but due to the lack of success in introducing both neutral and cationic brushes to PPVMI 3.1 and PPEMI 3.2.2 it was decided to favour ARGET ATRP. Also in order to tackle the poor solubility of the SPA, several methods were examined to improve the reaction conditions. It was hoped to prepare grafted
polymers with the physical properties of poly 3-(acryloyloxy)propane-1-sulfonate (PSPA) whilst still maintaining the photophysical properties of the CP backbones.

6.2 Results and Discussion

In order to synthesise the poly-sulfopropyl acrylate (PSPA) molecular brushes, considering the optimised grafting polymerisation methods in the previous chapters, the same ARGET ATRP procedure, which was used in previous chapter was applied. Initial trials grafting PSPA using IIB 1.11, PPVMI 3.1 and PPEMI 3.2.2 in DMSO showed that although DMSO is a good solvent for the initiators, the ATRP monomer was considerably less soluble. Such an inhomogeneity in reaction conditions was even more pronounced when performing grafting polymerisation with PPVMI 3.1 and PPEMI 3.2.2, due to their high molecular weight compared to monomer 1.11.

To address this solubility issue, the grafting polymerisations were conducted in a more diluted reaction mixture. Although the dilution improved SPA solubility, it was not completely successful. The grafted polymers precipitated very rapid after starting the grafting reactions, which resulted in a low rate of grafting. Attempting to improve this by modifying the pH of the reaction from 2 to 9 was found unsuccessful and the newly formed polymer was still seen to quickly precipitate.

In order to overcome this solubility issue and low rate of brush growth, it was decide to employ phase transfer complexation (PTC) to improve the solubility of SPA in organic solvents.433,434 It is well known that crown ethers can be used to coordinate potassium ions which results in complexes that are more soluble in organic solvents. Therefore, it was decided to attempt to form the supramolecular complex of crown ether (18-crown-6) and the potassium salt of SPA (Scheme 6.1).

![Scheme 6.1. Phase transfer complexation of ATRP monomer and 18-Crown-6.](image-url)
It is hypothesised that PTC method would improve monomer solubility, and also improve the solubility of the grafted polymers in the DMSO solvent.

To verify successful implementation of the PTC method, the complex formation between 18-C-6 and ATRP monomer was tracked through $^1$H NMR (Fig 6.3).

**Fig 6.3.** $^1$H NMR spectra of 18-Crown-6 (A), SPA (B) and SPA-18-Crown-6 complex (C) in DMSO.
Comparing the NMR spectra of 18-Crown-6 and SPA after complexed to SPA showed a chemical shift of the of the methylene groups of 18-Crown-6 from 3.53 ppm to 3.57 ppm, confirming a complex had formed between the SPA and 18-Crown-6. Also comparing $^1$H NMR of SPA to its complex shows CH$_2$ next to sulfonate group shifting from 2.57-2.70 nm to 2.43-2.56 nm (Fig 6.4).

By achieving a homogeneous monomer-complex solution in DMSO, enables further polymerisation reaction by ARGET ATRP. In order to optimise ARGET ATRP reaction condition, various ligands and reducing agents were trialled with TPMA, PMDETA, tin(II) 2-ethylhexanote and ascorbic acid subsequently used.$^{277,280}$ Analysing the results showed that PMDETA is the best ligand for the synthesis of the indicated grafted anionic polymers. It was found that the results when trialling different ligands for grafting PSPA with ARGET ATRP was not the same as the optimal ligand for grafting polymerisation of the nBA (Chapter four) and the previously studied of poly(glycidyl methacrylate) and methyl methacrylate grafting polymerisation.$^{282,438}$ However, the conditions used for the grafting of cationic molecular brushes in Chapter five gave better results. Such results supports the idea of greater compatibility of grafting polymerisation of more polar brushes when using PMDETA.
The choice of reducing agent was also examined and optimized for PSPA grafting polymerisation, using both tin(II) 2-ethylhexanoate and ascorbic acid. It was found that tin(II) 2-ethylhexanoate was the best reducing agent for the grafting, while the ascorbic acid was not as successful, with an approximately 40% reduction in overall grafting polymerisation yields being observed. Such a result may be attributed to the anionic nature of the monomer which may interact with ascorbic acid reducing its effectiveness. Therefore the reaction proceeds more effectively with the stronger reducing agent tin(II) 2-ethylhexanoate.439

For the grafting polymerisation of IIB-g-PSPA 6.1, PPV-g-PSPA (6.2 and 6.3) and PPE-g-PSPA (6.4 and 6.5) via ARGET ATRP, the brominated initiators in DMSO were added to the monomer-complex solution in DMSO (Scheme 6.2, 6.3 and 6.4). Anisole was added as an internal standard for the kinetic study using 1H NMR, and conversion was calculated by comparing the integration of reference anisole versus monomer signal. Monomer conversion for PPV and PPE grafted polymers for both low molecular weight brushes (using 250 equivalent of monomer) and high molecular weight (using 500 equivalent of monomer) were calculated.

Purification of the final grafted polymers was conducted through dialysis using first 1,4-dioxane to precipitate the final product into the dialysis bag while dissolving 18-Crown-6 into the 1,4-dioxane and then prolonged with pure water to remove remaining monomer.

Scheme 6.3. Synthesis of PPV-g-PSPA (6.2 and 6.3).
Characterization of the grafted polymers by $^1$H NMR was performed and comparison of the $^1$H NMR spectra of the initiators and the grafted polymers reveals that the polymer backbone signals have effectively disappeared (Fig 6.5). This is related to the very low proton concentration of the polymer backbones compared to the grafted molecular brushes.

Comparing the $^1$H NMR spectra of the SPA to the grafted polymers shows a disappearance of the (CH$_2$=CH) signals in the area of 5.6-6.3 ppm, while a shifting of these signals to 2.43 ppm and 1.94-1.60 ppm is observed. This is in addition to broadening of all the other monomer signals. These $^1$H NMR results indicate the successful polymerisation of the acrylate monomer to the bromo-ester functionalised groups in the initiators. The successful removal of the 18-Crown-6 after dialysis with 1,4-dioxane is apparent by $^1$H NMR spectra, where the methylene groups peak at 3.56 ppm are not present (Fig 6.5).
Fig 6.5. $^1$H NMR spectra of (A) potassium sulfopropyl lacrylate, (B) PPVM 3.1 and (C) PPV-g-PSPA 6.3
The kinetics of the ARGET ATRP was studied using $^1$H NMR spectroscopy during the grafting polymerisation on both PPEMI 3.2.2 and PPVMI 3.1. Kinetic study results are shown below, through monomer conversion percentage against time (Fig 6.6).

Examining the kinetic results it was found that the initial polymerisation process is fast as within 20 min of the reaction almost 20 % monomer conversion in both PPVMI and PPEMI is observed. In both case the kinetic plot shows an almost linear relationship after the first 20 min of grafting polymerisation. Due to the results found in chapter four, separate kinetic experiments were conducted for the synthesis of low molecular weight brushes (6.2. and 6.4) and high molecular weight brushes (6.3 and 6.5). As it is inferred from both kinetic models (Fig 6.6), grafting polymerisation rate of both high and low molecular weight grafted molecular brushes are very similar except in overall conversion. Such a variation in overall conversion when comparing high and low molecular weight grafting polymerisation may be attributed to the lower abundance of the ATRP monomer.258,440,441

### 6.3 Molecular Weight Determination

Gel Permeation Chromatography (GPC) was used to assess the molecular weight of the IIB-g-PSPA 6.1, PPV-g-PSPA (6.2 and 6.3) and PPE-g-PSPA (6.4 and 6.5). Using dextran standards calibration curve and water (0.02% NaN$_3$) as an eluent, the number-average molecular weight (M$_n$), average molecular weight (M$_w$) and the typical dispersity of the grafted polymers were analysed.
GPC analyses of the IIB-g-PSPA 6.1 calculated the average molecular weight to be 21969 gmol\(^{-1}\) and the typical polydispersity was measured to be 1.36.

Further molecular weight experiments were also conducted to evaluate high and low molecular weight of PPV-g-PSPA (6.2 and 6.3) based on the same above mentioned procedure average molecular weights of 19907 gmol\(^{-1}\) and 77649 being measured, respectively. Experimental molecular weight suggest the addition of approximately 98 and 384 units of SPA monomer onto the PPVMI 3.1 for polymers 6.2 and 6.3. Typical polydispersity was measured as almost 1.37 and 1.70 for the low and high molecular weight grafted PPV (6.2 and 6.3).

Molecular weight measurements were also conducted within the same procedure to determine molecular weight of high and low molecular weight grafted PPEs (6.4 and 6.5). The GPC experiments show the average molecular weights are 22059 gmol\(^{-1}\) and 77483 gmol\(^{-1}\) for low and high molecular weight PPE-g-PSPA, respectively (6.4 and 6.5). Here also experimental molecular weight suggest addition of approximately 109 and 383 units of SPA monomer onto the PPVMI 3.1 for polymers 6.2 and 6.3. Typical polydispersity was measured in grafted PPEs to be almost 1.41 and 1.68 for low and high molecular weight grafted PPEs (6.4 and 6.5).

Comparing polydispersity results it is understood that better controllability achieved both in low molecular weight grafted PPV 6.2 and PPE 6.4. Better controllability could be attributed to the lower availability of SPA, particularly in the first 20 min of the reaction, which can effectively reduce the polydispersity indexes of the low molecular weight grafted polymers comparing to the high molecular weight ones.\(^{44}\)

Based on these polydispersity results, it can be concluded that overall the synthesis of the grafted PSPA polymers has good controllability. Grafting polymerisation controllability was further investigated by comparing the GPC experimental molecular weight of both PPVs (6.2 and 6.3) and PPEs (6.4 and 6.5) grafted polymers with theoretical calculations using the \(^1\)H NMR conversion rates. The theoretical molecular weight of each grafted polymer was calculated taking into account the monomer ratio used as well as the observed conversion ratio. The comparison of the measured theoretical molecular weight and the actual ones are summarized below (**Table 6.1**).
<table>
<thead>
<tr>
<th>Polymer</th>
<th>Theoretical $M_w$</th>
<th>Actual $M_w$</th>
<th>$M_n$</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPV-g-PSPA</td>
<td>19907</td>
<td>22867</td>
<td>16721</td>
<td>1.37</td>
</tr>
<tr>
<td>(LM$_w$) 6.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PPV-g-PSPAA</td>
<td>77649</td>
<td>78079</td>
<td>46192</td>
<td>1.72</td>
</tr>
<tr>
<td>(HM$_n$) 6.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PPE-g-PSPA</td>
<td>22059</td>
<td>22434</td>
<td>16385</td>
<td>1.41</td>
</tr>
<tr>
<td>(LM$_w$) 6.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PPE-g-PSPAA</td>
<td>75079</td>
<td>77483</td>
<td>45889</td>
<td>1.68</td>
</tr>
<tr>
<td>(HM$_w$) 6.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6.1. Actual and theoretical molecular weight results of grafted PPV and PPE.

It can be inferred from these results that although the growth of molecular brushes was not initially linear the theoretical molecular weight results of both grafted PPV and PPE are in close agreement to the experimental molecular weights.

**6.4 Photophysical Properties of the Grafted Poly-3-sulfopropyl Acrylate Polymers**

With samples of PPV-g-PSPA 6.2 and PPE-g-PSPA 6.4 prepared we wished to examine their photophysical properties to determine the effect of adding the anionic grafted brushes. Photophysical analysis of IIB-g-PSPA, was not studied due to the non-photoluminescence of the compound.

**6.4.1 Photophysical Properties of the PPV-g-PSPA**

To observe the photoluminescent efficiency after grafting, the UV absorption of PPV-g-PSPA 6.2 after grafting polymerisation, was recorded. To evaluate the effect of grafting polymerisation on the conjugated backbone, the maximum absorption of the grafted PPV was compared to ungrafted polymers 2.2 and 3.1 (Fig 6.7).
As is shown in Fig 6.7 the maximum absorption of PPV-g-PSPA 6.2 solution in water appeared at 357 nm. Compared to PPVMI 3.1, a large spectral blue shift of around 99 nm is observed for the grafted PPV. Although water is a good solvent for the anionic molecular brushes, it is a poor solvent for the mostly organic conjugated backbone, therefore the blue shift may be related not only to the loss of conjugation after grafting polymerisation but also to solvent effects. This blue shift is comparable to that seen in PPV-g-PnBA 4.1 which appears at 375 nm and showed an almost 73 nm blue shift after grafting polymerisation. However, comparing the blue shift of PPV-g-PSPA 6.2 (99 nm blue shift) with cationic PPV-g-PTMAEMA 5.7, shows considerably more change in anionic polymer 6.2. Considering these, such variations in spectral shifts after grafting polymerisation may be mostly attributed to the monomer nature and its steric hindrance during the grafting polymerisation, whilst all the other reaction variables were kept consistent. Although the spectral blue shifting after grafting polymerisation is more pronounced in PPV-g-PSPA comparing to the previously reported grafted PPV, but it is still comparable with the maximum absorption of the previously reported PPV derivatives.358,382,442,443

The effect of grafting on the conjugated PPV backbone was also studied by calculating the optical band gap energy of PPV-g-PSPA 6.2. Optical band gap measurement for PPV-g-PSPA 6.2 was performed using the same procedure which was used for the PPV-g-PnBA 4.1 and PPV-g-PTMAEMA 5.7, calculated using the polymer UV-Vis absorption. A 3.48 eV optical
band gap energy was calculated for PPV-g-PSPA 6.2, which shows an almost 1180 meV increase in optical band gap compared to PPVMI 3.1. Such an increase in optical band gap energy illustrates that conjugation is reduced during grafting polymerisation. It also implies the large blue shift of this grafted polymers is more related to the conjugation loss rather than the conformational changes of the polymer backbone.

Next the photoluminescent properties of the PPV backbone was examined through measuring the maximum emission wavelength and the maximum fluorescent intensity of the grafted PPV 6.2 and compared to PPVMI 3.1 (Fig 6.8).

![FL spectra of PPVOH 2.2, PPVMI 3.1 and PPV-g-PSPA 6.2.](image)

It was observed that the maximum emission wavelength was 470 nm, which was a 75 nm blue shift compared to the PPVMI 3.1. Maximum emission wavelength of PPV-g-PSPSA 6.2 was measured in water, which is not similar to the condition used for the PPV backbones (2.2 and 3.1) therefore results may not be directly comparable. It is also seen that, after grafting polymerisation, the fluorescent intensity was 1.7 times lower than the PPV backbone (2.2 and 3.1), which is attributed to the lower solvent compatibility of the PPV backbone in the aqueous solution similar to what was observed for PPV-g-PTMAEMA 6.7.
To further analyse both UV-Vis and fluorescent spectral results, the effect of change in solvent polarity on the photophysical properties of the grafted polymers was further studied. A series of experiments on PPV-g-PSPA 6.2, using the same procedure that was used for PPV-g-PTMAEMA 5.7, using a water-methanol solvent system was employed. The resulting maximum fluorescent intensities and the maximum emission wavelengths of the resulting polymer when using different ratios of water to methanol were compared (Fig 6.9).

As can be seen changing the solvent polarity affects fluorescence intensity of the grafted PPV polymer, most likely due to the solubility of the polymer in the various solvent mixtures. PPV-g-PSPA 6.2 shows a small blue shift of around 10 nm, which may be attributed to better solubility for the PPV backbone with increasing methanol. The change in fluorescence in PPV-g-PSPA 6.2 with changes in solvent polarity, is summarised in Fig 6.10. It is shown that the behaviour of PPV-g-PSPA with solvent polarity is consistent with what was previously observed in both PPV-g-PnBA 4.1 and PPV-g-PTMAEMA 5.7, which in all these three cases a slight blue shift and fluorescent intensity decrease were observed.
The effect of grafting ratio and molecular weight in PPV-g-PSPA was also studied. $\lambda_{\text{max em}}$ and fluorescent intensity were measured for both the high 6.3 and low 6.2 molecular weight PPV-g-PSPA (Fig 6.11).
It can be seen from Fig 6.11 that $\lambda_{\text{max, em}}$ of both high 6.3 and low 6.2 molecular weight of PPV-g-PSPA occurs at 470 nm which shows that graft length has no spectral shift is observed while increasing the graft lengths. High molecular weight grafted PPV 6.3 shows about 50 % decrease in fluorescent intensity. Such a decrease in fluorescent intensity may be attributed to the lower solubility of the high molecular weight PPV-g-PSPA 6.3 compared to the low molecular weight polymer.

Quantum yield measurements were also conducted with grafted PPVs (6.2 and 6.3) and compared to the PPVMI 3.1 to identify the effect of molecular weight on the photoluminescent characteristic of grafted PPVs (Table 6.2).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\lambda_{\text{max, em}}$ (nm)</th>
<th>$\phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPVMI 3.1</td>
<td>545</td>
<td>0.94</td>
</tr>
<tr>
<td>PPV-g-PSPA(LMW) 6.2</td>
<td>470</td>
<td>0.43</td>
</tr>
<tr>
<td>PPV-g-PSPA(HMW) 6.3</td>
<td>470</td>
<td>0.17</td>
</tr>
</tbody>
</table>

Table 6.2. Photoluminescent characteristics of the grafted PPVs (6.2 and 6.3) Comparing to PPVMI 3.1.

Analysing these results, it is understood that quantum yield efficiency decreases after grafting water soluble anionic brushes onto the PPV backbone. This is similar effect as what was observed for PPV-g-PTMAEMA 5.7 such a decrease in quantum yield is also more intense when increasing the grafting ratio. Therefore, it is understood, that although the PPV backbone shows inherent photophysical properties in polar and aqueous medium because of its flexibility, grafting anionic hydrophilic molecular brushes reduces its photoluminescence efficiency.

Such an effect can be better explained when looking at the hydrophilic nature of the grafted molecular brushes which is in contrast to the hydrophobic PPV conjugated backbone. The interchain interactions of the PPV conjugated backbone were not reduced as was observed in PPV-g-PnBA 4.1. This theory is also best understood when comparing the quantum yield of the low molecular weight and high molecular weight grafted PPVs. Increase interchain interactions in the high molecular weight PPV reduces quantum yield efficiency by around 2.10 times compared to the low molecular weight PPV. This is in addition to the above mentioned conjugation loss of through grafting which also decreases quantum yield. Comparing quantum yields of the high 5.8 and low 5.7 molecular weight PPV-g-PTMAEMA to high 6.3 and low 6.2 molecular weight PPV-g-PSPA shows approximately 47 % and 25 %
decreases in quantum yields of high 6.3 and low 6.2 molecular weight PPV-g-PSPSA, respectively. Such quantum yield reduction is mostly due to the PPV backbone configuration that coming along with the steric hindrance of the 18-crown-6 complex of SPA which might affect CP core length of the final grafted polymer comparing to the PPV grafted cationic polymers. Quantum yield reduction is also inconsistence with what it was previously observed through large UV-Vis blue shifting.

### 6.4.2 Photophysical Properties of PPE-g-PSPA

The optical properties of the grafted PPE was then studied. The UV absorption spectra of PPE-g-PSPA 6.4 was recorded and the maximum absorption of grafted PPE was compared to its ungrafted polymer backbone (Fig 6.12).

![Graph](image)

**Fig 6.12.** UV-Vis spectra of PPEOH 2.3, PPEMI 3.2.2 and PPE-g-PSPA 6.4.

As shown in fig 6.12, the maximum absorption of a PPE-g-PSPA 6.4 solution in water is 422 nm. Compared to PPEMI, a small blue shift of 12 nm in the grafted PPE was identified. Although water is a good solvent for grafted molecular brushes, it is not a good solvent for the PPE conjugated backbone, similar to what was observed previously for grafted PPV 6.2.
Although the blue shift after grafting polymerisation in the PPE is less than that observed for PPV 6.2 backbone, such a blue shift may be attributed to the PPE conjugation loss after grafting polymerisation. It is understood that PPE has less conjugation loss than PPV and this again shows that PPE is more resistant to loss of conjugation during grafting.

Effect of grafting on the conjugated PPE backbone was then measured by calculating optical band gap energy of PPE-g-PSPA 6.4. Optical band gap calculations for the PPE-g-PSPA 6.4 was performed using the same procedure that was used for PPE-g-PnBA 4.2, based on polymer UV-Vis absorption. A 2.51 eV optical band gap energy was calculated for PPE-g-PSPA 6.4 which shows an almost 70 meV increase in optical band gap energy compared to PPEMI 3.2.2. Such an increase in optical band gap energy also illustrates a decrease in PPE conjugation during grafting polymerisation.

The fluorescent efficiency of PPE-g-PSPA 6.4 was then measured and compared to its non-grafted backbone (Fig 6.13). The maximum emission wavelength of PPE-g-PSPA 6.4 is 470 nm. Compared to $\lambda_{\text{max em}}$ of PPEMI 3.2.2, a blue shift of around 1nm is seen. However a considerable reduction in intensity was observed compared to the ungrafted CPs. It should be noted that the solvents for each measurements are not the same as PPEMI 3.2.2 is not soluble in water.

![Fluorescent spectra of PPEOH 2.3, PPEMI 3.2.2 and PPE-g-PSPA 6.4.](image)

Fig 6.13. Fluorescent spectra of PPEOH 2.3, PPEMI 3.2.2 and PPE-g-PSPA 6.4.
Due to the amphiphilic nature of PPE-g-PSPA 6.4, the effect of solvent polarity was again considered and a series of experiments were performed using different ratios of water-methanol solvent system (Fig 6.14).

Increasing the methanol ratio results in a small decrease in $\lambda_{\text{max em}}$ of around 7 nm when changing solvent from only water to a 1:20 water-methanol solvent system. It can also be seen that maximum fluorescent intensity decreases to approximately 60% of the maximum value when using water-methanol 1:20 (Fig 6.15). This is attributed to a lower overall solubility of the grafted PPE with increasing the methanol ratio. Therefore, it might be concluded that in the case of PPE-g-PSPA 6.4, the effect of decreasing solubility, as methanol is added, is more influential than solvent polarity effects. This is in contrast with what was previously observed in the case of PPE-g-PTMAEA. It would therefore appear that the cationic brushes in PPE-g-PTMAEMA 5.7 have a greater interaction with solvent that the anionic brushes of PPE-g-PSPA 6.4, which results in a greater solvent effect.
The effect of molecular weight on the photoluminescent characteristics of PPE-g-PSPA 6.4 was also studied through the study of photoluminescence properties and quantum yield measurements of the high 6.5 and low 6.4 molecular weight grafted PPE. The results of fluorescent intensity measurements are depicted in Fig 6.16.
Fluorescent spectra of high 6.5 and low 6.4 molecular weight grafted PPEs show decreasing in fluorescent intensity for the high molecular weight grafted PPE which is also accompanied by a small spectral red shift. Although the spectral shift is not large, the fluorescent intensity decrease by almost 2.3 times can be attributed to a lower solubility of the high molecular weight grafted PPE compared to the low molecular weight grafted PPE (Fig 6.17).

![Fig 6.17](image.png)

**Fig 6.17.** Image of high (a) and low (b) molecular weight (6.5 and 6.4) PPE-g-PSPA in water (5 mg mL⁻¹).

The effect of molecular weight and the grafting ratio in grafting PPEs was also studied through quantum yield measurements (Table 6.3).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>λ&lt;sub&gt;max em&lt;/sub&gt; (nm)</th>
<th>φ</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPEMI 3.2.2</td>
<td>545</td>
<td>0.87</td>
</tr>
<tr>
<td>PPE-g-PTMAEA(LM&lt;sub&gt;w&lt;/sub&gt;) 6.4</td>
<td>470</td>
<td>0.52</td>
</tr>
<tr>
<td>PPE-g-PTMAEA(HM&lt;sub&gt;w&lt;/sub&gt;) 6.5</td>
<td>474</td>
<td>0.25</td>
</tr>
</tbody>
</table>

**Table 6.3.** Photoluminescent characteristics of the grafted PPEs (6.4 and 6.5) compared to PPEMI 3.2.2.

Through these results, it is understood that the quantum yield efficiency decreases after grafting water soluble molecular brushes onto the PPE backbone, this is the same as what was observed in PPV grafted polymers, which is also followed by a further reduction in quantum yield in high molecular weight grafted PPE. Therefore, it is understood that although the PPE backbone is still be able to exhibit its inherent photophysical properties even in polar and aqueous
medium, grafting hydrophilic molecular brushes does not allow the same level of photoluminescence efficiency as the backbone PPE, in organic solvents.

Such an effect could be explained based on the hydrophilic nature of grafted molecular brushes, which is in contrast to the hydrophobic PPE conjugated backbone. The interchain interactions in the grafted PPE appear to be greater than before grafting. This may be due to increased aggregation of the PPE CP’s as they limit their interactions with the aqueous solvent.

**6.5 Summary**

A synthetic route using ARGET ATRP was developed for the direct synthesis of IIB-g-PSPA 6.1, PPV-g-PSPAA (6.2 and 6.3) and PPE-g-PSPA (6.4 and 6.5). To successfully produce grafted polymers, 18-Crown-6 was used to address solubility issue of the 3-(acryloyloxy)propane-1-sulfonate (SPA) in the DMSO solvent. Based on our current knowledge this is the first reported synthesis for the direct grafting polymerisation of the anionic molecular brushes onto the conjugated backbone. Cu(II)Cl was found to be the as the best catalyst with ligand PMDETA and tin(II) ethylhexanoate gave the optimal yields of grafted polymers.

The molecular weight of the grafted polymers were analysed and confirm a good growth of molecular brushes. The resulted molecular weights were compared with theoretical predictions which were calculated using the kinetic study. It was concluded that the actual and theoretical molecular weights were in close agreement which indicates that although the kinetic behaviour of the grafting polymerisation in both PPVMI 3.1 and PPEMI 3.2.2 is not initially linear the molecular weight is still controllable.

Photophysical studies were also conducted in order to characterise the grafted PPV and PPE polymers results, which were then compared to that of the backbones. Spectral blue shifts in the UV-Vis spectra of both grafted PPV 6.2 and PPE 6.4 were observed at 99 nm and 12 nm, respectively. Such shifts were also examined through measuring the fluorescence. A spectral blue shift of around 75 nm was observed in PPV-g-PSPA 6.2 with only 1 nm blue shift for PPE-g-PSPA 6.4. Through these results it is observed that for grafting of SPA the grafting from PPEMI 3.2.2 is considerably more favourable, with less loss of conjugation.
The photoluminescence behaviour of both grafted PPV 6.2 and PPE 6.4 were examined through fluorescence studies while changing solvent polarity. It was noted that PPV-g-PSPA 6.2 showed little changes while varying solvent polarity. The behaviour of PPV-g-PSPA 6.2 to changes in solvent polarity is similar to what was previously observed with PPV-g-PnBA 4.1 and PPV-g-PTMAEMA 5.7.

In the case of PPE-g-PSPA 6.4, decreasing solvent polarity resulted in a blue shift and a decrease in fluorescent intensity. Although this behaviour towards changes in polarity is not as marked as was observed in PPE-g-PnBA 4.2 and PPE-g-PTMAEA 5.9, such spectral shifts still show the rigid structural effect in PPE. Therefore, it was further realized that owing to the rigid structure of the conjugated PPE in polar medium, it prefers to aggregate together and interchain interactions lead to reduced quantum efficiency, when this is compared to the grafted PPV 6.2 however, the much larger blue shift in the PPV may be due to aggregation and folding of the more flexible polymer backbone.

6.6 Experimental Procedures

$^1$H NMR spectra for IIB-g-PSPA 6.1, PPV-g-PSPA (6.2 and 6.3) and PPE-g-PSPA (6.4 and 6.5) were recorded on 400 MHz Bruker instrument using deuterium oxide as reference or internal deuterium lock. The chemical shift data for each signal are given in units of (ppm). UV-Visible absorption spectra were measured with a Pharmaspec UV-1700, spectrophotometer. Fluorescence spectra were measured with a Perkin Elmer LS 55 spectrophotometer with a 3-Q-10 mm rectangular quartz cell. Solution state quantum yields were determined using either PPV or PPE grafted polymer samples in water relative to Anthracene 314 in ethanol ($\phi = 0.27$). The molecular weights of the grafted polymers were determined by Gel Permeation Chromatography (GPC) running with filtered water through 0.02 µm Nylon membrane filter (Grace) containing 0.02% NaN$_3$ as the eluent versus dextran standards (Sigma-Aldrich) using Viscotek TDAmax from Malvern Instruments equipped with the 2 x A5000 (300 mm x 8 mm each) Viscotech columns and A7Guard (50 mm x 8 mm) Guard column. Chemicals were purified and dried by standard techniques. Also all air and water-sensitive synthetic manipulations were performed under nitrogen atmosphere using standard techniques. All other chemicals were of reagent grade and used as received.
The controllability of ARGET ATRP reactions was studied tracking the polymerisation using $^1$H NMR. Therefore, at specific time intervals, 100 μL samples were taken from the reaction. The monomer conversion was tracked while calibrating the integration of anisole signal, as an internal standard, at 4.7 ppm in D$_2$O as a unit and measuring the integral of the monomer signal compared to anisole.

**Synthesis of High Molecular Weight IIB-g-PSPA 6.1**

A solution of IIB 2.11 (15 mg, 0.02 mmol) in DMSO (5 mL) was added to a solution of 3-(acryloyloxy)propane-1-sulfonate (2.077 g, 10 mmol) and 18-Crown-6 (2.65 g, 10.1 mmol) in DMSO (10 mL). Separately the ligand-catalyst complex was prepared by adding PMDETA (7.5 mg, 0.041 mmol) to a solution of Cu(II)Cl (2 mg, 0.0148 mmol) in anisole (1 mL) and stirring the mixture at 67 °C for 3 hours. This solution was added to the reaction mixture at 60 °C. A solution of tin (II) 2-ethylhexanoate (1.8 mL, 5.56 mmol) in anisole (1 mL) was added slowly to the reaction and the mixture left for 24 h under an atmosphere of nitrogen, at 60 °C. The reaction was quenched by cooling the mixture with liquid nitrogen and exposing the mixture to air. A white precipitate was collected and then dissolved in water. The product was re-precipitated using acetone (100 mL), collected with centrifuge and purified using dialysis with 1,4-dioxane, water and KCl (2 M) to achieve a white solid 6.1 (78 mg, 42 %).
δ_H (400 MHz; D_2O): 1.11-1.90 (2H, m, CH_2), 1.98-2.12 (2H, m, CH_2), 2.27-2.50 (1H, m, CH), 2.82-3.02 (2H, m, CH_2), 4.02-4.30 (2H, m, CH_2). **GPC**: M_w: 21.97×10^3 g mol^-1, M_n: 16.20×10^3 g mol^-1, M_w/M_n: 1.35.

**Synthesis of High Molecular Weight 6.3 and Low Molecular Weight 6.2 PPV-g-PSPA**

A solution of PPVMI 3.1 (270 mg, 0.02 mmol) in DMSO (5 mL) was added to a solution of 3-(acryloyloxy)propane-1-sulfonate (2.08 g, 10 mmol) and 18-Crown-6 (2.65 g, 10.1 mmol) in DMSO (10 mL). Separately the ligand-catalyst complex was prepared by adding the PMDETA (7.5 mg, 0.041 mmol) to a solution of Cu(II)Cl (2 mg, 0.0148 mmol) in anisole (1 mL) and stirring the mixture at 67 °C for 3 h. This complex was added to the reaction mixture at 60 °C. A solution of tin(II)2-ethylhexanoate (1.8 mL, 5.56 mmol) in anisole (1 mL) was added slowly to the reaction and the mixture left for 24 h under an atmosphere of nitrogen at 60 °C. The reaction was quenched by cooling the mixture with liquid nitrogen and exposing the mixture
to air. An orange precipitate was collected and then dissolved in water. The product re-precipitated using acetone (100 mL), collected with centrifuge and purified using dialysis with 1,4-dioxane, water and KCl (2 M) to achieve polymer 6.3 as a bright orange solid (430 mg, 55 %).

δ<sub>H</sub> (400 MHz; D<sub>2</sub>O): 1.14-1.19 (2H, m, CH<sub>2</sub>), 2.02-2.14 (2H, m, CH<sub>2</sub>), 2.29-2.51 (1H, m, CH), 2.85-3.04 (2H, m, CH<sub>2</sub>), 4.05-4.33 (2H, m, CH<sub>2</sub>). **GPC**: M<sub>w</sub>: 78.08×10<sup>3</sup> g mol<sup>-1</sup>, M<sub>n</sub>: 46.19×10<sup>3</sup> g mol<sup>-1</sup>, M<sub>w</sub>/M<sub>n</sub>: 1.72. **UV** (3.5 mg mL<sup>-1</sup>, water) λ<sub>max</sub> abs = 357 nm. **PL** (175 µg mL<sup>-1</sup>, water) λ<sub>max</sub> em = 470 nm.

The same procedure was used to achieve the low molecular weight PPV-g-PSPA 6.2, except using 3-(acryloyloxy)propane-1-sulfonate (1.04 g, 5 mmol) and 18-Crown-6 (1.32 g, 5 mmol) in DMSO (5 mL) and a solution of tin(II)2-ethylhexanoate (1100 µL, 3.40 mmol) in anisole (1 mL) to achieve polymer 6.2 as a bright orange solid (53 mg, 23 %).

δ<sub>H</sub> (400 MHz; D<sub>2</sub>O): 1.12-1.12 (2H, m, CH<sub>2</sub>), 2.03-2.15 (2H, m, CH<sub>2</sub>), 2.31-2.61 (1H, m, CH), 2.85-3.04 (2H, m, CH<sub>2</sub>), 4.07-4.38 (2H, m, CH<sub>2</sub>). **GPC**: M<sub>w</sub>: 22.87×10<sup>3</sup> g mol<sup>-1</sup>, M<sub>n</sub>: 16.72×10<sup>3</sup> g mol<sup>-1</sup>, M<sub>w</sub>/M<sub>n</sub>: 1.37. **UV** (3.5 mg mL<sup>-1</sup>, water) λ<sub>max</sub> abs = 357 nm. **PL** (175 µg mL<sup>-1</sup>, water) λ<sub>max</sub> em = 470 nm.
Synthesis of High Molecular Weight 6.5 and Low Molecular Weight 6.4 PPE-g-PSPA

A solution of PPEMI 3.1 (220 mg, 0.02 mmol) in DMSO (5 ml) was added to a stirring solution of the 3-(acyloyloxy)propane-1-sulfonate (2.077 g, 10 mmol) and 18-Crown-6 (2.65 g, 10.1 mmol) in DMSO (10 mL). Separately the ligand-catalyst complex was prepared by adding PMDETA (7.5 mg, 0.041 mmol) to a solution of Cu(II)Cl (2 mg, 0.0148 mmol) in anisole (1 mL) and stirring the mixture at 67 °C for 3 h. This complex was added to the reaction mixture at 60 °C. A solution of tin(II)2-ethylhexanoate (1.8 mL, 5.56 mmol) in anisole (1 mL) was added slowly to the reaction and the mixture left for 24 h under an atmosphere of nitrogen, at 60 °C. The reaction was quenched by cooling the mixture with liquid nitrogen and exposing the mixture to air. The yellow precipitate was collected and then dissolved in water. The product was re-precipitated using acetone (100 mL), collected with centrifuge and purified using dialysis with 1,4-dioxane, water and KC (2 M) to achieve polymer 6.5 as a bright yellow solid (387 mg, 50%).
δH (400 MHz; D2O): 1.12-1.90 (2H, m, CH2), 1.98-2.12 (2H, m, CH2), 2.27-2.48 (1H, m, CH), 2.82-3.02 (2H, m, CH2), 4.03-4.31 (2H, m, CH2). GPC: Mw: 77.48×10^3 gmol⁻¹, Mn: 45.89×10^3 gmol⁻¹, Mw/Mn: 1.68. UV (3.5 mgmL⁻¹, water) λmax abs = 422 nm. PL (175 µgmL⁻¹, water) λmax em = 474 nm.

The same procedure was used to achieve the low molecular weight PPE-g-PSPA 6.4, except using 3-(acryloyloxy)propane-1-sulfonate (1.04 g, 5 mmol) and 18-Crown-6 (1.32 g, 5 mmol) in DMSO (5 mL) and a solution of tin(II)2-ethylhexanoate (1100 µL, 3.40 mmol) in anisole (1 mL) to achieve polymer 6.4 as a bright yellow solid (61 mg, 27 %).

δH (400 MHz; D2O): 1.17-1.95 (2H, m, CH2), 2.05-2.15 (2H, m, CH2), 2.32-2.54 (1H, m, CH), 2.88-3.07 (2H, m, CH2), 4.07-4.35 (2H, m, CH2). GPC: Mw: 22.43×10^3 gmol⁻¹, Mn: 16.38×10^3 gmol⁻¹, Mw/Mn: 1.41. UV (3.5 mgmL⁻¹, water) λmax abs = 422 nm. PL (175 µgmL⁻¹, water) λmax em = 470 nm.
Chapter 7: Antibacterial Activity of Grafted Polymers
7.1 Introduction

Vancomycin-resistant enterococci (VRE) are one of the highly resistant bacteria, which have become common in many hospitals throughout the world and once established, are very difficult to eradicate.\textsuperscript{444} The emergence of multidrug-resistant and vancomycin-resistant enterococci during the last decade has made it difficult to treat nosocomial infections, two of which (\textit{Enterococcus faecalis} and \textit{Enterococcus faecium}) are responsible for the majority of human infections.\textsuperscript{445} On the other hand \textit{Staphylococcus} aureus is a major cause of nosocomial infections, which in recent years the prevalence of methicillin-resistance \textit{staphylococcus aureus} (MRSA) has got more attentions than before.\textsuperscript{446}

In order to control the spread of multidrug resistant bacteria, strategies to more effectively use antibiotics and prevent bacterial transmission between patients carriers are needed.\textsuperscript{447,448} Such interventions include developing new classes of biocides that have enhanced antimicrobial efficacy and which can be used to decontaminate surfaces in both food and hospital environments.

The importance of novel antibacterial compounds in order to combat bacterial transmission and contamination has resulted in the development of various antibacterial polymer systems.\textsuperscript{386,449} In particular, conjugated polyelectrolytes (CPEs) have attracted much attention in recent years as a new class of materials.\textsuperscript{386,450–453} Within the diverse categories of synthesised CPEs, charged CPEs have been shown to demonstrate antibacterial efficiency, with enhanced efficacy due to the addition of charged pendants.\textsuperscript{29–32,454–457} PPE derivatives with positively charged quaternary ammonium or alkylpyridinium or negatively charged sulfonate pendants have been found to be active against both Gram-negative and Gram positive bacteria.\textsuperscript{30,450–452,456} It is hypothesized that the addition of these groups enable these polymers to disrupt bacterial cell walls.\textsuperscript{454,458,459} The antibacterial efficiency of modified PPV has been demonstrated against \textit{Bacillus subtilis} and \textit{Escherichia coli} where an increase in antimicrobial activity was again attributed to the addition of charged pendants.\textsuperscript{460} One strategy to further improve the antibacterial efficiency of CPEs is to amplify the charge density, which could be achieved by grafting of the charged group onto a polymer backbone. Further, it may be advantageous to use amplified positively charged CPs since charge amplification has demonstrated notably increased antimicrobial effects.\textsuperscript{461–465}
Amongst the various grafting polymerisation methods, atom transfer radical polymerisation (ATRP) has been used for the synthesis of polymeric brushes, which later demonstrated antifouling efficiencies for example, poly2-(dimethylamino)ethyl methacrylate (PDMAEMA) molecular brushes grafted onto glass or paper have demonstrated significant antimicrobial efficacy against *E. coli* and *B. subtilis* due to membrane disruption. Other compounds produced using ATRP, include microsphere surfaces grafted with quaternised PDMAEMA or poly(butylmethacrylate)-block-poly(Boc-aminoethyl methacrylate) copolymer have also demonstrated antimicrobial activity Fig 7.1.

![Fig 7.1](image)

The antibacterial activity of conjugated polymers with shortly charged, side chains has been previously studied, showing mainly that PPEs and PPVs with cationic groups had antibacterial activity [G2 + PPV antibacterial G3]. Some of previously studied copolymers are shown in Fig 7.2.
It was reported that the positively charged PPEs bearing quaternary ammonium pendants such as 7.1, 7.2 and 7.3 had greater bactericidal activity against *Pseudomonas aeruginosa* and *E. coli* compared to other compounds. It is also concluded that the advantage of the PPE derivatives with the quaternary ammonium groups arise from a combination of quaternary ammonium sites and their lipophilic interactions. Further studies also indicated that the ability of CPs to sensitise singlet oxygen is responsible for increasing the antibacterial activities. This effect is more apparent when these CPs are exposed to light. Structural modification of the PPE backbone was also reported by Whitten and co-workers substituting one phenyl ring for a thiophene which gave CPE 7.4, which is darker active. More recently
Chunlei Zhu and co-workers have studied PPVs 7.5 which have quaternary ammonium and ethylene glycol groups.\textsuperscript{460} The antibacterial efficiency of these modified PPVs was tested against subtilis, a gram positive bacteria and the E. coli a gram negative bacteria. Testing results indicates that 7.5 is active against both gram-negative and the gram positive bacteria but more darker active against the gram negative bacteria due to difference in the cell walls of these bacteria. This polymer 7.5 had better selectivity to bacterial cells when compared to mammalian cells which was predominantly attributed the ethylene glycol groups. Whitten and co-workers also observed that although anionic polymer 7.6 is active at higher concentration, it is less active compared to the other mentioned positively charged polymers.

7.2 Antibacterial Testing

7.2.1 Zones of Inhibition MIC and MBC Testing

Due to the previously reported antibacterial activities of charged CPEs we wished to determine if the polymers prepared in this project would also have these activities. We also wished to see if charge amplification would result in greater activity to those previously compounds which have less charged groups.

To test the effectiveness of the brush CPs polymers, the CP backbones (2.2 and 2.3), neutral grafted brush polymers 4.1 and 4.2, cationic grafted brush polymers 5.6, 5.7, 5.8, 5.9 and 5.10 and anionic polymers 6.1, 6.2, 6.3, 6.4 and 6.5 were tested against a range of bacteria including Enterococcus.faecium, Listeria.monocytogenes, MRSA, Staphylococcus.epidermidis, Acinetobacter.baumannii, Klebsiella.Pneumoniae, Paeruginosa, E.coli. Antibacterial testing was conducted with the assistance of collaborator Prof. Katheryn Whitehead at Manchester Metropolitan University, UK.

It was clearly shown that the cationic polymers were particularly effective against all the gram positive bacteria and also against gram negative E. coli (Fig 7.3). With the exception of some minor antimicrobial activity of the PPV backbone 2.2 against MRSA, the neutral compounds 4.1 and 4.2 and anionic compounds 6.1, 6.2, 6.3, 6.4 and 6.5 polymers did not demonstrate any antimicrobial activity. Interestingly, the none-conjugated polymer 5.6 with grafted cationic side chains also did not demonstrate antimicrobial activity. It therefore appears that the nature of both the CP backbone and the brush influences the antimicrobial efficacy of the compound.
Overall the PPEs derivatives 5.9 and 5.10 showed greater activity than the PPVs. It is also clear that the lower molecular weight polymers either PPV 5.7 or PPE 5.9 were more effective than their corresponding high molecular weight molecules 5.8 and 5.10 respectively.

\[ 
\text{Fig 7.3. Antimicrobial activity of the compounds against a range of Gram negative (}\ A.\ baumannii,\ K.\ pneumoniae,\ P.\ aeruginosa,\ E.\ coli\ )\ and\ Gram\ positive\ bacteria\ (}\ E.\ faecium,\ L.\ monocytogenes,\ MRSA,\ S.\ epidermidis).\n\]

\textit{E. faecium} was then used as the bacteria of choice to further determine the antimicrobial efficacy. \textit{E. faecium} was chosen since the polymers had demonstrated good antimicrobial efficacy towards it in the zone of inhibition testing and it is also medically important in terms of being antimicrobial resistant. The minimum inhibitory concentration (MIC) is the lowest concentration of an antimicrobial that will inhibit the visible growth of a microorganism after overnight incubation. The minimum bactericidal concentration (MBC) is the lowest concentration of an antibacterial agent required to kill a particular species of bacteria.

The compounds were tested to determine the MIC and MBC including neutral 4.1 and 4.2 polymers, non-conjugated grafted polymers 5.6 with grafted cationic CPs 5.7, 5.8, 5.9 and 5.10 and the anionic grafted CPs 6.2, 6.3, 6.4 and 6.5. It was again determined that none of the anionic compounds (6.2, 6.3, 6.4 and 6.5) or the non-conjugated grafted polymer (5.1) appeared to have any inhibitory or biocidal effect, whereas all of the conjugated grafted cationic compounds (5.7, 5.8, 5.9 and 5.10) did have activity (Fig 7.4). The MIC was determined at 78
µg mL⁻¹ in PPV-g-PTMAEMA (HMw) 5.8, 39 µg mL⁻¹ in PPE-g-PTMAEMA (LMw) 5.9, 19 µg mL⁻¹ in PPE-g-PTMAEMA (HMw) 5.10, which suggests the best antibacterial activity of PPE-g-PTMAEMA 5.10 which, results in an antibacterial activity of almost 0.25 µM. The observed antibacterial results of PPE-g-PTMAEMA 5.10 is four times higher than what it was previously observed with Whitten et al. The PPE and PPV backbones (2.2 and 2.3) also demonstrated some antimicrobial efficacies but only at high concentrations at almost 1000 µg mL⁻¹ of polymer concentration (Fig 7.4).

The MBC results demonstrated that PPE-g-PTMAEMA 5.10 with high molecular weight of quaternary amine acrylic (cationic) and PPE-g-PTMAEMA low molecular weight 5.9 were the most active. This was followed closely by the PPV-g-PTMAEMA 5.8 high molecular weight of quaternary amine acrylic 5.8 with followed by the less activity of the PPV-g-PTMAEMA (LMw) 5.7. The PPE 2.3 and PPV 2.2 backbones also demonstrated some antimicrobial kill but at high concentrations (almost 2500 µg mL⁻¹) (Fig 7.5).
As concluded in the both MIC and MBC, the conjugated grafted cationic polymers all have some level of biocidal activity, whilst the non-conjugated grafted cationic polymer 5.6 has no apparent effect.

### 7.2.2 Polymers Synergy Testing

Considering the efficient antibacterial activities of PPV-g-PTMAEMA (5.7 and 5.8) and PPE-g-PTMAEMA (5.9 and 5.10) (both with high and low molecular weight) It was decided to test them to see if combining them increased their antimicrobial activity to evaluate their synergy effect. However, the results for synergy of MIC demonstrated combination of the cationic compounds did not increase their efficacy with unchanged MICs at all combinations tested (Fig 7.6).
The antimicrobial effects of a cationic grafted polymers (5.7, 5.8, 5.9 and 5.10), and the polymer backbones (2.2 and 2.3) on bacteria and the inhibitory and biocidal effects of these compounds on *E. faecium* have been studied. All the cationic compounds showed results in the zones of inhibition, MIC and MBC tests.

Interestingly the different compounds were found to affect the bacteria in slightly different ways. For example, both high and low molecular weight PPE-g-PTMAEMA 5.9 and 5.10, were the most effective compounds against *E. faecium* and *E. coli* but were the least effective against *S. epidermidis*. However, low molecular weight PPV-g-PTMAEMA 5.7 was the most effective against *L. monocytogenes* and high molecular weight PPE-g-PTMAEMA 5.10 was the most effective against *S. epidermidis*. This suggests two ideas; either the compounds could be altered to make them more broad spectrum, or that the compounds could be adapted and synthesised to target specific bacteria, making them into more narrow spectrum biocides and potentially antimicrobials. This would be of particular interest in medical fields where the natural good bacteria within the body need to be maintained, but specific pathogenic bacteria need to be targeted. Further, this work demonstrates that the CP backbone and the length and nature of
the brushes influence the polymers efficacy against bacteria. In the future this could be further investigated in more detail to produced narrow or broad spectrum antimicrobials.

7.4 Experimental Procedures

Bacteria

The Gram-positive bacteria included, *Staphylococcus aureus, Staphylococcus epidermis, Listeria monocytogenes* and *Enterococcus faecium*.

The Gram-negative bacteria included, *Escherichia coli, Pseudomonas aeruginosa, Acinetobacter baumannii* and *Klebsiella pneumoniae*.

Zones of Inhibition

Zones of inhibition assays were carried out to determine the efficacy of the antimicrobial compounds. The compound was placed on a disc or into a well cut into an agar plate that had been seeded with bacteria. If the antimicrobial was effective, a clear zone is observed where the bacteria cannot grow (Fig 7.7). The diameter of the zone was measured and is the value reported.

*Fig 7.7.* Zone of inhibition assay demonstrating the clear zone were the antimicrobial has inhibited growth.

*Minimum inhibitory concentration (MIC) and Minimum bactericidal concentration (MBC)*

Bacteria, broth, a respiratory dye and the antimicrobials at different concentrations are added to wells in a microtitre plate (Fig 2). When the bacteria are growing, the bacteria/ cultures in the wells turn blue since they activate the respiratory dye added to the medium; this allows for
ease of differentiation (**Fig 7.8**). For the synergy testing the same method was carried out, but two compounds were added to the wells rather than one.

**Fig 7.8.** Microtitre plate with cultures growing (blue wells) used to determine the MIC and MBC. The brown wells occur when the bacteria have been inhibited or killed.
Chapter 8: Ion Sensitivity of Grafted Cationic Poly(para-phenylene vinylene)
8.1 Introduction

Conjugated polymers (CPs) have received much attention in recent years due to their potential in a wide range of applications such as optical and electrical devices,478–482 solar cells,7,483–487 surface engineering,488–490 medical and biological devices491–493 as well as sensors and actuators.302,318,413,414,494 Many researchers have focused on the specific detection of inorganic ions; a useful function in a range of biological applications.11,495–499 Within biological sensing, some ions, including iodide, have received a significant amount of attention.500–502

Due to the essential role of iodide ions in neurons and thyroid gland activity, in addition to its potential use in the pharmaceutical and chemical industry, several studies have been conducted relating to the development of iodide sensing methods and sensors.503–507

A major desirable factor in biological and environmental sensing is the water solubility of the sensors. This has been difficult to achieve, and approaches to improve water solubility in CP-based sensors has been centred around design of the conjugated backbone. Rigid, conjugated backbones are less soluble in an aqueous phase, and several ionic10,508 and non-ionic28,509–511 groups have been introduced to the conjugated backbone as pendants in an effort to improve solubility. Amongst these modified CP-based sensors, some have shown a capability for sensing anions, including iodide.505

Comparing the sensing ability of CPs with previously-used small molecules, greater sensitivity is achieved and it is well understood that the enhanced sensing ability of CPs is mostly achieved through amplification of the responsive sites.10,322,361,512

Considering the heightened sensing ability of CPs due to amplification of responsive sites, the most recent development in CP-based components has been the use of CP-grafted molecular brushes.345,357,513–515 This is due to not only high performance capability but also because of their exceptional structural efficiency.516,517 A unique feature of CP-based grafted molecular brushes arises from the conformational changes of the backbone and molecular brushes when exposed to different conditions.361 These changes were seen in Chapter five where different conformation forms occur in solvents of various polarities. The segregation of the responsive sites on the brushes from the CP backbone can result in stimuli-responsive materials.514 These materials are of particular interest to researchers in the pharmaceutical, biomedical and environmental sectors.
We therefore decided to test the ability of the cationic grafted PPV 5.7 to sense a range of anions. Considering the more flexible conformation of PPV-g-PTMAEA 5.7 compared to PPE-g-PTMAEMA 5.9, which was observed in chapter five while studying solvent polarity changes, the grafted PPV was chosen rather than the PPE. Also considering the better water solubility of low molecular weight grafted PPV 5.7 ion sensing experiments was decided to perform using this polymer rather than higher molecular weight derivative 5.8.

8.2 Effect of Hofmeister Series of Anions on Cationic Grafted PPV 5.7

Sensing in CP-based sensors is often observed when the brush-to-globule transition alters the polymer’s luminescent properties. The effect of the polymer response can often be easily monitored using anions in the Hofmeister series. It has been previously reported that the Hofmeister series interacts more strongly with long sidechains. It was therefore decided to test an anion array through the Hofmeister series, using their sodium and potassium salts, to determine both the selectivity and sensitivity of 5.7 in water.

The effect of adding each anions effects on both the UV-Vis and fluorescent spectra of a solution of 5.7 in water in the presence of different anions in various concentrations were analysed. This was done by recording the UV-Vis spectrum of a solution of 5.7 (2 mg mL⁻¹) in water and in 25 μM solutions of the indicated salts (Fig 8.1).

As is shown in Fig 8.1, the maximum absorption of grafted PPV 5.7 is around 435 nm and there was a slight spectral red shift with exposure to almost all of the salts tested, with the largest red shift being almost 10 nm in KBr, KCl, NaOH and NaI solutions. To identify if there was any relationship between the amount of red shift and anion concentration, the UV-Vis spectra of 2 mg mL⁻¹ polymer solutions with various concentrations (2.5, 4.0, 5.0 and15 μM) of iodide was studied. As can be seen in Fig 8.2 there was no relationship between the red shift in the UV spectra and iodide concentration using potassium iodide through these changes in absorption intensity (Fig 8.2).
Fig 8.1. (a) UV-Vis spectra and (b) absorption intensity changes, of polymer solution in water of Hofmeister salts.

Fig 8.2. Effect of iodide concentration changes on absorption intensity changes using KI solutions.

Next the change in fluorescent intensity of polymer solutions (2 mg mL\(^{-1}\)) in either water or the abovementioned Hofmeister series salt (25 μM) were studied after excitation at 435 nm (Fig 8.3).
The maximum emission wavelength of the polymer solution in water is observed at around 535 nm. It was also observed that in all cases, the fluorescent intensity of the polymer solution in salt solutions decreased compared to the polymer solution in water only. This decrease in fluorescent intensity was more pronounced in the presence of iodide compared to other anions (Fig 8.3b). As well as a decrease in intensity a small, 5 nm and 10 nm, spectral blue shift in KI and NaI solutions, respectively, was observed.

To further analyse the effect of iodide on the photoluminescence properties of the 5.7, the changes in fluorescent intensity of polymer solutions in NaI and KI at different concentrations (2.5, 5.5, 10, 15 and 25 μM) of anion were then measured (Fig 8.4).
As is shown in Fig 8.4, the fluorescent intensity increases in magnitude with decreasing iodide concentration, both in NaI and KI solutions.

The fluorescence intensity of the grafted PPV 5.7 when exposed to each of the various anions at different concentrations was then measured (Fig 8.5).
As is seen in Fig 8.5, the polymer 5.7 shows maximum response to changes in iodide salt concentration compared to other anions with decreasing fluorescent intensity as iodide concentration increases. A smaller reduction in intensity is also observed with hydroxide, see section 8.3 below for details on pH effects.

The decrease in fluorescence intensity was then measured for iodide ion concentration at lower concentrations, between 1 μM and 6.5 μM using KI solutions of 5.7 (Fig 8.6).

![Fig 8.6. Relative fluorescence intensity changes of PPV-g-PTMAEA with increasing iodide ion concentration at λ<sub>max</sub> = 535 nm.](image)

It was observed that the decrease in fluorescence intensity has a positive linear relationship in this range with iodide ion concentration ($R^2 = 0.98$). Further detection limit (DL) was calculated using IUPAC equation (Equation 8.1), which shows the DL of $1 \times 10^{-8}$ molL$^{-1}$.

$$DL = 3 \times \sigma$$

Equation 8.1. IUPAC Detection limit formula
Where in Equation 8.1 $\sigma$ is the standard deviation of the samples signals being repeated for repetitions.

### 8.3 Evaluating pH Effect on Iodide Sensing

Due to the reduced fluorescent intensity upon exposure to hydroxide the effect of pH on the iodide sensing ability of grafted PPV 5.7 was examined. The fluorescence intensity at 535 nm of polymer 5.7 in 25 $\mu$M of KI solution was monitored while changing pH from 2 to 14. The unaltered pH of grafted PPV 5.7 in an aqueous solution is 7.5. Reducing the pH from 7.5 to 2 (using 2 M HCl) showed no significant changes in either spectral shift or fluorescence intensity. Increasing the pH from 7.5 to 14 (by adding 2 M NaOH) exhibited an effect on the fluorescence. Increasing the pH between 7.5 and 12 (by adding 2 M NaOH) shows a reduction in fluorescence intensity of approximately 30 % with no red shifting. Further increasing the pH from 12 to 14 resulted in gradual red shift as well as further decrease in fluorescent intensity of almost 46 % of the value of pH 7.5 (Fig 8.7).

![Fig 8.7. Iodide sensing variations at pH ≥ 7.5.](image-url)
It is also of note that these results are in accordance with what was observed in the behaviour of the polymer with hydroxide in the Hofmeister series effects discussed earlier. Therefore, such a decrease in fluorescent intensity can probably be attributed to the synergic effect of highly concentrated hydroxide and iodide ions, which induces further fluorescence quenching as well as maximum emission spectral shift. It could be concluded that iodide sensing using grafted PPV 5.7 is best achieved below pH 12.

8.4 Evaluating the Effect of Temperature

To investigate the effect of temperature on the spectroscopic properties and sensing ability of grafted PPV 5.7, the fluorescence intensity measurements were taken at 535 nm using 1.5 mg mL\(^{-1}\) of grafted polymer in water, while increasing temperature from 25 °C to 70 °C (Fig 8.8).

**Fig 8.8.** (a) Actual, and (b) Relative fluorescence intensity changes of PPV-g-PTMAEA in varying temperatures.
As is observed, the fluorescent spectrum of grafted PPV showed an approximately 22 % decrease in fluorescence intensity and no observable spectral shift in maximum emission wavelength with increasing temperature from 25 °C to 70 °C (Fig 8.8.a). Fluorescent intensity decreased linearly with increasing temperature across the temperature range studied (Fig 8.8.b).

A further experiment was also conducted using 1.5 mg mL⁻¹ of polymer 5.7 in 25 μM KI solution (Fig 8.9), in this case results show a non-linear decrease in the relationship between temperature and relative fluorescence intensity. The non-linear relationship may be attributed to the variation in solution turbidity with increasing temperature, which results in random movement of iodide ions.

8.5 Reversibility of Iodide Sensing

One important future for the development of chemical sensors is their reversibility so future sensing is not compromised after each test run. To initially test the reversibility of the fluorescence quenching by iodide random amounts of KCl solution (2.5 M) was added into a solution of polymer 5.7 (1.5 mg mL⁻¹) in KI solution. It was noticed that the colour of the polymer solution changed from dark red to yellow upon addition of chloride. This yellow
colour formed was seen for all the polymer-anion solutions except those containing iodide. This suggested displacement of iodide with chloride by the polymer.

To quantitatively determine this reversibility, 1.5 mg mL\(^{-1}\) solutions of polymer in 2.5 µM KI were tested with increasing concentrations of KCl, and the change in fluorescence intensity at 535 nm was monitored. It is proposed that such a high KI concentration might induce a collapse in conformation of the grafted molecular brushes.\(^{361}\) To this end, 100 µL of concentrated KCl solution was directly added into the 2 mL polymer sample for each experiment in order to prevent a dilution effect. It was discovered that the fluorescent intensity of the grafted polymer increased with increasing concentrations of KCl (Fig 8.10).

![Fig 8.10](image)

Fig 8.10. (a) Reversibility of iodide sensing against changes in fluorescence intensity changes and (b) relationship of fluorescence intensity and KCl concentration.
Analysing the changes in fluorescence intensity shows a minor improvement in fluorescent intensity when adding less than 0.23 mM of KCl. Despite a small increase in fluorescence intensity, a spectral blue shift of around 15 nm is observable; a behaviour opposite observed to that shown in the presence of increasing iodide ions. The fluorescence intensity at the highest KCl concentration (2 mM) is approximately 1.8 times that at the lowest KCl concentration measure (0.025 mM), showing a roughly linear, positive relationship between KCl concentration and fluorescence intensity (Fig 8.10). Initial polymer solution at the presence of 2 mM KCl solution showed fluorescent intensity increasing up to 86 a.u. Although this fluorescent intensity is lower than that observed of a solution of polymer 5.7 in water, it shows that some reversibility over iodide sensing though not complete is observed.

8.6 Iodide Sensing Mechanism

The changes in fluorescent intensity of grafted PPV 5.7 upon exposure to iodide can be rationalised by understanding the effect of anions on the cationic grafted brushes. To evaluate this transduction response mechanism, the effect of iodide, as a chaotrope ion in the Hofmeister series, on the configuration of the grafted brushes should be considered.

As was discussed in Chapter five, water is a good solvent for the highly charged grafted brush polymers but in contrast is a poor solvent for the lipophilic PPV backbone. Considering previous studies in such complex solvent conditions, steric interactions of water-soluble grafted molecular brushes prevents the multimolecular polymer aggregation, which consequently results in a completely water soluble grafted polymer with a star shape brush-g-globule structure. Because of this, it was hypothesized that grafted PPV 5.7 solution in water could also exhibit such a star shape configuration, which is related to the positively charged quaternary ammonium brushes Fig 8.11.

Fig 8.11. Schematic structure of PPV-g-PTMAEMA in water and in iodide solution.
Adding iodide as a strong chaotrope ion may then disrupt intramolecular interactions of the grafted PPV which induces salting out, which occurs through the disruption of the hydrogen bonding network between water and molecular brushes, followed by a collapse of the grafted molecular brushes. Consequently, the collapsed grafted molecular brushes could further reduce intermolecular interaction because of a decrease in charged repulsion.

To investigating such effects, Atomic Force Microscopy (AFM) as well as Dynamic Light Scattering (DLS) studies were conducted as methods to monitor conformational changes of the polymer when exposed to iodide ions. Tapping mode AFM was used to generate images, deposited on mica, of the polymer in both water and an iodide solution (25 µM). A clear conformational change can be seen between these two conditions (Fig 8.12) with large aggregates present for the polymer deposited from the iodide solution.

![AFM images of PPV-g-PTMAEA 5.7 in water (A, C) and iodide solution (B, D). Scan size 10 µm in A and B, and 2 µm in C and D. The vertical scale is 20 nm in A, 300 nm in B and 80 nm in C and D.](image)

Additionally, the size distribution of freshly made solutions of the PPV-g-PTMAEA 5.7 in water and iodide solution in different concentrations were examined using DLS (Fig 8.13).
It can be seen through the DLS results, that increasing iodide ion concentration using either KI or NaI solutions results an increase in polymer size distribution from almost 120 nm to 900 nm. Both results clearly show increased aggregation upon addition of iodide.

**8.7 Summary**

In conclusion the obtained results revealed that PPV-g-PTMAEMA afforded good selectivity for iodide ion within the Hofmeister series while comparing the changes in fluorescence intensity of the grafted polymer. A detection limit for iodide ion sensitivity was determined to be $1 \times 10^{-8}$ M.

The mechanism of iodide ion sensing was studied using DLS and AFM, which indicates aggregation of the grafted molecular brushes at the presence of iodide ion. Results also clarify that the other factors such as temperature and pH can affect the iodide sensing procedure though only moderately.
8.8 Experimental Procedure

8.8.1 Materials and Measurements

UV-Visible absorption spectra were measured with a Pharmaspec UV-1700, Shimadzu UV-Visible spectrophotometer. Fluorescence spectra were measured with a Perkin Elmer LS 55 spectrophotometer with a 3-Q-10 mm rectangular quartz cell.

Dynamic light scattering (DLS) measurements were also conducted using wide angle light scattering photometer from Malvern Zetasizer. The light source with red badge at \( \lambda_0 = 632.8 \) nm emitting vertically polarized light. The cells were placed into the DLS-5000 compact goniometer system and sat in vat of \textit{cis}-decahydronaphthalene, which matched the index of refraction of the glass cell. The scattered light was detected by a S90 and ZS90 instruments use optics that have a 90° scattering detector angle. Angular was consisted of scattering angles between 12.8° and 175°. All DLS experiments were implemented in water and potassium iodide solution with particular concentrations.

8.8.2 Spectroscopic Measurements

UV-Vis spectroscopy measurements of PPV-g-PTMAEA 5.7 were conducted using 1 mg mL\(^{-1}\) of the polymer solution dissolved either in pure mili Q water (resistivity at 25 °C filter, 18.2 \( \Omega \)) or Hofmeister series salt solutions (2.5-25 \( \mu \)M). The spectral shift of the \( \lambda_{\text{max abs}} \) was monitored.

In order to conduct fluorescence spectroscopy measurements 1 mg mL\(^{-1}\) of the grafted polymer solution was further diluted to 25 \( \mu \)g mL\(^{-1}\), preventing further polymer self-quenching. Spectral shifts of the \( \lambda_{\text{max emis}} \) as well as the fluorescent intensity changes were tracked using various Hofmeister series salts at different concentrations.
8.8.3 Light Scattering Measurements

Dynamic light scattering measurements were conducted using wide angle light scattering photometer. In order to compare polymer sizes 10 μL of 1 mg mL⁻¹ polymer in water and potassium iodide solutions, with various concentrations (2.5 μM-25 μM), was added directly into 1.5 mL milli Q water. All the experiments were done at room temperature in plastic disposable cuvettes and adjusting angular range between 30° and 150°.

8.8.4 Atomic Force Microscopic Measurements

AFM was performed using an Asylum Research Cypher ES instrument (Oxford Instruments, US). Images were acquired in air using tapping mode with a Tap150 probe (resonance frequency 175 kHz, force constant 1.5 N/m to 15 N/m) from Budget Sensors (Bulgaria). During the post-processing of images, the background of the images were flattened, while the features were preserved by masking.

Samples for AFM were prepared on freshly cleaved mica, which was exposed to a drop of diluted polymer solution (2 mg mL⁻¹) in water or potassium iodide solution (25 μM) and allowed to dry overnight.
Chapter 9: Conclusion and Future Work
9.1 Summary of the Research

The aim of this project was to prepare grafted, brush-like, conjugated polymers based on PPV and PPE scaffolds. This initially required the synthesis of functionalised monomers to allow preparation of these CPs. Four functionalised monomers (2.4, 2.10, 2.5 and 2.11) were desired. In order to achieve such functionalised monomers Stille and Sonogashira reactions were utilised on monomer 2.6 to finally afford monomers 2.4 and 2.10 respectively. Hydroxyl functionalised monomer 2.5 was successfully synthesised and was then used for the synthesis of bromoester functionalised monomer 2.11.

Afterwards, Heck and Sonogashira polymerisation reactions were conducted combining monomers 2.4 and 2.5, as well as 2.5 and 2.10 for the synthesis of hydroxyl functionalised PPV and PPE. Using monomers 2.4 and 2.10 resulted in the either PPV 2.2 or PPE 2.3 backbones having lateral triglycol pendants as spacer, which were designed to space out and separate the grafted polymers. The hydroxyl functionality was incorporated for post polymerisation esterification, which was succesful on PPVOH 2.2. However poor esterification reactions of PPEOH 2.3 resulted in the direct synthesis of PPEMI 3.2.2 utilising monomers 2.10 and 2.11 based on Sonogashira polymerisation reaction. The successful synthesis of hydroxyl functionalised (2.2 and 2.3) and bromoester functionalised (3.1 and 3.2.2) PPV and PPE were confirmed using 1H NMR and FT-IR. Comparing with PPVOH 2.2 and PPEOH 2.3, macroinitiators (3.1 and 3.2.2) showed better processability in an organic solvents, which was favourable for the further grafting polymerisation.

Having successfully established the synthesis pathway of the PPVMI 3.1 and PPEMI 3.2.2, grafting polymerisation were conducted to introduce neutral, cationic and anionic lateral grafted molecular brushes. It was determined that ARGET ATRP was best suited for grafting polymerisation of neutral, cationic and anionic molecular brushes. When grafting anionic molecular brushes, it was determined that due to solubility issues with the SPA monomer, a phase transfer complexation process using 18-crown-6 was necessary to use in order to successfully achieve the desired grafts.

All of the grafted polymers (4.1, 4.2, 5.6, 5.7, 5.8, 5.9, 5.10, 6.1, 6.2, 6.3, 6.4 and 6.5) all had appropriate molecular weights and good chemical yields when compared to the same compounds achieved using conventional ATRP. It is proposed that the reduced susceptibility
of the ARGET ATRP to oxygen allowed greater controllability in the synthesis of these grafted polymers especially under the more polar conditions used.

In all grafting polymerisations, loss of conjugation in the CP backbones was observed using UV-Vis and was more dominant in PPV grafted polymers compared to the PPEs. It is proposed that reduced loss of conjugation is related to increased rigidity and stability in the PPEs compared to the PPVs. The loss of conjugation was also confirmed using the fluorescence spectra of both PPV-g-nBA 4.1 and PPE-g-nBA 4.2 which all indicated spectral blue shifting after grafting polymerisation. Both PPV 4.1 and PPE 4.2 grafted PnBA molecular brushes adapted the physical properties of the acrylate grafted brushes rather than the PPV and PPE backbones. After grafting polymerisation both grafted polymers (4.1 and 4.2) exhibited increased photophysical properties compared to the CP backbones, which resulted in solid state fluorescence. Such solid state fluorescence is due to the reduction of interchain interactions, which occurs by separation of the CP backbones after PnBA grafting. The CP backbone extension and separation results from the organic solvent compatibility of the both CP backbones and grafted brushes in PPV-g-PnBA 4.1 and PPE-g-PnBA 4.2.

Next the grafting of both cationic and anionic molecular brushes PPV-g-PTMAEMA (5.7 and 5.8), PPE-g-PTMAEMA (5.9 and 5.10) and PPV-g-PSPA (6.2 and 6.3) and PPE-g-PSPA (6.4 and 6.5) was achieved. Similar to what was observed in both 4.1 and 4.2, the charged grafted polymers also had physical properties of the grafted molecular brushes. It was found that polymers with increased grafting (5.8, 5.10, 6.3 and 6.5) had reduced aqueous solubility due to their increased molecular weight.

Photophysical studies of the charged grafted PPVs and PPEs determined that these polymers are still photophysically active. A noticeable spectral blue shift in the UV-Vis spectra was observed after grafting polymerisation for all of the charged grafted polymers and was more dominant in grafted PPVs, most particularly in an anionic polymer 6.2.

Photoluminescence studies of the charged grafted polymers showed spectral red shifting in both PPE-g-PTMAEMA 5.9 and PPE-g-PSPA 6.4, which was not observed in the corresponding PPVs (5.7 and 6.2). Considering the reduced physical compatibility of the CP backbones with the charged grafted molecular brushes, solvent polarity studies were conducted using different water-methanol solvent systems. Also, to better understand the sensitivity of the grafted CPs to the solvent polarity, the photoluminescent properties of neutral grafted PPV-g-
PnBA 4.1 and PPE-g-PnBA 4.2 in THF-EtOAc solvent systems was also examined. It was discovered that for both neutral and charged grafted polymer cases, the PPVs showed less change when the solvent polarity was altered and this was attributed to greater PPV flexibility compared to PPEs, which enables PPV grafted polymers to be folded and achieve micellar conformations within polar environments. However, the rigid structures of the PPE backbones, in all of the charged and neutral grafted PPEs, resulted in spectral red shifting in the fluorescent spectra as the polarity was increased, which suggests increased aggregation rather than the micelle formation.

After successfully synthesising grafted molecular brushes their applications were investigated. Considering the well established antibacterial properties of the quaternary ammonium compounds, the antibacterial activity of the all of the neutral and charged grafted polymers as well as the ungrafted CP backbones were studied using a range of bacteria. It was determined that all of the cationic CPEs were antibacterial, while the neutral and the anionic grafted polymers showed no activity. It was discovered that the non-conjugated cationic grafted polymer 5.6 was not active. This determined that the antibacterial activity of the cationic CPEs was dependant on both the conjugated backbone and the density of the positively charged groups. The high molecular weight PPE-g-PTMAEMA 5.10 showed the best antibacterial activity with greater activity than the less densely grafted polymer 5.9. The antibacterial activity of the high molecular weight PPE-g-PTMAEMA 5.10 is observed to be even higher than what it was previously observed with Whitten et al showing that amplification of charged sites by grafting can lead to more active compounds.

The increased aqueous solubility of the lower molecular weight and less densely grafted polymers allowed an investigation of their use as sensors. In particular low molecular weight PPV-g-PTMAEMA 5.7 was chosen to study the anion sensing ability using series of Hofmeister series ions. It was determined using the photoluminescence spectra that in most case the fluorescence intensity decreased with increasing ion concentration. The ion sensitivity was more noticeable in case of iodide, which was clearly observed while studying photoluminescence spectra of different concentrations of NaI or KI. The interaction of anions with grafted PPV 5.7 resulted in changes in the conformation of the brushes, which is transduced to the PPV backbone. The selectivity to iodide is proposed to be due to its size and iodide salting out property, which consequently results in trapping iodide ion within the grafted molecular brushes and breaking down of the hydrogen bonding network of the water around.
the PPV-g-PTMAEMA 5.7. This results in reduced solubility in water and results in aggregation. This mechanism was verified using DLS and AFM testing, which both confirmed aggregation.

9.2 Future Work

Synthesis of neutral, cationic and anionic grafted molecular brushes using the PPV and PPE macroinitiators has successfully established in this project within ARGET ATRP. However, of ARGET ATRP is known to be incompatible with a range of acrylates and acylamides especially to more polar acrylate monomers such as zwitterionic ones.197,525,526 In this case RAFT polymerisation could be used as an alternative method to prepare brushes of these types.

Considering this, monomers 9.1 could be synthesised from previously prepared bromoester 2.11. The thiocarbamate in 9.1 allows RAFT polymerisations at this site. Alternatively the thiocarbamate could be added post-polymerisation to PPVOH 2.2 or PPEOH 2.3. The proposed synthesis pathway using RAFT polymerisation is depicted in Scheme 9.1.

Scheme 9.1. Retro synthesis pathway of the RAFT initiator.
In regard to the antibacterial activity of these polymers Whitten et al. showed that better antibacterial activity could be obtained using a thiophene substituted PPE (Fig 9.1).\textsuperscript{32} It would be interesting to investigate whether grafting of cationic brushes from such a PPE derivative has greater activity than that on solely PPE backbone reported in this thesis.

![Fig 9.1. Proposed structure of the new ATRP functionalised PPE.](image)

Additionally, due to the ion sensing ability of the cationic grafted PPV \textsuperscript{5.7}, it might be possible to explore if such polymer could be further attached to the surface to achieve a surface grafted cationic polymer, which may have application as a solid sensor (Fig 9.2).
Fig 9.2. Proposed structure of the cationic surface grafted PPE.
References
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