Soft Polymeric Nanoparticles as Additives for CO$_2$ Separation Membranes

by

ANDRI HALIM
B. Eng (Hons, I)

Submitted in total fulfillment of the requirements of the degree of
Doctor of Philosophy

2014

Department of Chemical and Biomolecular Engineering
The University of Melbourne
Abstract

The use of polymeric membranes for gas separation has experienced a major expansion in the past few decades with current applications which include the separation of CO$_2$ from flue gas. Various approaches have been explored to fabricate membranes with superior separation performance that can exceed the current upper performance limit. These include the incorporation of hard inorganic nanoparticles into polymers to form mixed-matrix membranes (MMMs).

The performance of MMMs can be further enhanced if they can be fabricated into asymmetric morphology. The fabrication of asymmetric membranes, in the form of a thin film composite (TFC) membrane, is more commercially viable due to the increased flux and reduced consumption of expensive nanoparticles. TFC membranes are typically composed of a porous support coated with a highly permeable gutter layer, which is in turn coated with a thin active layer. However, the development of effective asymmetric MMMs has been limited. This is due to the difficulty in fabricating nanoparticles in a size that does not exceed the thickness of the active layer and in avoiding defects in the resulting composite structure.

The fabrication of next generation mixed-matrix gas separation membranes is also hampered by the need to ensure a defect-free polymer/inorganic particle interface. A similar approach can be applied to the addition of soft polymeric nanoparticles into a selective polymer matrix. In this case, the problem of defects occurring between the particle and the matrix can be avoided through the engineering of particles that are compatible with the polymer matrix.

Hence, this thesis aims to synthesize novel soft polymeric nanoparticles with well-defined architectures and utilize these as additives to be incorporated into the thin active layer of TFC membranes. The requirements for these nanoparticles include (a) a soft and CO$_2$ permeable core and (b) a corona which is compatible with the polymer
The best candidate nanoparticles are then blended with a selective polymer matrix to form the active layer of TFC membranes, which are tested for their CO₂ separation from N₂. The size of the soft polymeric nanoparticles are significantly smaller than the thickness of the active layer and overcome the problem of blending larger inorganic nanoparticles to form asymmetric MMMs.

The first soft polymeric nanoparticles studied were based on triblock copolymers containing polyimide (PI) and poly(dimethylsiloxane) (PDMS). Well-defined difunctional PI was initially prepared via step-growth polymerization. Subsequently, PI was functionalized and chain extended with different molar ratios of PDMS-monomethacrylate (PDMS-MA) via atom transfer radical polymerization (ATRP) to form a series of triblock copolymers. Self-assembly of triblock copolymers in a selective solvent for PI, followed by cross-linking via hydrogen abstraction, resulted in the formation of well-defined nanoparticles with a soft PDMS core.

The second soft polymeric nanoparticles developed in this study was based on diblock copolymers containing poly(ethylene glycol) (PEG) and PDMS. Commercially available PEG was utilized as a substitute for the PI block due to the difficulty in synthesizing well-defined polymers via step-growth polymerization. Three different molecular weights of monomethyl ether PEG were initially functionalized to form macroinitiators suitable for ATRP. These macroinitiators were then chain extended with PDMS-MA and photoactive anthracene moieties in different molar ratios to afford a series of photoresponsive diblock copolymers. Self-assembly of diblock copolymers in a selective solvent for PEG, followed by photocross-linking via [4+4] photodimerization of anthracene moieties, resulted in the formation of another well-defined soft polymeric nanoparticles with various structures that range from spherical micelles to large compound micelles.

The preparation of soft polymeric nanoparticles through the self-assembly of block copolymers is generally carried out in low concentration to avoid aggregation of nanoparticles. This hinders the preparation of nanoparticles on a larger scale. The
third soft polymeric nanoparticles explored in this thesis were based on PEG and PEG-
b-PDMS grafted star polymers that were synthesized via the ‘core-first’ approach. This
method allows the preparation of nanoparticles in high yields as the crude reaction
mixture only requires separation from unreacted monomers. Various grafted star
polymers with different PEG and PDMS molar ratios were synthesized in high yields
and high conversions utilizing a four-arm ATRP initiator. These grafted star polymers
were then utilized as additives for existing gas separation membranes.

TFC membranes were prepared from commercially available selective poly(amide-\textit{b-}
ether) (Pebax® 2533) that was blended with a series of PEG and PEG-\textit{b}-PDMS grafted
star polymers. These blends formed a thin film on microporous polyacrylonitrile
substrates which have been pre-coated with a PDMS gutter layer. Their ability to
selectively separate CO\textsubscript{2} from N\textsubscript{2} was studied at 35 °C and an upstream pressure of 3.4
bar. The addition of soft polymeric nanoparticles into the thin active layer of TFC
membranes resulted in greatly improved flux as these particles are able to form
localized, high flux, soft domains within a selective polymer matrix. These results
create an interesting route to further develop and utilize soft polymeric nanoparticles
as additives in membranes for gas separation processes.
This is to certify that

(i) This thesis comprises only my original work towards the PhD,

(ii) Due acknowledgement has been made in the next to all other material used,

(iii) This thesis is less than 100,000 words in length, exclusive of tables, figures, bibliography and appendices.

Andri Halim
February 2014
The tetra-functional initiator described in Chapter 4 was synthesized by Dr Anton Blencowe.
Completing my PhD degree has probably been the most challenging, yet exciting and fulfilling activity in my life. The best and worst moments of the journey have been shared with many people who are very close to my heart.

First and foremost, I would like to express my heartfelt gratitude to Professor Greg Qiao. I would like to thank him for giving me uncountable opportunities, from designing parts of undergraduate modules, to peer-reviewing publications for many highly-ranked international journals. Most importantly, I would like to thank Greg for his ideas and enthusiasm towards the completion of this thesis. I am truly grateful for his guidance that has shaped me to be a better researcher and communicator in science. Greg definitely has brought out the best in me.

Special thanks to my second supervisor, Professor Sandra Kentish, for her warm encouragement and thoughtful guidance. I would also like to thank Sandra for giving me the opportunity to be involved in organizing the 2013 International Membrane Science and Technology Conference (IMSTEC). This experience has helped hone my time management and organization skills, both of which were essential given the tight deadlines for the conference and my thesis.

I would like to thank Dr Paul Gurr and Dr Qiang Fu. Thank you Paul for being there for me from the very first day. Thank you Qiang for all your help and the meaningful discussions. Both of you have been of great help and I am very grateful for that.

Many thanks to Dr Anton Blencowe – thank you for always sharing your immense knowledge and for always being there when I needed help. I would not have completed my PhD without your inputs and guidance.
My time at the Polymer Science Group was made enjoyable due to many friends that became a part of my life. Many thanks to Mr Jing Ming Ren who always helped me when I encountered problems with polymer synthesis. Thanks to the three sisters, Dr Stefanie Nina Guntari, Ms Shereen Tan and Ms Enhyung Nam, for the endless jokes, who never fail to make me laugh even at my most stressful times.

I am very humbled to have received many sources of funding throughout my PhD journey. I would like to thank the Cooperative Research Centre for Greenhouse Gas Technologies (CO2CRC) for providing me with my living stipend and The University of Melbourne for the Melbourne International Fee Remission Scholarships (MIFRS) that covers tuition costs. I am also truly honoured to have received the prestigious Eugen Singer Award, as well as the Melbourne Abroad Travel Scholarship (MATS) and Particulate Fluid Processing Centre (PFPC) Travel Grant. These have provided funding for my travel to South Korea to visit the Membrane Laboratory in Hanyang University and Taiwan to attend the 13th Pacific Polymer Conference.

I would also like to thank all my good friends whom I cannot possibly list out completely. They have always believed in me, more than I do myself. Thank you all.

Last but not least, I would like to thank my family for their endless love and support. They have provided me with more than I could ever ask for, and have never failed to make me feel that I am blessed.
Peer-reviewed Journal Papers

Chapter 2

“Synthesis and self-assembly of polyimide/poly(dimethylsiloxane) brush triblock copolymers”


*Polymer.* **2013**, *54*, 520 – 529.

Chapter 3

“Soft nanoparticles assembled from linear poly(ethylene glycol) and linear brush poly(dimethylsiloxane) diblock copolymers”

Andri Halim, Timothy D. Reid, Jing M. Ren, Qiang Fu, Paul A. Gurr, Anton Blencowe, Sandra E. Kentish and Greg G. Qiao.


Chapter 4 and 5

“Soft polymeric nanoparticles additives for next generation gas separation membranes”

Andri Halim, Qiang Fu, Qiwyn Yong, Paul A. Gurr, Sandra E. Kentish and Greg G. Qiao.


Other Publications

“Highly permeable membrane materials for CO₂ capture”

Qiang Fu, Andri Halim, Jinguk Kim, Joel M. P. Scofield, Paul A. Gurr; Sandra E. Kentish and Greg G. Qiao.
"The effect of crosslinking temperature on the permeability of PDMS membranes: evidence of extraordinary CO₂ and CH₄ permeation"


“Novel mixed matrix membranes for CO₂ capture”

**Andri Halim**, Paul A. Gurr, Chun Yong Tan, Anton Blencowe, Sandra E. Kentish and Greg G. Qiao

- All Energy Conference (Melbourne, Australia), 6 – 7 October 2010 (Poster)

*Awarded the Best Poster Presentation: Australian Institute Energy Postgraduate Award 2010 – 1st Prize for General Energy Project*

- CO2CRC Research Symposium 2010 (Melbourne, Australia), 1 – 3 December 2010 (Poster)

“Self-assembly as a route to fabricating membranes with superior separation characteristics”

**Andri Halim**, Wilcent Chua, Paul A. Gurr, Anton Blencowe, Sandra E. Kentish and Greg G. Qiao

- CO2CRC Research Symposium 2011 (Adelaide, Australia), 29 November – 1 December 2011 (Poster)

*Awarded the People’s Choice for Best Poster*

“Nano-flowers to capture CO₂”

**Andri Halim**, Paul A. Gurr, Anton Blencowe, Sandra E. Kentish and Greg G. Qiao

- All Energy Conference (Melbourne, Australia), 10 – 11 October 2012 (Poster)

*Awarded the Best Poster Presentation: Australian Institute Energy Postgraduate Award 2012 – 1st Prize for Fossil Fuel Projects*

- Australian Institute Energy National Conference (Sydney, Australia), 16 – 19 November 2012 (Poster)

*Awarded the Highly Commended Poster Presentation*
“Novel permeable additives for gas separation membranes”

Andri Halim, Paul A. Gurr, Sandra E. Kentish and Greg G. Qiao

- CO2CRC Research Symposium 2012 (Sunshine Coast, Australia), 27 – 29 November 2012 (Oral)

Awarded the Best Oral Presentation in Materials and Process Development

"Novel grafted star polymers for advanced composite gas separation membranes"

Andri Halim, Qiang Fu, Paul A. Gurr, Anton Blencowe, Sandra E. Kentish and Greg G. Qiao

- 13th Pacific Polymer Conference (Kaohsiung, Taiwan), 17 – 22 November 2013 (Oral)
- 8th International Membrane Science and Technology Conference (Melbourne, Australia), 25 – 29 November 2013 (Oral)
# Chapter 1: Polymer Gas Separation Membranes: Past, Present and Future Challenges

1.1 Background ........................................................................................................................................1

1.2 Membrane technology ..........................................................................................................................3
  1.2.1 Gas transport mechanism ................................................................................................................4
    1.2.1.1 Solubility .....................................................................................................................................5
    1.2.1.2 Diffusivity ...................................................................................................................................8
    1.2.1.3 Permeability ..............................................................................................................................8
    1.2.1.4 Selectivity ..................................................................................................................................9

  1.2.2 Membrane configuration ................................................................................................................10

1.3 Polymer science .....................................................................................................................................11
  1.3.1 Polymeric membrane materials ........................................................................................................11
    1.3.1.1 Polyimides ................................................................................................................................12
1.3.1.2 Poly(dimethylsiloxane) .................................................................13
1.3.1.3 Poly(ethylene glycol) ....................................................................13

1.3.2 Polymerization techniques ..................................................................14
  1.3.2.1 Step-growth polymerization .........................................................14
  1.3.2.2 Chain-growth polymerization .......................................................15

1.3.3 Polymeric architectures .......................................................................19
  1.3.3.1 Micelles ..........................................................................................19
  1.3.3.2 Star polymers ................................................................................21

1.4 Current challenges in CO\textsubscript{2} separation membranes .................23
  1.4.1 Block copolymers for CO\textsubscript{2} separation ......................................25
    1.4.1.1 Well-defined block copolymer .......................................................26
    1.4.1.2 Multi block copolymers .................................................................28
  1.4.2 Mixed-matrix membranes ................................................................29
    1.4.2.1 Dispersion of particles .................................................................30
    1.4.2.2 Interfacial morphology .................................................................31

1.5 Objectives ..................................................................................................32

1.6 Thesis outline ..........................................................................................34

1.7 References ................................................................................................38

**Chapter 2:** Soft Polymeric Nanoparticles Based on Linear Polyimide and Linear Brush Poly(dimethylsiloxane) Triblock Copolymers

1.1 Chapter perspective ..................................................................................45

1.2 Introduction .............................................................................................46

1.3 Result and discussion ..............................................................................50
  1.3.1 Synthesis of $\alpha,\omega$-diamino poly(6FDA-co-TMPD) .......................50
  1.3.2 Synthesis of $\alpha,\omega$-dibromo poly(6FDA-co-TMPD) macroinitiator ...........................................................................................................51
  1.3.3 Synthesis of polyimide/poly(dimethylsiloxane) triblock copolymers ...........................................................................................................55
Chapter 3: Soft Polymeric Nanoparticles Based on Linear Poly(ethylene glycol) and Linear Brush Poly(dimethylsiloxane) Diblock Copolymers

3.1 Chapter perspective ..........................................................67
3.2 Introduction .....................................................................................68
3.3 Result and discussion ........................................................................71
  3.3.1 Synthesis of α-methyl, ω-bromo functionalized poly(ethylene glycol) macrorinitiators ..........................................................71
  3.3.2 Synthesis of poly(ethylene glycol)/poly(dimethylsiloxane) diblock copolymers ..........................................................75
  3.3.3 Self-assembly of poly(ethylene glycol)/poly(dimethylsiloxane) diblock copolymers ..........................................................80
  3.3.4 Photocross-linking of poly(ethylene glycol)/poly(dimethylsiloxane) diblock copolymers ..........................................................85
3.4 Chapter summary................................................................................89
3.5 References .........................................................................................90

Chapter 4: Soft Polymeric Nanoparticles Based on Poly(ethylene glycol) and Poly(ethylene glycol)-b-poly(dimethylsiloxane) Grafted Star Polymers

4.1 Chapter perspective ........................................................................93
Chapter 5: Soft Polymeric Nanoparticles as Additives for CO₂ Separation Membranes

5.1 Chapter perspective .............................................................................................................107
5.2 Introduction ..........................................................................................................................108
5.3 Membrane preparation ........................................................................................................111
  5.3.1 Preparation and characterization of cross-linked PDMS gutter layers ........................................112
  5.3.2 Preparation and characterization of active layers ................................................................112
5.4 Result and discussion ...........................................................................................................113
  5.4.1 Pure gas permeation characteristics of thin film composite membranes ..................................113
  5.4.2 Pure gas permeation characteristics of active layers ..........................................................117
  5.4.3 Effect of PDMS content on CO₂ permeability ....................................................................119
5.5 Chapter summary ..................................................................................................................121
5.6 References ...........................................................................................................................122

Chapter 6: Conclusions and Future Perspective

6.1 Conclusions ...........................................................................................................................125
6.2 Future perspective .................................................................................................................128
  6.2.1 High performance polyimide-based thin film composite membranes ......................................128
7.2.6 Cross-linking of polyimide/poly(dimethylsiloxane) triblock copolymers ................................................................. 139
7.2.7 Imaging of uncross-linked polyimide/poly(dimethylsiloxane) triblock copolymers ............................................................... 140
7.2.8 Imaging of cross-linked polyimide/poly(dimethylsiloxane) triblock copolymers ............................................................... 140

7.3 Experiments for chapter 3 ................................................................. 140
7.3.1 Materials ................................................................. 140
7.3.2 Synthesis of α-methyl, ω-bromo functionalized poly(ethylene glycol) macroinitiators ......................................................... 141
7.3.3 Synthesis of 2-(methacryloyloxy)ethyl anthracene-9-carboxylate ........................................................................ 141
7.3.4 Synthesis of poly(ethylene glycol)/poly(dimethylsiloxane) diblock copolymers ................................................................. 142
7.3.5 Self-assembly of poly(ethylene glycol)/poly(dimethylsiloxane) diblock copolymers ................................................................. 143
7.3.6 Photocross-linking of poly(ethylene glycol)/poly(dimethylsiloxane) diblock copolymers ......................................................... 143
7.3.7 Photocleavage of poly(ethylene glycol)/poly(dimethylsiloxane) diblock copolymers ................................................................. 143
7.3.8 Imaging of uncross-linked and photocross-linked poly(ethylene glycol)/poly(dimethylsiloxane) diblock copolymers ............. 144

7.4 Experiments for chapter 4 .................................................................... 144
7.4.1 Materials ........................................................................... 144
7.4.2 Synthesis of tetra-functional initiator .................................................. 144
7.4.3 Synthesis of poly(ethylene glycol) grafted star polymers ...................... 145
7.4.4 Synthesis of poly(dimethylsiloxane) grafted star polymers ................... 145
7.4.5 Synthesis of poly(ethylene glycol)-b-poly(dimethylsiloxane) grafted star polymers ................................................................. 146

7.5 Experiments for chapter 5 .................................................................... 147
7.5.1 Materials ........................................................................... 147
7.5.2 Membrane preparation .................................................................147
7.5.3 Gas permeation experiments .........................................................148
7.5.4 Imaging of thin film composite membranes cross-section............149
7.6 References .........................................................................................150

Appendices

Chapter 2 Appendix ..............................................................................151
Chapter 3 Appendix ..............................................................................156
Chapter 4 Appendix ..............................................................................165
Chapter 5 Appendix ..............................................................................166
List of Figures

Chapter 1

Figure 1.1 The process of carbon capture and storage.

Figure 1.2 A typical post-combustion capture of CO₂.

Figure 1.3 Gas separation driven by pressure difference across a membrane.

Figure 1.4 The three different mechanisms for membrane separation.

Figure 1.5 Gas sorption isotherm in a glassy polymer represented by the dual mode sorption model.

Figure 1.6 Relationship between the polymer specific volume and temperature in amorphous polymers.

Figure 1.7 Three different membrane configurations.

Figure 1.8 The general chemical structure of polyimide; R₁ and R₂ refer to the dianhydride and diamine moieties.

Figure 1.9 The general structure of poly(dimethylsiloxane).

Figure 1.10 The general structure of poly(ethylene glycol).

Figure 1.11 Robeson’s trade-off curve for CO₂ and N₂ gas pair.
**Figure 1.12** \(\text{CO}_2/\text{N}_2\) selectivity versus \(\text{CO}_2\) permeance trade-off plot comparing the performance of commercially available membranes, the Polaris™ membrane and various developmental membranes reported in the literature. The shaded region indicates the optimum membrane properties for the separation of \(\text{CO}_2\) from flue gases as proposed by Merkel et al. Open circles (〇) are data points for Kai et al. and Duan et al.; the filled triangle (▕) is reported by Bao and Trachtenberg; the filled diamond (◆) is data of Kim et al.; the open square (□) is data of Cai et al.; the open diamond (◇) is data of Hanoioka et al.; the filled star (★) is data from Zhao et al.; the inverted triangles (▼) are data from Hendriks et al.

**Figure 1.13** Development of well-defined block copolymers since 1970.

**Figure 1.14** Various interfacial morphologies of mixed-matrix membranes adapted from Chung et al.

**Figure 1.15** Design of soft polymeric nanoparticles.

**Figure 1.16** *Research theme of this thesis:* soft polymeric nanoparticles as additives for \(\text{CO}_2\) separation membranes.

**Figure 1.17** *Chapter 2:* Soft polymeric nanoparticles based on linear polyimide and linear brush poly(dimethylsiloxane) triblock copolymers.

**Figure 1.18** *Chapter 3:* Soft polymeric nanoparticles based on linear poly(ethylene glycol) and linear brush poly(dimethylsiloxane) diblock copolymers.

**Figure 1.19** *Chapter 4:* Soft polymeric nanoparticles based on poly(ethylene glycol) and poly(ethylene glycol)-b-poly(dimethylsiloxane) grafted star polymers.

**Figure 1.20** *Chapter 5:* Soft polymeric nanoparticles as additives for \(\text{CO}_2\) separation membranes.
Chapter 2

**Figure 2.1** $^1$H NMR spectra (CDCl$_3$) of poly(6FDA-co-TMPD) (a) P1 and (b) P2.

**Figure 2.2** MALDI ToF mass spectra of (a) diamino poly(6FDA-co-TMPD) P1 and (b) dibromo macroinitiator P2 recorded in linear/positive mode using DCTB and AgTFA as the matrix and cationization agent, respectively. The numbers on the peaks denote the number of repeat units (n, 573 m/z).

**Figure 2.3** GPC differential refractive index chromatograms of polyimide/poly(dimethylsiloxane) triblock copolymers P3-1 to P3-3 and their precursors, macroinitiator P2 and PDMS-MA macromonomer. The molecular weight of PDMS-MA could not be determined via GPC as a result of weak light scattering signals, however, the manufacturer specifies a molecular weight of 600-800 Da.

**Figure 2.4** $^1$H NMR spectrum (CDCl$_3$) of fractionated polyimide/poly(dimethylsiloxane) triblock copolymers P3-3. The asterisk denotes residual THF solvent.

**Figure 2.5** (a) Correlation function and (b) intensity-average hydrodynamic diameter distributions of polyimide/poly(dimethylsiloxane) triblock copolymers self-assemblies.

**Figure 2.6** (a, c) Correlation function and (b, d) intensity-average hydrodynamic diameter distributions of polyimide/poly(dimethylsiloxane) triblock copolymers self-assemblies upon the addition of benzoyl peroxide and post cross-linking.

**Figure 2.7** (a) TEM image of P3-2, (b) STEM image of P3-2 and its elemental analysis recorded at a single point marked ‘x’, (c) TEM image of cross-linked P3-2 and (d) STEM image of cross-linked P3-2 and its elemental analysis recorded at a single point marked ‘x’.

xxi
Chapter 3

**Figure 3.1** $^1$H NMR spectra ($d_6$-DMSO) of macroinitiator $\textbf{P1}_5$.

**Figure 3.2** MALDI-ToF mass spectra of (a) 5 kDa MeOPEG and (b) its bromo-functionalized derivative, $\textbf{P1}_5$, recorded in linear/positive mode using DCTB and NaTFA as the matrix and cationization agent, respectively. The numbers on the peaks represent the number of EO repeat units (n, 44 m/z).

**Figure 3.3** $^1$H NMR spectrum (CDCl$_3$) of poly(ethylene glycol)/poly(dimethylsiloxane) diblock copolymers $\textbf{P2}_{5/9}$. The asterisks denote resonances corresponding to the double bond of unreacted PDMS-MA macromonomer.

**Figure 3.4** GPC ultraviolet (UV) chromatograms at 230 (---) and 390 nm (----) of poly(ethylene glycol)/poly(dimethylsiloxane) diblock copolymers and their macroinitiator $\textbf{P1}$ and PDMS-MA macromonomer. The manufacturer specifies a molecular weight of 600-800 Da for the PDMS-MA macromonomer.

**Figure 3.5** (a, c, e) Intensity autocorrelator and (b, d, f) intensity-average hydrodynamic diameter distributions of poly(ethylene glycol)/poly(dimethylsiloxane) diblock copolymers $\textbf{P2}$ self-assemblies.

**Figure 3.6** Intensity-average hydrodynamic diameter ($d_{4,4}$) of self-assembled nanoparticles as a function of poly(PDMS-MA) number-average molecular weight determined from $^1$H NMR spectroscopic analysis.

**Figure 3.7** Illustrated structure of large compound micelles formed from (a) $\text{PS}_{200-b}$-PAA$_4$ and (b) $\textbf{P2}_1$ series of linear-linear brush diblock copolymers.

**Figure 3.8** TEM images of (a) $\textbf{P2}_{1/5}$, (b) photocross-linked $\textbf{P2}_{1/5}$, (c) $\textbf{P2}_{5/7}$ and (d) photocross-linked $\textbf{P2}_{5/7}$. Scale bar = 100 nm.
**Figure 3.9** Random polystyrene-\textit{alt}-maleic anhydride-\textit{graft}-poly(ethylene oxide).

**Figure 3.10** Ultraviolet-visible spectra of P2_{5/4} upon exposure to UV radiation (365 nm) for 4 hours.

**Figure 3.11** (a, c, e) Intensity autocorrelation and (b, d, f) intensity-average hydrodynamic diameter distributions of poly(ethylene glycol)/poly(dimethylsiloxane) diblock copolymers P2 self-assemblies post photocross-linking.

**Chapter 4**

**Figure 4.1** $^1$H NMR spectra (CDCl$_3$) of the tetra-functional initiator I.

**Figure 4.2** GPC differential refractive index chromatograms of poly(ethylene glycol) grafted star polymers P0 and MeOPEG-MA macromonomer. The macromonomer has a molecular weight of 300 Da, as specified by the manufacturer.

**Figure 4.3** $^1$H NMR spectra (CDCl$_3$) of poly(ethylene glycol) grafted star polymers P0$_{24/0}$. An insert of 10 times magnification shows the methacrylate characteristics of unreacted MeOPEG-MA macromonomers which is marked by asterisks.

**Figure 4.4** GPC differential refractive index chromatograms of poly(ethylene glycol)-\textit{b}-poly(dimethylsiloxane) grafted star polymers P2 and their precursors, macroinitiator poly(dimethylsiloxane) grafted star polymers P1 and PDMS-MA macromonomer. The macromonomer has a molecular weight of 600 – 800 Da, as specified by the manufacturer.

**Figure 4.5** $^1$H NMR spectra (CDCl$_3$) of (a) poly(dimethylsiloxane) grafted star polymer P1$_{0/9}$ and (b) poly(ethylene glycol)-\textit{b}-poly(dimethylsiloxane) grafted star polymer P2$_{72/10}$. The asterisk denotes unreacted PDMS-MA macromonomers.
Chapter 5

Figure 5.1 Thin composite Pebax® membranes blended with soft polymeric nanoparticles in the form of grafted star polymers.

Figure 5.2 Cross-section of (a) PAN substrate pre-coated with PDMS gutter layer and (b) Pebax® 2533/PEG-b-PDMS grafted star polymers TFC blend membranes.

Figure 5.3 CO₂ and N₂ permeance of Pebax® 2533 and Pebax® 2533/grafted star polymers TFC blend membranes as a function of grafted star polymers (P₀ and P₂) content tested at 35 °C and 3.4 bar.

Figure 5.4 CO₂/N₂ selectivity of Pebax® 2533 and Pebax® 2533/grafted star polymers TFC blend membranes as a function of grafted star polymers (P₀ and P₂) content tested at 35 °C and 3.4 bar.

Figure 5.5 (a) CO₂ and N₂ permeance, (b) CO₂/N₂ selectivity of Pebax® 2533 and Pebax® 2533/grafted star polymers blend active layers as a function of grafted star polymers (P₂) content tested at 35 °C and 3.4 bar.

Figure 5.6 The performance of Pebax® 2533 and Pebax® 2533/PEG-b-PDMS grafted star polymers TFC blend membranes and the corresponding active layers developed in this study relative to other membranes reported in the literature.

Figure 5.7 The effect of PDMS content in the active layer on CO₂ permeability.

Chapter 6

Figure 6.1 Chemical structures of various high performance polyimides.
Chapter 7

Figure 7.1 Schematic diagram of the apparatus for gas flow measurements.

Appendices

Figure A2.1 $^1$H NMR spectrum (CDCl$_3$) of $\alpha,\omega$-diamino poly(6FDA-co-TMPD) P1. The asterisk denotes CDCl$_3$. An inset of 10 times magnification is included to show the absence of resonances corresponding to carboxylic protons (typically in the $\delta_H$ 10.5 - 13 ppm region).

Figure A2.2 $^{13}$C NMR spectrum (CDCl$_3$) of $\alpha,\omega$-diamino poly(6FDA-co-TMPD) P1. The asterisk denotes CDCl$_3$.

Figure A2.3 $^1$H NMR spectrum (CDCl$_3$) of $\alpha,\omega$-dibromo poly(6FDA-co-TMPD) P2. The asterisk denotes CDCl$_3$. An inset of 10 times magnification is included to show the absence of resonances corresponding to carboxylic protons (typically in the $\delta_H$ 10.5 - 13 ppm region).

Figure A2.4 $^{13}$C NMR spectrum (CDCl$_3$) of $\alpha,\omega$-dibromo poly(6FDA-co-TMPD) P2. The asterisk denotes CDCl$_3$.

Figure A2.5 MALDI ToF mass spectra of $\alpha,\omega$-amino poly(6FDA-co-TMPD) recorded in linear/positive using (a) DCTB/KTFA and (b) DCTB/NaTFA. The numbers on the mass spectra denote the number of repeat units (n, 573 m/z) and the mass values.

Figure A2.6 MALDI ToF mass spectra of functionalized $\alpha,\omega$-amino poly(6FDA-co-TMPD) recorded in linear/positive using (a) DCTB/KTFA and (b) DCTB/NaTFA. The numbers on the mass spectra denote the number of repeat units (n, 573 m/z) and the mass values.
Figure A3.1 $^{13}$C NMR spectra ($d_6$-DMSO) of bromo-functionalized 5 kDa MeOPEG macroinitiator, $P_{15}$.

Figure A3.2 $^1$H NMR spectra (CDCl$_3$) of 2-(methacryloyloxy)ethyl anthracene-9-carboxylate.

Figure A3.3 $^{13}$C NMR spectra (CDCl$_3$) of 2-(methacryloyloxy)ethyl anthracene-9-carboxylate.

Figure A3.4 $^1$H NMR spectra ($d_6$-DMSO) of (a) bromo-functionalized 1 kDa MeOPEG macroinitiator $P_{11}$, and (b) bromo-functionalized 10 kDa MeOPEG macroinitiator $P_{110}$.

Figure A3.5 MALDI ToF mass spectra of (a) 1 kDa MeOPEG and (b) its bromo-functionalized derivative, $P_{11}$, recorded in linear/positive mode using DCTB and NaTFA as the matrix and cationization agent, respectively. The numbers on the mass spectra denote the number of EO repeat units (n, 44 m/z).

Figure A3.6 MALDI ToF mass spectra of (a) 10 kDa MeOPEG and (b) its bromo-functionalized derivative, $P_{110}$, recorded in linear/positive mode using DCTB and NaTFA as the matrix and cationization agent, respectively. The numbers on the mass spectra denote the number of EO repeat units (n, 44 m/z).

Figure A3.7 MALDI ToF mass spectra of PDMS-MA macromonomer recorded in linear/positive mode using no matrix and KTFA as the cationization agent. Series a refers to the PDMS-MA while series b refers to the unfunctionalized PDMS. Each peak in both series is separated by 74 m/z which are indicative of PDMS repeat unit.

Figure A3.8 Ultraviolet-visible spectra of $P_2$’s self-assemblies upon exposure to UV radiation (365 nm) for 4 hours.
Figure A3.9 Ultraviolet-visible spectra of various photocross-linked nanoparticles upon exposure to UV radiation (254 nm) for 20 hours.

Figure A4.1 $^{13}$C NMR spectra of tetra-functional initiator I.
List of Schemes

Chapter 1

Scheme 1.1 Mechanisms of step-growth polymerization.

Scheme 1.2 Mechanisms of conventional free radical polymerization.

Scheme 1.3 Equilibrium between the active and dormant species in living/controlled radical polymerization.

Scheme 1.4 General scheme of copper-catalyzed atom transfer radical polymerization.

Scheme 1.5 Synthetic approaches for preparation of star polymers via (a) grafting-from ('core-first'), (b) grafting-to, and (c) grafting-to/from (arm-first) approaches, adapted from Blencowe et al.

Chapter 2

Scheme 2.1 Synthetic outline for the preparation of soft polymeric nanoparticles based on linear polyimide and linear brush poly(dimethylsiloxane) triblock copolymers.

Scheme 2.2 The mechanism of radical induced cross-linking of PDMS proposed by Charlesby.
Chapter 3

Scheme 3.1 Synthetic outline for the preparation of soft polymeric nanoparticles based on linear poly(ethylene glycol) and linear brush poly(dimethylsiloxane) diblock copolymers.

Scheme 3.2 Mechanism for photodimerization and photocleavage of anthracene molecules.

Chapter 4

Scheme 4.1 Synthetic outline for the preparation of poly(ethylene glycol) and poly(ethylene glycol)-b-poly(dimethylsiloxane) grafted star polymers.

Chapter 5

Scheme 5.1 The fabrication of thin film TFC blend membrane. (i) The PDMS gutter layer was formed by cross-linking amino-terminated PDMS and trimesoyl chloride. (ii) The TFC blend membrane was prepared by spin-coating the mixture of Pebax® 2533 and grafted star polymers onto the PDMS gutter layer.
List of Tables

Chapter 1

Table 1.1 Various grades of Pebax® copolymers.

Table 1.2 The general effects of various interfacial morphologies on gas transport properties.

Chapter 2

Table 2.1 Molecular weight characterization of polyimides P1 and P2.

Table 2.2 Synthesis and characterization of polyimide/poly(dimethylsiloxane) triblock copolymers.

Table 2.3 Intensity-average hydrodynamic diameter distributions of polyimide/poly(dimethylsiloxane) triblock copolymers self-assemblies.

Table 2.4 Intensity-average hydrodynamic diameter distributions of polyimide/poly(dimethylsiloxane) triblock copolymers self-assemblies before and after cross-linking.

Chapter 3

Table 3.1 Molecular weight characterization of MeOPEG macroinitiator P1.

Table 3.2 Synthesis and characterization of poly(ethylene glycol)/poly(dimethylsiloxane) diblock copolymers.
Table 3.3 Intensity-average hydrodynamic diameter distributions of poly(ethylene glycol)/poly(dimethylsiloxane) diblock copolymers self-assemblys.

Table 3.4 Graft copolymers composition and size analysis of graft copolymers micelles.

Table 3.5 Extent of photodimerization of the anthracene groups over 4 hours.

Chapter 4

Table 4.1 Synthesis and characterization of grafted star polymers.

Chapter 5

Table 5.1 Gas separation performance of TFC blend membranes and the corresponding active layers tested at 35 °C and 3.4 bar.

Chapter 6

Table 6.1 Gas transport properties of various polyimides.

Table 6.2 Gas transport properties of Pebax® 1657 and cross-linked PEG.

Appendices

Table A3.1 Extent of photocleavage of the anthracene moieties over 20 hours.

Table A5.1 PDMS and PEG weight fractions of the synthesized grafted star polymers.

Table A5.2 CO₂ and N₂ flux of PDMS-coated support and fabricated TFC membrane.
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>6FDA</td>
<td>4,4’-Hexafluoroiso propyldene</td>
</tr>
<tr>
<td>AgTFA</td>
<td>Silver trifluoroacetate</td>
</tr>
<tr>
<td>AR</td>
<td>Analytical reagent</td>
</tr>
<tr>
<td>ATRP</td>
<td>Atom transfer radical polymerization</td>
</tr>
<tr>
<td>BAFL</td>
<td>9,9- Bis(4-aminophenyl)fluorene</td>
</tr>
<tr>
<td>BCP</td>
<td>Block copolymer</td>
</tr>
<tr>
<td>BIBB</td>
<td>2-Bromoiso butyrylbromide</td>
</tr>
<tr>
<td>BP</td>
<td>Benzoyl peroxide</td>
</tr>
<tr>
<td>BuOH</td>
<td>Butanol</td>
</tr>
<tr>
<td>CCS</td>
<td>Carbon capture and storage</td>
</tr>
<tr>
<td>CDCl$_3$</td>
<td>Deuterated chloroform</td>
</tr>
<tr>
<td>CF$_3$</td>
<td>Trifluoromethyl</td>
</tr>
<tr>
<td>CMC</td>
<td>Critical micelle concentration</td>
</tr>
<tr>
<td>CPVV</td>
<td>Constant pressure variable volume</td>
</tr>
<tr>
<td>CRP</td>
<td>Controlled radical polymerization</td>
</tr>
<tr>
<td>CuBr</td>
<td>Copper (I) bromide</td>
</tr>
<tr>
<td>CVVP</td>
<td>Constant volume variable pressure</td>
</tr>
<tr>
<td>DCM</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>DCTB</td>
<td>Trans-2-[3-(4-tert.-butyl-phenyl)-2-methyl-2-propenylidene]-malononitrile</td>
</tr>
<tr>
<td>DLS</td>
<td>Dynamic light scattering</td>
</tr>
<tr>
<td>DMAc</td>
<td>N,N-Dimethylacetamide</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N-Dimethylformamide</td>
</tr>
<tr>
<td>DMS</td>
<td>Dual mode sorption</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl sulfoxide</td>
</tr>
<tr>
<td>DP</td>
<td>Degree of polymerization</td>
</tr>
<tr>
<td>EO</td>
<td>Ethylene oxide</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Compound/Method Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>Et₂O</td>
<td>Diethyl ether</td>
</tr>
<tr>
<td>EtOH</td>
<td>Ethanol</td>
</tr>
<tr>
<td>FFV</td>
<td>Fractional free volume</td>
</tr>
<tr>
<td>GPC</td>
<td>Gel permeation chromatography</td>
</tr>
<tr>
<td>GPU</td>
<td>Gas permeation unit</td>
</tr>
<tr>
<td>HCl</td>
<td>Hydrogen chloride</td>
</tr>
<tr>
<td>HEMAM</td>
<td>2-Hydroxyethyl methacrylate</td>
</tr>
<tr>
<td>HPLC</td>
<td>High-performance liquid chromatography</td>
</tr>
<tr>
<td>IPA</td>
<td>Propan-2-ol</td>
</tr>
<tr>
<td>kDa</td>
<td>Kilodalton</td>
</tr>
<tr>
<td>KTFA</td>
<td>Potassium trifluoroacetate</td>
</tr>
<tr>
<td>M</td>
<td>Monomer</td>
</tr>
<tr>
<td>MALDI ToF</td>
<td>Matrix-assisted laser desorption/ionization time of flight</td>
</tr>
<tr>
<td>Me₆TREN</td>
<td>Tris[2-(dimethylamino)ethyl]amine</td>
</tr>
<tr>
<td>MEA</td>
<td>Monoethanolamine</td>
</tr>
<tr>
<td>MEAC</td>
<td>2-(Methacryloyloxy)ethyl anthracene-9-carboxylate</td>
</tr>
<tr>
<td>MeOH</td>
<td>Methanol</td>
</tr>
<tr>
<td>MeOPEG</td>
<td>Monomethyl ether poly(ethylene glycol)</td>
</tr>
<tr>
<td>MeOPEG-MA</td>
<td>Poly(ethylene glycol) methyl ether methacrylate</td>
</tr>
<tr>
<td>MgSO₄</td>
<td>Magnesium sulphate</td>
</tr>
<tr>
<td>MHz</td>
<td>Megahertz</td>
</tr>
<tr>
<td>MI</td>
<td>Macroinitiator</td>
</tr>
<tr>
<td>MM</td>
<td>Macromonomer</td>
</tr>
<tr>
<td>MMM</td>
<td>Mixed-matrix membrane</td>
</tr>
<tr>
<td>MS</td>
<td>Mass spectroscopy</td>
</tr>
<tr>
<td>NaCl</td>
<td>Sodium chloride</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>Sodium hydrogen carbonate</td>
</tr>
<tr>
<td>NaOH</td>
<td>Sodium hydroxide</td>
</tr>
<tr>
<td>NaTFA</td>
<td>Sodium trifluoroacetate</td>
</tr>
<tr>
<td>NF</td>
<td>Nano-flower</td>
</tr>
<tr>
<td>NH₂-PDMS-NH₂</td>
<td>Aminopropyl terminated poly(dimethysiloxane)</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>NMP</td>
<td>Nitroxide-mediated polymerization</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>ODA</td>
<td>4,4'-Oxydianiline</td>
</tr>
<tr>
<td>PA</td>
<td>Polyamide</td>
</tr>
<tr>
<td>PAN</td>
<td>Polyacrylonitrile</td>
</tr>
<tr>
<td>PB</td>
<td>Polybutadiene</td>
</tr>
<tr>
<td>PBT</td>
<td>Poly(butylene terephtalate)</td>
</tr>
<tr>
<td>PDMS</td>
<td>Poly(dimethylsiloxane)</td>
</tr>
<tr>
<td>PDMS-MA</td>
<td>Monomethacryloxypropyl terminated poly(dimethylsiloxane)</td>
</tr>
<tr>
<td>PDI</td>
<td>Polydispersity index</td>
</tr>
<tr>
<td>PE</td>
<td>Polyether</td>
</tr>
<tr>
<td>PEt</td>
<td>Polyethylene</td>
</tr>
<tr>
<td>PEG</td>
<td>Poly(ethylene glycol)</td>
</tr>
<tr>
<td>PEO</td>
<td>Poly(ethylene oxide)</td>
</tr>
<tr>
<td>PEP</td>
<td>Poly(ethylene-propylene)</td>
</tr>
<tr>
<td>PI</td>
<td>Polyimide</td>
</tr>
<tr>
<td>PMDETA</td>
<td>$N,N,N',N'',N'''$-Pentamethyldiethylenetriamine</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>PTMO</td>
<td>Poly(tetramethylene oxide)</td>
</tr>
<tr>
<td>PTMSP</td>
<td>Poly(1-trimethylsilyl-1-propyne)</td>
</tr>
<tr>
<td>QELS</td>
<td>Quasi-elastic light scattering</td>
</tr>
<tr>
<td>RAFT</td>
<td>Reversible addition-fragmentation chain transfer</td>
</tr>
<tr>
<td>ROMP</td>
<td>Ring-opening metathesis polymerization</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SOCl₂</td>
<td>Thionyl chloride</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning transmission electron microscopy</td>
</tr>
<tr>
<td>TEA</td>
<td>Triethylamine</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TFC</td>
<td>Thin film composite</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Name</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>TH</td>
<td>Transfer agent</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>TMC</td>
<td>Trimesoyl chloride</td>
</tr>
<tr>
<td>TMPD</td>
<td>2,3,5,6-Tetramethyl-1,4-phenyldiamine</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>Ultraviolet-visible</td>
</tr>
</tbody>
</table>
List of Notations

- $b$: Block
- $brs$: Broad singlet
- $C$: Concentration of penetrant gas
- $C'_H$: Saturation capacity for uptake in the excess free volume
- $C_D$: Concentration of the gas molecules absorbed
- $C_H$: Standard Langmuir relationship
- $d_H$: Hydrodynamic diameter
- $dn/dc$: Specific refractive index increment
- $d$: Deuterated
- $D$: Diffusivity coefficient
- $J$: Flux of a penetrant
- $K_d$: Henry's law constant
- $K_p$: Ratio of rate coefficients between adsorption and desorption
- $l$: Thickness
- $m$: Multiplet
- $M_n$: Number-average molecular weight
- $M_w$: Weight-average molecular weight
- $N_{VT}$: Total volumetric flux
- $p$: Applied partial pressure
- $P$: Permeability coefficient
- $quin$: Quintet
- $R_{AL}$: Resistance through the active layer
- $R_G$: Resistance through the gutter layer
- $R_S$: Resistance through the microporous substrate
- $R_T$: Total resistance
- $s$: Singlet
- $S$: Solubility coefficient
\( t \) \quad \text{Triplet}

\( \textit{tert.} \) \quad \text{Tertiary}

\( T_g \) \quad \text{Glass transition temperature}

\( x \) \quad \text{Mole fraction}

**Greek letter**

\( \alpha \) \quad \text{Ideal selectivity}
Polymeric Gas Separation Membranes: Past, Present and Future Challenges

1.1 Background

The use of membranes for gas separation applications has experienced a major expansion in the past few decades. One of the major potential applications includes the separation of CO$_2$ from flue gases to reduce greenhouse gas emissions [1-3].

Carbon capture and storage (CCS) involves capturing, purifying, compressing, transporting and storing CO$_2$ that would otherwise be emitted from coal-fired power stations to the atmosphere (Figure 1.1) [4]. The three ways to capture CO$_2$ from a coal-fired power station are post-combustion, oxy-fuel combustion and pre-combustion capture. Post-combustion capture involves CO$_2$ capture after the fossil fuel has been combusted with air. Oxy-fuel combustion involves burning fossil fuel with an oxygen-enriched gas stream to give a stream containing up to 90% CO$_2$ with a balance of impurities, while pre-combustion capture is a process where fossil fuel is converted to H$_2$ and CO$_2$ prior to combustion. In pre-combustion capture, CO$_2$ must be separated from H$_2$ upstream of the combustor [5].

![Figure 1.1 The process of carbon capture and storage.
(reprinted from www.co2crc.com.au)](image-url)
Post-combustion capture is challenging as it involves CO₂ separation at atmospheric pressure from a gaseous stream with low CO₂ content, typically 5 – 15 % (Figure 1.2). Nonetheless, this option also corresponds to the most widely applicable option as it can be retrofitted to existing power stations [6].

![Figure 1.2 A typical post-combustion capture of CO₂.](reprinted from www.co2crc.com.au)

The cost of capturing CO₂ contributes approximately 80% to the total cost of CCS. Hence, developing an efficient way of separating CO₂ from a mixture of gases is essential. Absorption of CO₂ in basic solvents such as monoethanolamine (MEA) is currently the most mature technology available as it is able to achieve high CO₂ purity and recovery. However, this technology suffers from the need for solvent regeneration, a large plant footprint and high energy penalties. Furthermore, basic solvents are corrosive and are prone to degradation by impurities present in the flue gas [6].

The use of membranes for gas separation has been studied for more than 150 years, with membranes having been used commercially since 1980 [2]. When compared to solvent technology, membrane technology offers advantages such as the ease of scale up and the potential of having higher energy efficiency. Furthermore, the area required to install membrane systems is much smaller when compared to solvent systems, hence making retro-fitting easier and cheaper [7].
1.2 Membrane technology

The concept of membrane separation is based on the principle that only selected components in a mixture of fluids are able to pass through a barrier, i.e. membrane. The separation is driven by the pressure difference across the membrane as illustrated in Figure 1.3 [8]. Gas separation membranes can be fabricated from either organic or inorganic materials. Inorganic membranes typically show exceptional separation performance as well as chemical and thermal stability [9-15]. However, the fabrication of inorganic membranes is difficult since they are brittle which results in an increase in their cost of production [16-19]. Conversely, polymeric membranes have been widely used as they are easy to fabricate and entail low production costs [1].

![Figure 1.3](reprinted from www.co2crc.com.au)

Polymeric membranes are commonly classified as either ‘glassy’ and ‘hard’ or ‘rubbery’ and ‘soft’ structures, which are categorized by their glass transition temperatures ($T_g$). Glass transition is commonly defined as a reversible phase transition between a glassy to a rubber-like state [20]. Glassy polymers have been widely reported in the literature and provide better selective performances due to their more restricted segmental motions, while rubbery polymers give higher flux due to their greater free volume [21, 22]. The concept of free volume will be further detailed in Section 1.2.1.1.
1.2.1 Gas transport mechanism

The gas transport mechanism through polymeric membranes typically follows either one of the three mechanisms shown in Figure 1.4, depending on the type of membranes used. Knudsen diffusion occurs for gas transport through a porous membrane with pore diameters larger than that of the kinetic diameter of the gases. Low molecular weight molecules can diffuse at a faster rate when compared to heavier molecules because of the greater interaction between the lighter species and the pore walls [23]. The rate of mass transport through Knudsen diffusion can be further enhanced by surface diffusion in which molecules are absorbed onto the surfaces of the pores and diffuse along this surface [24].

![Figure 1.4 The three different mechanisms for membrane separation.](www.co2crc.com.au)

Reductions of membrane pore size to diameters larger than one gaseous component yet smaller than another, results in an entirely different separation mechanism, commonly termed molecular sieving, which operates simply via size exclusion. Gas molecules that are small enough to ‘fit’ through the pore can diffuse through the membrane while larger ones are excluded.

Gases may also diffuse through a non-porous membrane by a solution-diffusion mechanism. In this model, the penetrant molecules dissolve into the retentate face of the membrane, diffuse through the bulk of the membrane and desorb from the
permeate face of the membrane [25]. Penetrant transport properties are typically related to the solubility and diffusivity in the membrane.

The dependence of gas transport properties upon both solubility and diffusivity allows for more flexibility with respect to tuning of membrane properties. Physically larger molecules can permeate more quickly than smaller molecules if their respective solubilities are suitably manipulated with an appropriate polymer [26]. This separation mechanism is commonly termed ‘reverse-selective’ and is not possible with Knudsen diffusion or molecular sieving-based processes. High permeability rubbery polymers utilize this principle to achieve separation of higher hydrocarbons from small penetrant molecules such as N₂ or H₂ [26].

The separation of penetrants through glassy polymers is dependent primarily on the penetrant’s kinetic diameter, whereby penetrant molecules move through gaps within the polymer structure. These gaps are related to the free volume that the membrane exhibits due to the movement of the polymer chains and allows penetrant molecules to “jump” from one gap to another. The size and size distribution of the gaps can be manipulated to achieve selective gas transport [27]. As a result, diffusivity selectivity is the dominant factor dictating the performance of glassy polymers and is used for the separation of light gases such as CO₂ removal from N₂ and H₂ [28]. It is worthwhile noting that glassy polymers with ultra-high permeability such as poly(1-trimethylsilyl-1-propyne), PTMSP, exhibit higher permeabilities for large organic vapours than smaller gases. However, this is unusual for glassy polymers and represents a variation on the typical solution-diffusion mechanism [29].

1.2.1.1 Solubility

The dissolution of penetrant gas into a polymer matrix was historically described using Henry’s law which states that the gas concentration in the liquid is linearly proportional to the applied pressure and solubility coefficient. Henry’s law is represented by the following equation [30]:

\[ C_D = K_d \cdot p \]  

(1)
where $C_0$ is the concentration of the gas molecules absorbed, $K_d$ is the Henry’s law constant and $p$ is the applied partial pressure.

This relationship has been found to adequately describe the concentration of gases in rubbery polymers at low concentration [26]. Glassy polymers, on the other hand, do not obey this relationship. The polymer’s penetrant concentration exhibits proportionality to the applied fugacity that is far from linear. The concentration-pressure plot for the overall sorption is often concave with respect to the pressure axis as shown in Figure 1.5. The dual mode sorption (DMS) describes such non-linear behaviour.

![Figure 1.5 Gas sorption isotherm in a glassy polymer represented by the dual mode sorption model.](image)

DMS differs from Henry’s law in that it regards glassy polymers having two domains into which penetrant can sorb. The first domain is the standard model of Henry’s law of dissolution in which penetrant literally dissolves into free volume between adjacent polymer chains. Variations in the polymer structure, which result in the fluctuation of chain molecular diameters, provide opportunities for gases to dissolve. The second domain is called the Langmuir region and is central to the DMS theory. It allows for penetrant gas to be adsorbed into excess free volume. Excess free volume may be thought of as microscopic voids that are created due to the imperfect packing of polymer chains. These voids are only
present in the glassy state and not the rubbery state. Hence, the concentration of penetrant gas described in the dual mode sorption model can be written as [31]:

\[ C = C_D + C_H = K_d \cdot p + \frac{C_H \cdot K_p}{1 + K_p} \] (2)

where \( C_H \) is the standard Langmuir relationship, \( C'_H \) is the saturation capacity for uptake in the excess free volume and \( K_p \) is the ratio of rate coefficients between adsorption and desorption (\( K_p = K_H/K_D \)).

The above equation is useful to correlate and compare experimental data, however it is not predictive as the parameters are not directly related to the chemical structures of the polymers [32].

**Figure 1.6** shows a conceptual model for the relationship between polymer specific volume and temperature. For glassy polymers, the excess free volume region is considered the volume into which Langmuir adsorption occurs. Above the \( T_g \), there are no packing defects and hence the disappearance of this excess free volume (\( C'_H \rightarrow 0 \)) occurs. The remaining fraction of the overall free volume is considered to be void space in which gas may dissolve according to Henry’s law. Void space persists in both glassy and rubbery polymers as this is a manifestation of irregular polymer chain diameters.

**Figure 1.6** Relationship between the polymer specific volume and temperature in amorphous polymers [33]
1.2.1.2 Diffusivity

Diffusion is a process in which penetrants are transported from one part of the membrane to the other as a result of random molecular motion, driven by either chemical potential, concentration gradient or fugacity gradient. The diffusivity coefficient is a proportional constant that describes the relationship between the molar flux of the penetrant and the concentration gradient.

The diffusivity of a molecule depends on the size of the molecule, the size of the voids and the size distribution of these voids in the polymer. Since fractional free volume (FFV) represents the proportion of space between polymer chains, i.e. void size and its size distribution, it can also be correlated to the diffusivity of a penetrant according to Fujita’s free volume theory [34-36]:

\[ D = A_D \exp \left( \frac{-B_D}{FFV} \right) \]  

(3)

where \( D \) is the diffusion coefficient while \( A_D \) and \( B_D \) are constants which are functions of kinetic diameter. This correlation can be applied to structurally related polymers or a single polymer system, with high accuracy [36].

1.2.1.3 Permeability

Mass transfer rates can be quantified in terms of flux of penetrant through the membrane. Fick’s first law is a common approach to describe the flux of a penetrant, \( J \) (mol/m²s), moving from regions of high concentration to regions of low concentration across a membrane:

\[ J = -D \frac{\partial C}{\partial z} \]  

(4)

where \( D \) is the diffusivity coefficient (cm² s⁻¹; a measure of the mobility of the molecules within the membrane)

However, it is more common to express flux as:

\[ J = \frac{P \Delta p}{l} \]  

(5)

where \( P \) is the permeability coefficient (cm³ (STP) cm⁻¹ s⁻¹ cmHg⁻¹), \( \Delta p \) is the partial pressure driving force and \( l \) is the thickness of the membrane. Barrer (10⁻¹⁰ cm³ (STP) cm⁻¹ s⁻¹ cmHg⁻¹) is the common measurement of \( P \).
For rubbery polymers, where **Equation 1** applies, these two equations can be readily related by:

\[ P = D \cdot S \]  

(6)

where \( S \) is the solubility coefficient (\( \text{cm}^3 \text{ (STP)} \ \text{cm}^{-3} \text{ cmHg}^{-1} \); a measure of the solubility of gas molecules within the membrane). The solubility coefficient is also commonly defined as the concentration of penetrant sorbed in the polymer divided by the fugacity in the gaseous phase:

\[ S = \frac{c}{p} \]  

(7)

Non-ideal systems, including glassy polymers, often display solubilities that vary with penetrant concentration. In this case, permeabilities are commonly expressed as:

\[ P = D \cdot \frac{\partial c}{\partial p} \]  

(8)

Gas permeability can be determined through two methods. In the first method, a constant pressure of a gas is applied to the upstream side of a membrane and the gas volumetric flow rate can be measured from the permeate side of the membrane. This method is known as constant pressure variable volume (CPVV) permeation. Alternatively, the amount of permeating gas can be accurately determined as a function of time by allowing gas to permeate into a sealed chamber of known volume, while monitoring the change in permeate pressure. The latter method is more accurate at low permeance and is known as constant volume variable pressure (CVVP) permeation.

**1.2.1.4 Selectivity**

Membrane selectivity is an important criterion for judging the membrane performance. The ideal selectivity of a gas pair \((A/B)\), \(\alpha_{AB}\) is defined as:

\[ \alpha_{AB} = \frac{P_A}{P_B} \]  

(9)

where \(P_A\) is the permeability of gas A while \(P_B\) is the permeability of gas B.
This definition is a simplification of the real selectivity which can be determined by the ratio of the downstream (1) and upstream (2) mole fraction (x) of each component of the gas mixture A and B as described by the following equation:

\[ \alpha_{AB} = \frac{x_{A1}x_{B1}}{x_{A2}x_{B2}} \]  

(10)

### 1.2.2 Membrane configuration

Polymeric materials can be fabricated into either hollow fibre or spiral wound modules for industrial applications. Flat-sheet polymeric membranes are commonly utilized in a spiral wound format. A dense flat-sheet membrane contains only a homogeneous non-porous layer, whereas an asymmetric membrane consists of a thin non-porous active layer supported by a microporous sub-layer. Asymmetric membranes are commonly prepared via a dry/wet phase inversion technique [37]. When the porous sub-layer is made from a different material from the skin layer, it is known as a composite membrane ([Figure 1.7]) [8]. The development of thin film composite (TFC) membranes has attracted much attention due to increased flux and hence a higher efficiency for gas separation, and is the focus of this thesis. Higher flux can be achieved with a membrane that has a lower thickness as flux is inversely proportional to the membrane thickness ([Equation 5]).

![Figure 1.7 Three different membrane configurations.](image)

The three main ways of fabricating defect-free thin films are dip-coating [38], interfacial polymerization [39] and spin-coating [40]. Dip-coating is the most common method to fabricate thin films in large scale production as it is easy to implement [38]. Interfacial polymerization is an established method of fabricating polyamide membranes for water separation [41, 42]. Although spin-coating is the method of choice in the microelectronics industry and is widely used to fabricate TFC membranes within the laboratory, its application to large scale membrane production is not practical [43].
A gutter layer is also often coated on top of the highly porous substrate before application of the active layer. The introduction of this layer is mainly to provide a smooth surface before the coating of the active layer. In this case, it is important to utilize a permeable polymer that will provide the least resistance to flow \[43\].

The total resistance \((R_T)\) to permeation through the composite membrane can be expressed as the sum of resistances from the membrane active layer \((R_{AL})\), the gutter layer \((R_G)\) and the microporous substrate \((R_S)\):

\[
R_T = \frac{\Delta p}{N_{VT}} = R_{AL} + R_G + R_S
\]

(11)

where \(\Delta p\) is the pressure difference across the membrane and \(N_{VT}\) is the total volumetric flux.

The resistance of the active layer \((R_{AL})\) can then be determined by subtracting the resistance to flow provided by the microporous substrate and gutter layer, determined prior to active layer coating. The permeance of this active layer \((P_{AL})\) is then simply the inverse of this resistance. The permeability of gas through the active layer \((P_{AL})\) can then be calculated from:

\[
P_{AL} = \mathcal{P}_{AL} \times l
\]

(12)

where \(\mathcal{P}_{AL}\) is the permeance of the active layer in GPU and \(l\) is the thickness in \(\mu\)m. The estimation of permeability is highly dependent on the accuracy in determining the thickness of the active layer.

### 1.3 Polymer science

#### 1.3.1 Polymeric membrane materials

A large number of polymers, both glassy and rubbery, have been studied for their gas separation performance. The following section describes the main polymers that have been identified as promising membrane materials for CO\(_2\) separation.
1.3.1.1 Polyimides

Polyimides (PI) are a class of glassy polymers that are known to be chemically, mechanically and thermally stable [1, 7]. Additionally, these polymers exhibit higher permeability and selectivity when compared to other types of glassy polymers [32]. Therefore, polyimides have been extensively researched for their potential applications for gas separation membranes. Polyimides are generally synthesized by the reaction of a diamine with a dianhydride to form a polyamic acid, which then undergoes a polycondensation reaction and subsequently cyclodehydration to form the desired polyimide. The general structure of a polyimide is shown in Figure 1.8.

![Figure 1.8](image)

**Figure 1.8** The general chemical structure of polyimide; $R_1$ and $R_2$ refer to the dianhydride and diamine moieties.

Polyimides that incorporate hexafluoroisopropylidene-diphthalic anhydride (6FDA) groups have been extensively researched as they tend to give high permeability and selectivity. The main reasons for this excellent performance are [1]:

- The trifluoromethyl ($CF_3$) groups show a strong affinity for CO$_2$ due to their polar bonds which increases CO$_2$ solubility. Hence, selectivity is enhanced.
- The large $CF_3$ group also increases inter-chain spacing and reduces the effective chain packing; this leads to an increase in permeability through increased diffusivity.
- The effective chain packing is further reduced as the formation of charge-transfer complexes is reduced; this reduces the effective chain packing which leads to an increase in permeability.
1.3.1.2 Poly(dimethylsiloxane)

Poly(dimethylsiloxane) (PDMS) is a rubbery polymer that has received considerable attention as a potential candidate to fabricate membranes for gas separation. Studies have shown that PDMS shows much higher gas permeabilities when compared to other synthetic polymers; this is due to the flexible siloxane (-SiO-) linkages of this polymer (shown in red, Figure 1.9) [32]. Although it has high permeability (ca. 3800 Barrer), PDMS has low selectivity (selectivity of CO$_2$ over N$_2$ is ca. 9.5) [44].

![Figure 1.9](image.png)

Figure 1.9 The general structure of poly(dimethylsiloxane).

1.3.1.3 Poly(ethylene glycol)

Poly(ethylene glycol) (PEO) is known to possess a high affinity towards CO$_2$ as it contains a polar ether oxygen bond (shown in orange, Figure 1.10). This bond is able to produce quadrupolar interaction with CO$_2$ [6]. One drawback of using PEO is its high tendency to crystallize. There are three strategies to minimize the effect of crystallinity in PEO and these are [45]:

- Utilizing low molecular weight PEO.
- Designing block copolymers with short segments of PEO.
- Designing highly branched or cross-linked networks with high concentrations of PEO.

Other advantages of utilizing PEO include chemical stability, non-toxicity and biodegradability [46].

![Figure 1.10](image.png)

Figure 1.10 The general structure of poly(ethylene glycol).
1.3.2 *Polymerization techniques*

Polymerization techniques such as step-growth and/or chain-growth polymerization can be utilized to synthesize various polymeric materials with targeted morphology and architecture.

1.3.2.1 *Step-growth polymerization*

Step-growth polymerization involves the reaction between two different functional groups. These reactions include esterification, amidation, the formation of urethanes, aromatic substitution and others. Step-growth polymerization can be categorized into two groups depending on the type of monomer(s) used. The first involves two different bifunctional and/or polyfunctional monomers where each monomer possesses only one type of functional group; a bifunctional monomer is a monomer with two functional groups per molecule while a polyfunctional monomer is one with more than one functional group per molecule. The second involves a single monomer containing both types of functional groups [47]. The two groups of reactions is illustrated in Scheme 1.1 where A and B are the two different types of functional groups.

\[
\begin{align*}
\text{nA} - \text{A} & + \text{nB} - \text{B} \quad \rightarrow \quad \text{A} - \text{AB} - \text{B} \overset{n}{\rightarrow} \\
\text{nA} - \text{B} & \quad \rightarrow \quad \text{A} - \text{B} \overset{n}{\rightarrow}
\end{align*}
\]

**Scheme 1.1** Mechanisms of step-growth polymerization.

The synthesis of high molecular weight polymers using step-growth polymerization is generally difficult as high molecular weight can only be achieved at very high conversions, i.e. > 98 – 99% [47]. Additionally, A and B functional groups need to be present at very close to stoichiometric ratios to achieve high molecular weight polymers [47].

Step-growth polymerization proceeds at a relatively slow increase in molecular weight of the polymer as monomers are consumed early in the reaction far before the production of any polymer with sufficiently high molecular weight. In this polymerization process, two monomers can react to form a dimer, the dimer may react with another dimer to form a tetramer, or the dimer may react with
monomer to form a trimer. This process continues until the reaction terminates [47]. Hence, the rate of a step-growth polymerization can be summarized as the sum of the rates of reactions between molecules of various sizes.

1.3.2.2 Chain-growth polymerization

Chain-growth polymerization involves the addition of monomers having double bonds or ring structure to an active site at the end of a growing polymer chain. Traditionally, this class of polymerization was termed as addition polymerization [20]. The mechanism of chain-growth polymerization can be of coordination, ionic or free radical type. There are four reactions involve in a free radical chain-growth polymerization system and these include initiation, propagation, termination and chain transfer (Scheme 1.2) [48]. Initiation is a process whereby the first active centre is formed and the growth of the chain is initiated. Radicals can be formed from thermolysis or a photolysis initiator. Monomers then react with the initiator, resulting in the growth of polymer chain to form a propagating radical chain. This process is termed propagation. Growth is terminated by either combination or disproportionation of two propagating species. Chain transfer is another common reaction in radical polymerization. This process occurs when the reactive radical of a growing polymer chain abstracts hydrogen from another species, which can be an additional specific chain transfer agent, solvent, initiator, monomer, polymer, or impurities to produce a ‘dead’ polymer chain and a new radical species that can undergo further initiation.
Living/controlled radical polymerization

Living polymerization was first introduced by Scwarc in 1956. The mechanism is similar to that of conventional polymerization, however there is minimum termination or chain transfer reactions that can stop the polymerization process [49]. Hence, the polymer chain will keep on growing until the absolute consumption of monomers, changes in reaction conditions or the addition of appropriate terminating agents [50].

The basic principle of controlled radical polymerization (CRP) is the introduction of organic or organometallic catalysts, degenerative transfer agents, or radical capping agents to suppress irreversible conventional termination reactions by promoting equilibrium between the active and dormant species as shown in Scheme 1.3. This ensures that the instantaneous radical concentration is low,
which allows good control of polymer chain growth with narrow polydispersity [48]. Common CRP methodologies include atom transfer radical polymerization (ATRP) [51-54], nitroxide-mediated polymerization (NMP) [55, 56] and reversible addition-fragmentation chain transfer (RAFT) polymerization [57, 58]. For the research outlined in this thesis, only ATRP will be discussed in further detail.

**Scheme 1.3** Equilibrium between the active and dormant species in living/controlled radical polymerization.

ATRP was first reported independently by Matyjaszewski and co-workers, and Sawamoto and co-workers in 1995 [51, 54]. To date, it is one of the most versatile CRP methodologies. ATRP is a multi-component system that is composed of a monomer \( M \), an initiator with a transferable (pseudo)halogen \( X \), a metal complexing ligand and a metal catalyst. Other factors such as the solvent and temperature also must be taken into consideration for successful ATRP reactions [51]. The metal catalyst is the most important component of ATRP since it determines the position of the atom transfer equilibrium and the exchange dynamics between the dormant and active species. Various metal catalysts can be utilized to mediate the ATRP reactions, however, copper (Cu) catalysts are superior in terms of versatility and cost [51]. **Scheme 1.4** shows the general mechanism of Cu-catalyzed ATRP. The radicals, sometimes referred to as the active species, are generated through a reversible redox process by a transition metal complex (Cu\(^{l}\)-X/L\(_{n}\), where \( L \) is the metal complexing ligand) which undergoes a one-electron oxidation with concurrent abstraction of a (pseudo) halogen atom, \( X \), from a dormant species, \( A \cdot X \) [51, 59]. Propagation occurs in the same way as conventional radical polymerization. Termination reactions also occur in ATRP mainly through radical coupling and disproportionation, however no more than a few percent of the growing polymer chains undergo termination in a well-controlled ATRP reaction [51].
The main role of the initiator is to determine the number of growing polymer chains [51]. The theoretical molecular weight or degree of polymerization (DP) increases reciprocally with the initial concentration of initiator according to Equation 13.

\[
DP = \frac{[M]_0}{[\text{Initiator}]_0} \times \text{conversion} \tag{13}
\]

Alkyl halides are typically utilized as the ATRP initiator and the rate of the polymerization is first order with respect to the concentration of A-X. Other types of initiators that have been successfully used in ATRP include benzylic halides, \(\alpha\)-haloketones, \(\alpha\)-halonitriles and sulfonyl halides [51]. A variety of monomers have been successfully polymerized using ATRP. These include styrenes, (meth)acrylates, (meth)acrylamides, and acrylonitrile which contain substituents that can stabilize the propagating radicals [59, 60]. The main role of the ligand in ATRP is to solubilize the transition-metal salt in organic media and to adjust the redox potential of the metal centre for appropriate reactivity and dynamics for atom transfer [61]. Nitrogen-based ligands, ranging from bidentate to quadridentate ligands, work particularly well for Cu-mediated ATRP [61].

**Scheme 1.4** General scheme of copper-catalyzed atom transfer radical polymerization.
contrast, sulphur, oxygen or phosphorus ligands are less effective due to inappropriate electric effects or unfavourable binding constants [51].

1.3.3 Polymeric architectures

Major developments in synthetic polymer chemistry, which include the development of controlled living/controlled radical polymerization, have allowed the synthesis of well-defined polymers with precise composition, molecular weight and molecular architecture [51, 54, 62]. Nanoparticles with complex architecture including the formation of micelles and star-shaped polymers have been reported.

1.3.3.1 Micelles

A micelle is an aggregate of amphiphilic molecules and is the simplest form of nanoparticle. The amphiphilic molecules consist of two different blocks; polymers insoluble in the solvent which therefore associate together forming a core and a surrounding shell of soluble polymers that stabilize the micelle. The micellar structure is determined by an equilibrium between repulsive forces among the hydrophilic groups and short-range attractive forces among the hydrophobic groups. In other words, the chemical structure of a given micelle determines its size and shape [63]. A micelle typically has a spherical shape with hydrodynamic radius of 10 – 100 nm [64, 65]. The formation of larger micelles with diverse morphologies such as rod, ellipsoidal and lamella configurations have also been reported [66, 67]. Micelles have been extensively studied for a wide range of applications due to their simplicity and ease of formation [64, 68, 69].

A threshold concentration of surface active polymers is required prior to the formation of micelles. This concentration is known as the critical agglomeration concentration, or more commonly known as the critical micelle concentration (CMC) [64, 70]. Below the CMC, the entropic gains through the formation of a more thermodynamically stable structure are insufficient to drive the formation of micelles. This is mainly due to a greater loss of entropy gain due to the association of amphiphilic polymers rather than the release of rigid arrangements of solvent molecules. However, the situation is reversed above the CMC as micelles form
spontaneously driven by gains in free energy [64]. The CMC is an indication of the thermodynamic stability of the micelles where a lower CMC indicates higher thermodynamic stabilities. The CMC of a system is a function of many factors which include the composition of the amphiphilic block copolymer, the hydrophobic/hydrophilic block length, additives present, temperature and nature of the solvent [64]. In general, the length and nature of the hydrophobic (in the case of aqueous solvent) or hydrophilic (in the case of organic solvent) segment of the block copolymer has the greatest impact on the CMC [71, 72].

Micelles will dissociate into separate polymers upon dilution below the CMC [70]. The rate of dissolution is dependent on the kinetic stability of the micelle which in turn is dependent upon the association strength of the polymer segments in the core of the micelles [73]. Strong association is typically quantified by high core viscosities, low $T_g$ and high levels of chain entanglement in the core of the micelle. It is also known that the size of the core affects the kinetic stability of the micelle, i.e. a larger core size leads to less stable micelles [64, 70, 74].

The stability of micelles may be a crucial condition for some applications such as controlled drug delivery [75]. Several approaches have been utilized to stabilize micelles which include core [76, 77] and shell cross-linking [78, 79]. The stabilization of micelles was first studied by shell cross-linking and since then many studies have followed this regime via core-cross linking [77]. Many studies have focused on the stabilization of micelles through chemical reaction. There has also been a growing interest in designing micelles with a stabilization state that can be controlled by light. The use of light to trigger a desired reaction enables more temporal and positional control [80]. Light-induced cross-linking also provides a convenient route of stabilization with the avoidance of unwanted by-products [75].
1.3.3.2 Star polymers

Star polymers are a class of macromolecular structures which are comprised of a number of several linear arms connected to a central core (Scheme 1.5). They have been long studied for their unique properties which facilitate their application to advanced materials [76, 81-90]. Star polymers can be prepared via three different techniques and these are: (a) grafting-from ('core-first'); (b) grafting-to; and (c) a combination of grafting-to and from (arm-first) approach [76].

The three different techniques are all well established and have their own advantages and disadvantages, which make them suited for the preparation of a particular type of star polymers. The grafting-from ('core-first') approach utilizes a multifunctional initiator to initiate the polymerization forming the arms of the star polymers. This method allows the preparation of well-defined star polymers with a precise number of arms that can be controlled by the number of initiating sites present on the multifunctional initiator. Additionally, star polymers can be synthesized in high yields as the crude reaction mixture only requires the facile removal of any unreacted monomers. However, this technique only allows the synthesis of star polymers with a moderately low number of arms (< 30). The molecular weight of the arms also cannot be measured directly [76, 91]. Indirect methods such as end-group analysis, determination of branching parameters and cleavage of arms are often used to characterize the molecular weight of the arms. It is also difficult to ensure that every initiating site has equal reactivity which can lead to unequal length of arms.
Scheme 1.5 Synthetic approaches for preparation of star polymers via (a) grafting-from (‘core-first’), (b) grafting-to, and (c) grafting-to/from (arm-first) approaches, adapted from Blencowe et al. [76].
The grafting-to approach relies on the use of multifunctional coupling agents. This method involves the preparation of well-defined arms prior to coupling to a multifunctional linking agent which acts as the core. The preparation of star polymers with the greatest degree of control can be achieved via this approach as both the synthesis of arms and the core can be conducted in a very precise manner. The number of arms is controlled by the functionality of the multifunctional coupling agent provided that the coupling reaction is quantitative. However, a long reaction time with lengthy purification is required as the use of excess arms is generally required for quantitative conversion. Additionally, steric hindrance often leads to incomplete grafting and hinders the formation of star polymers with a large number of arms (>30) [76].

The grafting-to and from (arm-first) approach involves the reaction of living macromonomer (MM) or macroinitiators (MI) (i.e. the arms) with a di- or higher functional cross-linker to form core cross-linked star polymers. Star polymers with large number of arms (>100) can be synthesized via this technique. Additionally, the core size is larger (ca. 10 to 40% relative to the overall molecular weight of the polymer) when compared to star polymers synthesized via the two previously described techniques [76]. One drawback of using an arm-first approach is the synthesis of star polymers with broad arm number distributions [76, 92]. Extensive purification, such as fractional precipitation or dialysis protocols, is also required due to the incomplete conversion of the MI or MM.

1.4 Current challenges in CO₂ separation membranes

It is known that membrane technologies offer advantages over conventional gas separation processes such as reduced environmental impact and the potential for lower capital and operating costs [93]. The two main criteria to gauge the performance of a membrane are permeability and selectivity. However, Robeson has shown that there is a general trade-off between permeability and selectivity for polymeric membranes; membranes that have high permeability tend to have low selectivity and vice versa (Figure 1.11) [94, 95].
Figure 1.11 Robeson’s trade-off curve for CO$_2$ and N$_2$ gas pair [94].

More recently it has been noted that for CO$_2$ capture, permeance becomes a more important parameter than permeability in determining the performance of gas separation membranes. Permeance is controlled by both the permeability and the thickness of the active layer (Equation 5). Previous studies have recognized that there is a target range for permeance and selectivity that would make membrane processes cost-competitive for post combustion capture. This target range is shown in Figure 1.12 [96]. There are two criteria for membranes to fall within this region. Firstly, membranes are required to have high CO$_2$ permeance (≥ 1000 GPU) as membranes with lower CO$_2$ permeances will require too much membrane area. Membranes also need to have a selectivity of more than 20 but less than 150 to fall within this region. Membranes with a selectivity of less than 20 are unlikely to be selective enough, no matter what their permeance. Conversely, membranes with a selectivity of more than 150 are likely to be too selective and would require too much membrane area for a cost-competitive process.
Figure 1.12 CO$_2$/N$_2$ selectivity versus CO$_2$ permeance trade-off plot comparing the performance of commercially available membranes, the Polaris™ membrane and various developmental membranes reported in the literature. The shaded region indicates the optimum membrane properties for the separation of CO$_2$ from flue gases as proposed by Merkel et al. [96]. Open circles (O) are data points for Kai et al. [97] and Duan et al. [98]; the filled triangle (▲) is reported by Bao and Trachtenberg [99]; the filled diamond (♦) is data of Kim et al. [100]; the open square (□) is data of Cai et al. [101]; the open diamond (◇) is data of Hanioka et al. [102]; the filled star (★) is data from Zhao et al. [103]; the inverted triangles (▼) are data from Hendriks et al. [104].

Various approaches have been explored to fabricate polymeric membranes with superior separation performance; these include the synthesis of block copolymers which benefit from combining the intrinsic properties from different blocks to provide a tailored morphology. There has also been much interest in the incorporation of hard nanoparticles based on inorganic materials into existing polymeric membranes [19, 105, 106]. The application of each of these concepts is described in more detail below.

1.4.1 Block copolymers for CO$_2$ separation

Block copolymers (BCPs) are polymers with two or more different blocks covalently linked to form one macromolecule. BCPs have gained increasing interest
in their use for gas separation membranes with results showing superior separation performance [107], due to their ability to self-assemble into a variety of ordered nanostructures. Additionally, the properties of BCPs can be tuned by changing their chemical composition and block lengths. A key strategy for fabricating functional BCPs includes the formation of macromolecules that comprise ‘hard’ and ‘soft’ block segments. The ‘hard’ segment provides the mechanical strength as well as gas selectivity, while the ‘soft’ segment provides the flexibility to facilitate permeable gas transport [1].

Early studies focused on the gas permeation of simple BCPs such as diblock and triblocks [106]. With major developments in synthetic polymer chemistry, which include the development of controlled living radical polymerization (detailed in Section 1.3.2.2), gas separation studies on BCPs with precise composition and molecular weight have been made possible. However, the full potential of gas separation membranes fabricated from BCPs with precise composition and molecular weight has not been fully exploited due to the synthetic challenges faced by researchers.

1.4.1.1 Well-defined block copolymer

BCPs were first studied for gas separation in 1975. The studies utilized commercially available polystyrene (PS)/polybutadiene (PB) triblock copolymers (PS-b-PB-b-PS) and found that the performance was strongly dependant on the morphology and domain orientation of the film [108-112]. All of the studies suggested that a lamella structure with the microphase aligned normal to the film surface provided the best results [108].

Later studies reported the synthesis of BCPs with specific length and composition based on polyethylene/poly(ethylene-propylene) (PEt/PEP) diblock and PET/PEP/PET triblock copolymers [113-115]. The study suggested that the gas transport performance in semicrystalline BCPs was related to the corresponding changes in the morphology. A decrease in permeability was observed with increasing crystallinity as gas molecules are generally considered to be insoluble in polymer crystallites [113, 116]. The study was unsuccessful in preparing crack and
pinhole-free specimens for gas transport measurements. However, modelling was used to confirm the results of the previous studies that suggested a lamella structure aligned to the film gives the best separation performance [113].

Studies based on polystyrene (PS)/poly(ethylene oxide) (PEO) triblock copolymers (PS-\textit{b}-PEO-\textit{b}-PS) have been conducted to assess their potential as reverse selective membranes for CO$_2$ separation [117]. CO$_2$ permeability was enhanced by blending with poly(ethylene glycol) (PEG) as it has a high affinity for CO$_2$. Additionally, blending both amorphous and semicrystalline PEG promoted a morphology transition from alternating lamellar to polyether continuous morphology [117].

![Figure 1.13](image)

**Figure 1.13** Development of well-defined block copolymers since 1970.

The advent of controlled polymerization techniques (Section 1.3.2.2), has allowed for the fabrication of BCPs with more precise composition and molecular architecture. Recently, BCPs with one cross-linked phase and one bicontinuous phase have been developed. The cross-linked phase provides the mechanical stability that is required, with the gas transport mainly occurring through the bicontinuous phase. Various methods of cross-linking such as the use of photochromic moieties and reactive BCP precursors for ring-opening metathesis polymerization (ROMP) have been explored [118]. The best results for CO$_2$ separation were achieved with a cylindrical structure with the bicontinuous phase orientated perpendicular to the surface [119]. These studies have demonstrated that advanced materials for gas separation could be fabricated through the synthesis of functional BCPs and targeted self-assembly.
1.4.1.2 Multi block copolymers

Pebax® is a commercial poly(amide-\textit{b}-ether) copolymer have been widely used in sporting equipment. The multi BCP has recently received significant attention as a promising membrane material as it has shown potential for use in CO\textsubscript{2} separation membranes [120-122]. Pebax® is a thermoplastic polymer with two separated microphases; an aliphatic polyamide (PA) ‘hard’ segment and an amorphous polyether (PE) ‘soft’ segment [123]. The gas transport occurs mainly through the PE phase, while the PA phase provides the structural stability required for gas separation which may occur at high temperatures and pressures [120]. Various grades of Pebax® are available which are comprised of a varying number of PA and PE segments and block lengths as shown in Table 1.1.

<table>
<thead>
<tr>
<th>Grade</th>
<th>‘Hard’ segment</th>
<th>‘Soft’ segment</th>
<th>% of ‘soft’ segment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1657</td>
<td>Nylon 6</td>
<td>PEO</td>
<td>60</td>
</tr>
<tr>
<td>2533</td>
<td>Nylon 12</td>
<td>PTMO</td>
<td>86</td>
</tr>
<tr>
<td>4033</td>
<td>Nylon 12</td>
<td>PTMO</td>
<td>71</td>
</tr>
<tr>
<td>6333</td>
<td>Nylon 12</td>
<td>PTMO</td>
<td>37</td>
</tr>
</tbody>
</table>

Table 1.1 Various grades of Pebax® copolymers [124-127].

The performance of Pebax® copolymers can be further improved by various methods. The simplest and most studied way is through physical blending of additives. The selection of additives is crucial as the performance of the blend membranes is directly related to the nature of additives and polymer characteristics. Low molecular weight PEG has been widely utilized in this respect as the ether oxygen groups can interact with CO\textsubscript{2}, resulting in high CO\textsubscript{2} solubility [128-130]. Other methods to improve the separation performance of Pebax® copolymers include the blending of carbon nanotubes, and silver or silica particles [106]. The preparation of facilitated transport Pebax® copolymers have also been explored by the incorporation of amino or quaternary ammonium segments [131].

Polyactive™ is another example of a multi BCP that were not initially designed for CO\textsubscript{2} separation. This multi BCP is based on poly(ethylene oxide)-\textit{b}-poly(1-butylene
terephthalate) (PEO-b-PBT) and it was designed for medical applications [132]. Polyactive™ has two separated microphases; a ‘hard’ segment made of PBT and a ‘soft’ block made of PEO [43, 133]. As before, the ‘soft’ segment facilitates the gas transport while the ‘hard’ segment provides the structural stability. Past studies have indicated that this class of multi BCPs show exceptional CO₂ separation performance when fabricated into a thin composite membrane [43]. However, limited studies have been conducted with Polyactive™ due to the commercial nature of the material.

1.4.2 Mixed-matrix membranes

It is known that inorganic materials can show exceptional separation performance as well as chemical and thermal stability [9-15]. However, the fabrication of a purely inorganic membrane entails a high production cost as it is difficult to achieve continuous and defect-free membranes. Another drawback of fabricating inorganic membranes includes their inherent brittleness [16-18]. In view of this situation, an approach of combining both polymeric membranes and inorganic particles has been identified to fabricate membranes with superior separation characteristics. These are termed mixed-matrix membranes (MMMs) [19, 105].

MMMs consist of two phases; the bulk phase is the polymer matrix while the dispersed phase represents the inorganic particles. The main aim of MMMs is to preferentially transport gases through the inorganic particles rather than the polymer matrix phase [19].

MMMs can be fabricated in symmetric or asymmetric formats. A symmetric dense film is the most studied geometry due to the simplicity of the fabrication process. The main challenge of fabricating a symmetric dense film is forming a homogenous dispersion of the inorganic particles within the polymer matrix. Additionally, it is difficult to fully exploit the gas transport properties of the inorganic particles as typically loading levels cannot exceed 50% [134]. This is mainly due to the agglomeration of particles. Another drawback of fabricating symmetric dense films
includes the low flux due to the thickness of the fabricated membrane, typically more than 50 µm [135].

Loeba and Sourirajan reported the fabrication of an asymmetric membrane that composed of an ultra thin active layer coated onto a porous support layer [136]. This morphology overcame the issues associated with low flux that is commonly associated with symmetric dense films. The same concept can also be applied to further enhance the performance of MMMs. However, the fabrication of asymmetric MMMs has not been much explored. This is possibly due to the need to design nanoparticles with a size that does not exceed the thickness of the active layer.

Studies have shown that a good selection of membrane morphology does not guarantee good separation performance. Several challenges associated with the fabrication of MMMs can significantly affect the separation performance. These challenges include the (i) homogeneous dispersion of particles in the polymer matrix and (ii) a defect-free polymer/inorganic particle interface.

1.4.2.1 Dispersion of particles

In the production of MMMs, inorganic particles tend to agglomerate within the polymer matrix due to the difference in physical properties and density [19, 105]. The agglomeration of particles may cause voids that cannot be filled by the polymer chain segments. As a result, selectivity is reduced as these voids allow extra pathways for the gas molecules to pass through [19, 105]. Ways to avoid agglomeration include the “priming” of inorganic particles with a thin layer of polymer prior to mixing with the bulk polymer solution and adding inorganic particles into the solvent rather than the polymer solution before mixing the separate solutions together [137-140].

Sedimentation of inorganic particles is another challenge to overcome before homogenous dispersions can be achieved [19, 105]. High polymer concentrations can be used to slow the particle sedimentation [137, 138]. However, this may also
increase the chance of agglomeration. To date, the use of ultra-fine crystalline particles appears to be the best solution to avoid particle sedimentation [141].

1.4.2.2 Interfacial morphology

The gas transport properties of MMMs are strongly dependent on the polymer/inorganic particle interface [19, 105]. Figure 1.14 illustrates the various interfacial morphologies that can occur in MMMs. The supposed ideal morphology is shown in case 1 while the detachment of polymer chains from the inorganic particles is shown in case 2, which results in the generation of interfacial voids. Case 3 illustrates the rigidification of polymer chains while case 4 indicates the partial blockage of particle pores by the polymer chains.

![Figure 1.14 Various interfacial morphologies of mixed-matrix membranes adapted from Chung et al. [105].](image)

Interfacial voids are typically formed due to low adhesion between the inorganic particles and the polymer matrix [142, 143]. Small and contained voids can improve separation performance. However, most of the time, these voids are large and cause gas molecules to take non-selective and less resistant by-pass instead of passing through the pores of the particles [141]. Strategies such as the use of
mesoporous materials [144-146] and silane coupling agents [147] have been widely explored and led to improved adhesion. Better separation performance has been achieved with improved interfacial morphology [19].

Polymer chains may rigidify at the polymer/inorganic particle interface as the mobility of the polymer chains can be inhibited in the region directly contacting the particles relative to that for the bulk polymer [105]. Polymer rigidification often results in higher selectivity as diffusivity selectivity is enhanced with lower mobility of polymer chains [148]. Past studies have suggested that polymer matrix plasticization has offered a way to increase the mobility of a polymer chain that has rigidified [149].

For MMMs using porous fillers, partial or full pore blockage by the polymer chains often occurs [138, 150, 151]. Partial blockage could potentially improve separation performance if the reduced pore size is suitable for molecular sieving mechanism to occur [137, 147, 149]. However, in most cases pore blockage results in reduced permeability. Introducing a coupling agent to create a space between the polymer chain and inorganic particles could potentially reduce the problem of pore blockage [147].

**Table 1.2** The general effects of various interfacial morphologies on gas transport properties [105].

<table>
<thead>
<tr>
<th>Morphologies</th>
<th>Effect on permeability</th>
<th>Effect on selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interfacial voids</td>
<td>Increase</td>
<td>Decrease</td>
</tr>
<tr>
<td>Polymer rigidification</td>
<td>Decrease</td>
<td>Increase</td>
</tr>
<tr>
<td>Pore blockage</td>
<td>Decrease</td>
<td>Increase</td>
</tr>
</tbody>
</table>

1.5 **Objectives**

The fabrication of next generation mixed-matrix gas separation membranes through the incorporation of hard inorganic materials is hampered by the need to ensure a defect-free polymer/inorganic particle interface. In this thesis, a similar approach is applied to the addition of soft polymeric nanoparticles into a selective
polymer matrix. In this case, the problem of defects occurring between the particle and the matrix can be avoided through the engineering of particles compatible with the polymer matrix. It is envisaged that the addition of localized, gas permeable soft polymeric nanoparticles into a selective polymer matrix will lead to improvements in gas separation performance. The main aim of this thesis is to synthesize novel nanoparticles with well-defined architectures and utilize these as additives for existing gas separation membrane materials. The requirements for these polymeric nanoparticles include: (i) a soft and CO₂ permeable core and (ii) a corona which is compatible with the polymer matrix (Figure 1.15).

![Design of soft polymeric nanoparticles.](image)

Two design strategies are employed to build soft polymeric nanoparticles with well-defined architectures (Figure 1.16). The first strategy is based on macromolecular self-assembly and involves the formation of cross-linked micelles via the self-assembly of block copolymers, followed by stabilization through hydrogen abstraction and photochemical cross-linking. The second strategy is based directed macromolecular formation through the synthesis of star polymers via the grafting-from ('core-first') approach. The best candidate soft nanoparticles are then blended with a selective polymer matrix to form the active layer of thin film composite membranes, which are tested for their CO₂ separation from N₂. The size of the soft polymeric nanoparticles are significantly smaller than the thickness of the active layer and overcome the problem of blending larger inorganic nanoparticles to form asymmetric MMMs.
Figure 1.16 Research theme of this thesis: soft polymeric nanoparticles as additives for CO₂ separation membranes.

1.6 Thesis outline

In Chapter 2, the synthesis of a series of novel soft polymeric nanoparticles based on triblock copolymers containing ‘hard’ fluorinated PI and ‘soft’ PDMS is described. Well-defined difunctional PI was initially prepared via step-growth polymerization using precise control of the diamine and dianhydride ratio. Subsequent functionalization with tertiary alkyl halide afforded a telechelic macroinitiator suitable for ATRP. ATRP of PDMS-monomethacrylate (PDMS-MA) macromonomer using the macroinitiator in different molar ratios afforded a series of triblock copolymers with varying PDMS weight fractions. Self-assembly of the triblock copolymers was conducted in a selective solvent for the PI block, N,N-dimethylformamide (DMF), and afforded nanoparticles with a ‘hard’ PI shell and ‘soft’ PDMS core. Cross-linking of the nanoparticles was achieved via hydrogen abstraction through the thermal degradation of benzoyl peroxide. The size of the
self-assemblies and cross-linked derivatives were characterized via dynamic light scattering (DLS) while the morphology was characterized via transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM).

![Self-Assembly](image)

**Figure 1.17 Chapter 2: Soft polymeric nanoparticles based on linear polyimide and linear brush poly(dimethylsiloxane) triblock copolymers.**

**Chapter 3** explores the synthesis of novel soft polymeric nanoparticles based on linear PEG and linear brush PDMS diblock copolymer. Three different molecular weights of linear monomethyl ether PEG (MeOPEG) were initially functionalized with tertiary alkyl halide to afford a macroinitiator suitable for ATRP. The three different molecular weights macroinitiators were then chain extended with PDMS-MA macromonomer and photoactive anthracene moieties in different molar ratios to afford a series of photoresponsive amphiphilic diblock copolymers. Self-assembly of the diblock copolymers was conducted in a selective solvent for the PEG block, DMF, and afforded nanoparticles with various structures, ranging from spherical micelles to large compound micelles. Cross-linking of the nanoparticles was achieved via the [4+4] photodimerization of the anthracene moieties incorporated in the PDMS blocks upon exposure to UV-radiation (> 300 nm). The photocleavage of the anthracene moieties was studied by exposing the stabilized nanoparticles to UV-radiation with a wavelength of < 300 nm. Ultraviolet-visible (UV-Vis) spectroscopy was utilized to monitor the extent of photodimerization and photocleavage. The size of the self-assemblies and cross-linked derivatives were characterized via DLS while the morphology was characterized via TEM.
Chapter 3 outlines the synthesis of two other novel soft polymeric nanoparticles, PEG and PEG-\textit{b}-PDMS grafted star polymers. The grafted star polymers were synthesized \textit{via} ATRP and the 'core-first' approach. Initially, pentaerythritol was functionalized to afford a tetra-functional initiator suitable for ATRP. The tetra-functional initiator was subsequently chain extended with varying amounts of PEG methyl ether methacrylate (MeOPEG-MA) macromonomer to afford PEG grafted star polymers. The tetra-functional initiator was also chain extended with varying amounts of PDMS-MA macromonomer to afford PDMS grafted star polymer. The synthesized grafted star polymers were then further chain extended with varying amounts of MeOPEG-MA macromonomer to afford a series of PEG-\textit{b}-PDMS grafted star polymers.

Chapter 4 outlines the synthesis of two other novel soft polymeric nanoparticles, PEG and PEG-\textit{b}-PDMS grafted star polymers. The grafted star polymers were synthesized \textit{via} ATRP and the 'core-first' approach. Initially, pentaerythritol was functionalized to afford a tetra-functional initiator suitable for ATRP. The tetra-functional initiator was subsequently chain extended with varying amounts of PEG methyl ether methacrylate (MeOPEG-MA) macromonomer to afford PEG grafted star polymers. The tetra-functional initiator was also chain extended with varying amounts of PDMS-MA macromonomer to afford PDMS grafted star polymer. The synthesized grafted star polymers were then further chain extended with varying amounts of MeOPEG-MA macromonomer to afford a series of PEG-\textit{b}-PDMS grafted star polymers.

Figure 1.18 Chapter 3: Soft polymeric nanoparticles based on linear poly(ethylene glycol) and linear brush poly(dimethylsiloxane) diblock copolymers.

Figure 1.19 Chapter 4: Soft polymeric nanoparticles based on poly(ethylene glycol) and poly(ethylene glycol)-\textit{b}-poly(dimethylsiloxane) grafted star polymers.
Chapter 5 presents the first utilization of soft polymeric nanoparticles as additives for gas separation membranes. The best candidate soft polymeric nanoparticles, PEG-<i>b</i>-PDMS grafted star polymers as outlined in Chapter 4, were blended with commercially available poly(amide-<i>b</i>-ether) copolymers, Pebax® 2533. TFC membranes were prepared by blending grafted star polymers with Pebax® 2533 and spin coating these blends onto polyacrylonitrile (PAN) microporous substrate that have been pre-coated with a PDMS gutter layer. Scanning electron microscopy (SEM) was used to measure the thickness of the PDMS gutter layers and membrane active layers. The CO₂ and N₂ gas transport properties of these TFC membranes was determined at 35 °C with an upstream pressure of 3.4 bar, using a constant pressure variable volume (CPVV) apparatus. The performance of the TFC membranes and their corresponding active layer is compared to the performance of commercial natural gas membranes and current state-of-the-art membranes.

![Figure 1.20](image)

**Figure 1.20 Chapter 5:** Soft polymeric nanoparticles as additives for CO₂ separation membranes.

In Chapter 6, concluding remarks from each chapter are presented along with some proposed future directions for the work outlined in this thesis. Chapter 7 describes the characterization methods and detailed experimental procedures for all the work presented in this thesis.
1.7 References


Rizzardo E, Solomon DH. Polym Bull 1979;8:529-34.


Soft Polymeric Nanoparticles Based on Linear Polyimide and Linear Brush Poly(dimethylsiloxane) Triblock Copolymers

2.1 Chapter perspective

Soft materials such as micelles have been extensively used in the biomedical field while the application of such materials to separation technologies have been less explored. It is envisaged that the addition of soft polymeric nanoparticles into a selective polymer matrix could improve the gas separation performance, as they would be able to form localized, high flux, soft domains within the selective polymer matrix. In this chapter, soft polymeric nanoparticles based on block copolymers with 'hard' fluorinated polyimide and 'soft' poly(dimethylsiloxane) segments will be detailed. The 'hard' block is generally rigid in nature and provides the selective separation of the target gas from a mixture of gases. Additionally, it also provides the structural and mechanical support. The 'soft' block is flexible in nature and provides pathway for the transportation of gases.
2.2 Introduction

Polyimides (PIs) are a class of high performance rigid and glassy polymers that have attracted much attention due to their outstanding chemical, mechanical and thermal stability [1-3]. PIs have found application in the aerospace industry as composite materials, in microelectronics as inter-level insulators and as matrices for gas separation membranes [1, 2, 4]. Most PIs are poorly processable due to their planar hetero-aromatic structures and a major effort has been devoted to the development of PIs that possess good solubility [5, 6]. Monomers with hydrophobic trifluoromethyl groups, such as hexafluoroisopropylidene-diphthalic anhydride (6FDA), are often utilized in the synthesis of PIs to increase their solubility while maintaining their excellent chemical, mechanical and thermal stability [7, 8]. The presence of the hydrophobic trifluoromethyl (CF₃) groups also improves gas separation performance as it increases the stiffness of the polymer which allows more effective separation of molecules based on steric bulk, hence selectivity is enhanced. Additionally, the large trifluoromethyl groups increase the inter-chain spacing and reduce the effective chain packing which lead to an increase in permeability [9, 10]. Poly(dimethylsiloxane) (PDMS) is a rubbery polymer that is often covalently incorporated into PI to increase its solubility and processability [11, 12]. In addition, PDMS has been utilized to impart impact resistance, low dielectric constant, low moisture uptake and thermo-oxidative resistance [13]. More importantly, PDMS has been extensively studied for incorporation into gas separation membranes as it possesses high intrinsic permeability, and as such is a potential candidate for the fabrication of soft polymeric nanoparticles [14]. Several approaches have been reported to combine PDMS and PI; mainly through copolymerization or grafting. Covalently linked copolymers have included the grafting of PDMS along a polyimide backbone [13, 15], copolymerization of end-functionalized PDMS and PI [16-18], and end-capping of PI with linear PDMS [19]. In the past, studies involving siloxane-containing PIs have mainly focused on varying the weight fraction and the molecular weight of the siloxane segments and investigating the resulting effects on the thermal, mechanical, rheological, surface and dielectric properties of the copolymers [13, 15-19].
Block copolymers (BCPs) self-assembly has received considerable scientific attention as it represents one of the key strategies to prepare well-defined nanostructures with tunable chemical and physical properties [20, 21]. BCPs consist of several polymer blocks of different composition. Covalently linking two (or more) incompatible polymers allows the formation of ordered nano and microdomains. Novel properties not shown by the corresponding homopolymers can also be found for BCPs by adjusting the degree of incompatibility between different blocks, their molecular weight or the block sequence. In the past decades, scientists have exploited the thermodynamic incompatibility of BCPs to fabricate various functional nanomaterials [22-24]. For example, ABA triblock copolymers can self-assemble to form flower type micelles in selective solvents for the middle block. Flower type micelles display interesting properties, such as low entanglement and low viscosity at high concentrations [25-27]. Based on the architecture, this type of micelle is also referred to as a ‘nano-flower’ (NF) [28]. Micellization of ABA triblock copolymers to form NFs have been reported for poly(2-vinyl pyridine)-b-polystyrene-b-poly(2-vinyl pyridine) [25, 29, 30], poly(vinyl alcohol)-b-polystyrene-b-poly(vinyl alcohol) [31], poly(2-hydroxyethyl acrylate)-b-poly(ethylene oxide)-b-poly(2-hydroxyethyl acrylate) [32], poly(methyl methacrylate)-b-poly(ethylene oxide)-b-poly(methyl methacrylate) [33-35], and polystyrene-b-poly(ethylene oxide)-b-polystyrene copolymers [36, 37]. In these previous studies, the triblock copolymers are comprised of flexible polymer chains, however it is unclear if NF morphologies can still be formed if a copolymer with a very rigid middle block is employed.

This chapter describes the synthesis of novel soft nanoparticles based on well-defined PI/PDMS triblock copolymers with very rigid PI middle blocks. The triblock copolymers were synthesized by a combination of step- and chain-growth polymerizations. The end groups and molecular weight of the PI were accurately controlled by careful manipulation of the monomer ratios. Self-assembly of the triblock copolymers was investigated in N,N-dimethylformamide (DMF), which is a selective solvent for the PI block, and resulted in the formation of nanoparticles that were further stabilized following cross-linking via hydrogen abstraction. Both the self-assemblies and cross-linked derivatives were characterized to determine
their size, morphology and molecular structures. Given that the self-assembly is conducted in a selective solvent for the PI block it is proposed that the resulting nanoparticles could consist of a ‘hard’ PI shell, and a ‘soft’ PDMS core.
Scheme 2.1 Synthetic outline for the preparation of soft polymeric nanoparticles based on linear polyimide and linear brush poly(dimethylsiloxane) triblock copolymers.
2.3 Result and discussion

A combination of step- and chain-growth polymerizations was employed to prepare well-defined triblock copolymers (Scheme 2.1). Initially, ‘hard’ fluorinated PI, poly(6FDA-co-TMPD) (P1), with a very high proportion of amino end-groups was synthesized via step-growth polymerization and subsequently functionalized to afford the α,ω-dibromo terminated difunctional macroinitiator P2, suitable for atom transfer radical polymerization (ATRP). The well-defined diamino terminated PI and its functionalized derivative were characterized via gel permeation chromatography (GPC), nuclear magnetic resonance (NMR) spectroscopic analysis and matrix-assisted laser desorption/ionization time of flight (MALDI ToF) mass spectroscopy. The poly(6FDA-co-TMPD) macroinitiator P2 was subsequently chain extended with varying amounts of monomethacrylxypropyl terminated poly(dimethylsiloxane) (PDMS-MA) macromonomer to afford a series of novel block copolymers containing ‘hard’ and ‘soft’ segments, with constant and variable degrees of polymerisation (DP), respectively.

2.3.1 Synthesis of α,ω-diamino poly(6FDA-co-TMPD)

Fluorinated PI, poly(6FDA-co-TMPD) P1, with amino end-groups was synthesized via a standard two-step step-growth polymerization involving anhydride ring-opening and thermal cyclodehydration (Scheme 2.1). An exact molar ratio of 6FDA and TMPD (5:6) was utilized to control the DP and ensure a very high proportion of amino end-groups. In the presence of nucleophiles such as water, the anhydride groups of 6FDA are readily hydrolyzed to form ortho dicarboxylic groups, which are unreactive towards polymerization, thus the use of anhydrous solvents and inert environments are crucial to obtain well-defined polymers [1]. In this study, thermal imidization (also known as cyclodehydration) at 180 °C was conducted, since the commonly employed chemical imidization in the presence of drying agents (e.g., acetic anhydride) and base catalyst would have resulted in undesirable acetylation of the terminal amine groups [34]. Subsequently, the α,ω-diamino poly(6FDA-co-TMPD) P1 was isolated via precipitation. $^1$H NMR spectroscopic analysis confirmed that complete imidization was achieved as
indicated by the absence of resonances corresponding to carboxylic protons (typically in the $\delta_{H}$ 10.5-13 ppm region; Figure A2.1), and revealed the presence of aromatic methyl protons adjacent to the amine end-groups (Figure 2.1a). Integration of the characteristic end-group and backbone resonances provided a number-average molecular weight ($M_n$) of 3.8 kDa, which is very similar to the theoretical $M_n$ (3.2 kDa) based upon the monomer ratio employed. In comparison, the $M_n$ (5.2 kDa) determined by GPC based upon the assumption of 100% mass recovery, was slightly higher (Table 2.1).

MALDI ToF MS was utilized to determine the molecular weight and end-group composition of the PI P1. The mass spectrum of PI P1 obtained using silver trifluoroacetate (AgTFA) as the cationization agent revealed several series of peaks separated by ca. 573 m/z, which corresponds to the repeat unit of poly(6FDA-co-TMPD) (Figure 2.2a). The mass values of the major series of peaks were found to correlate well with the expected masses of the Ag$^+$ salt of $\alpha,\omega$-diamino poly(6FDA-co-TMPD). Importantly, no series of peaks corresponding to mono- or di-anhydride terminated poly(6FDA-co-TMPD) were observed. A very minor, unidentified series ($< 1.5\%$) was attributed to fragmentation of the PI during the MS ionization process. The very high extent of amino end-groups observed in the mass spectrum supports the NMR spectroscopy results, and is attributed to the excess of TMPD used in the polymerization. To ensure that the observed mass series correlates to the expected Ag$^+$ salt, other cations (e.g., Na$^+$ and K$^+$) were also employed in the analysis and resulted in characteristic shifts in the PI mass series corresponding to those salts (Figure A2.5). Determination of $M_n$ via MALDI ToF MS provided a value of 2.8 kDa, which is slightly lower than that calculated from NMR spectroscopy (Table 2.1). The observed discrepancy most likely results from preferential ionization of low molecular weight species during MS analysis [38].

2.3.2 Synthesis of $\alpha,\omega$-dibromo poly(6FDA-co-TMPD) macroinitiator

Functionalization of PI P1 with initiating moieties was achieved through reaction with 2-bromoisobutyryl bromide to afford the $\alpha,\omega$-dibromo poly(6FDA-co-TMPD) macroinitiator P2 in quantitative yield (Scheme 2.1) [39]. GPC analysis of
Macroinitiator $\textbf{P2}$ revealed an increase in $M_n$ from 5.2 kDa ($\textbf{P1}$) to 5.9 kDa ($\textbf{P2}$) (Table 2.1). $^1$H NMR spectroscopic analysis of $\textbf{P2}$ revealed a new resonance at $\delta_H$ 2.2 ppm (Figure 2.1b) corresponding to the methyl groups of the bromoisobutyramide end-groups, which was accompanied by a down-field shift of the adjacent aromatic methyl protons from $\delta_H$ 2.09 (Figure 2.1a) to 2.11 ppm (Figure 2.1b).

Figure 2.1 $^1$H NMR spectra (CDCl$_3$) of poly(6FDA-co-TMPD) (a) $\textbf{P1}$ and (b) $\textbf{P2}$. 
As for P1, MALDI ToF MS was used to characterize macroinitiator P2 using identical conditions (e.g., AgTFA) and revealed a series of peaks separated by ca. 573 m/z (Figure 2.2b). In theory, the addition of two bromoisobutyramide end-groups should result in a 298 m/z shift in the mass series to higher values relative to the diamino PI P1 mass series (Figure 2.2a). However, examination of the mass values revealed a shift of ca. 136 m/z instead of the expected value of 298 m/z, which is attributed to fragmentation of the bromine atoms during the MS ionization process. Taking this into account, the observed mass values were found to correlate well with the desired dibromo PI P2. The utilization of other cationization agents (e.g., Na⁺ and K⁺) resulted in characteristic shifts in the PI mass series corresponding to those salts (Figure A2.6), although fragmentation of the bromine atoms was observed in all cases (Table 2.1).

### Table 2.1 Molecular weight characterization of polyimides P1 and P2.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n^{\text{theor}}$ (kDa)$^a$</th>
<th>$M_n^{\text{NMR}}$ (kDa)$^b$</th>
<th>$M_n^{\text{MALDI ToF}}$ (kDa)$^c$</th>
<th>$M_n^{\text{GPC}}$ (kDa)$^d$</th>
<th>PDI$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>3.2</td>
<td>3.8</td>
<td>2.8</td>
<td>5.2</td>
<td>1.5</td>
</tr>
<tr>
<td>P2</td>
<td>3.5</td>
<td>4.1</td>
<td>3.1</td>
<td>5.9</td>
<td>1.5</td>
</tr>
</tbody>
</table>

$^a$ Number-average molecular weight based upon the precise monomer ratio of the diamine (TMPD) to dianhydride (6FDA) employed. $^b$ Number-average molecular weight calculated from $^1$H NMR spectroscopic analysis. $^c$ Number-average molecular weight determined by MALDI ToF MS analysis. $^d$ Number-average molecular weight and polydispersity index (PDI) measured by GPC based upon the assumption of 100% mass recovery; using this method $dn/dc$ was determined to be 0.132 for P1 and P2.
Figure 2.2 MALDI ToF mass spectra of (a) diamino poly(6FDA-co-TMPD) P1 and (b) dibromo macronitiator P2 recorded in linear/positive mode using DCTB and AgTFA as the matrix and cationization agent, respectively. The numbers on the peaks denote the number of repeat units (n, 573 m/z).
2.3.3 Synthesis of polyimide/poly(dimethylsiloxane) triblock copolymers

Triblock copolymers were synthesized via ATRP using Cu(I)/Me₆TREN as the catalyst/ligand system (Scheme 2.1) and α,ω-dibromo poly(6FDA-co-TMPD) P2 as the macronitiator and PDMS-MA as the macromonomer. Me₆TREN was chosen as the ligand as previous studies indicated that the use of other ligands with low rates of activation (kₐ), such as PMDETA or bipyridine, result in low conversions [40]. ATRP of PDMS-MA macromonomer initiated with P2 at various macromonomer to initiator ratios (Table 2.2) yielded the copolymers (P3-1 to P3-3) as pale yellow tacky solids. ¹H NMR spectroscopic analysis revealed high PDMS-MA macromonomer conversions, up to 94%, and $M_n$ values ranging from 10.1 to 23.3 kDa (Table 2.2). GPC analysis of P3-1 to P3-3 provided $M_n$ values in good agreement to those calculated by ¹H NMR spectroscopic analysis (Table 2.2).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Molar ratio [PDMSMA] : [P2]</th>
<th>Conversion (%)ᵃ</th>
<th>$M_n^{\text{NMR}}$ (kDa)ᵇ</th>
<th>$M_n^{\text{GPC}}$ (kDa)ᶜ</th>
<th>PDIᶜ</th>
<th>Yield (%)ᵈ</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3-1</td>
<td>5:1</td>
<td>88</td>
<td>10.1</td>
<td>9.7</td>
<td>1.9</td>
<td>94</td>
</tr>
<tr>
<td>P3-2</td>
<td>10:1</td>
<td>92</td>
<td>16.7</td>
<td>16.8</td>
<td>1.9</td>
<td>92</td>
</tr>
<tr>
<td>P3-3</td>
<td>15:1</td>
<td>94</td>
<td>23.3</td>
<td>22.8</td>
<td>1.9</td>
<td>87</td>
</tr>
</tbody>
</table>

ᵃ PDMS-MA macromonomer conversion was calculated from ¹H NMR spectroscopic analysis. ᵇ Number-average molecular weight of the copolymers calculated from ¹H NMR spectroscopic analysis. ᵅ Number-average molecular weight and polydispersity index (PDI) measured by GPC based upon the assumption of 100% mass recovery; using this method $dn/dc$ was determined to be 0.101 (P3-1), 0.085 (P3-2) and 0.078 (P3-3). ᵈ Isolated yield.

Closer examination of the GPC refractive index chromatograms of copolymers P3-1 to P3-3 revealed a shoulder at ca. 29 min, which corresponds to unreacted PDMS-MA macromonomer (Figure 2.3). Even though multiple precipitations were conducted, the association of unreacted PDMS-MA macromonomer with the high density brushes made it difficult to completely remove.
Figure 2.3 GPC differential refractive index chromatograms of polyimide/poly(dimethylsiloxane) triblock copolymers P3-1 to P3-3 and their precursors, macroinitiator P2 and PDMS-MA macromonomer. The molecular weight of PDMS-MA could not be determined via GPC as a result of weak light scattering signals, however, the manufacturer specifies a molecular weight of 600-800 Da.

$^1$H NMR spectroscopic analysis of the copolymers P3-1 to P3-3 (Figure 2.4), revealed characteristic methylene and methyl proton resonances (ca. $\delta_H$ 1.8 and 1.0 ppm) associated with the methacrylate polymer backbone, which in combination with the GPC results confirmed the successful synthesis of the PI/PDMS triblock copolymers. The integral ratios of the PI aromatic protons (ca. $\delta_H$ 8.0 ppm) and the methylene protons ($\delta_H$ 3.9 ppm) adjacent to the ester groups in the PDMS-MA block were used to calculate the $M_n$ values (Table 2.2).
Figure 2.4 $^1$H NMR spectrum (CDCl$_3$) of fractionated polyimide/poly(dimethylsiloxane) triblock copolymers P3-3. The asterisk denotes residual THF solvent.

2.3.4 Self-assembly of polyimide/poly(dimethylsiloxane) triblock copolymers

Self-assembly of the triblock copolymers in DMF afforded stable nanoparticles, which are proposed to consist of a ‘soft’ PDMS cores surrounded by a ‘hard’ PI shell. The intensity-average hydrodynamic diameters ($d_H$) of the PI/PDMS triblock copolymers after self-assembly in DMF were characterized via DLS (Figure 2.5) and found to range from 87 to 109 nm (Table 2.3). Correlation function plots revealed smooth profiles for all samples, implying a continuous distribution in the measured samples (Figure 2.5a). The polydispersity of all the samples was very large, but analysis revealed that there were no multiple peaks, which would be expected if aggregates were present (Figure 2.5).
The $d_H$ of the P3-1 nanoparticle is relatively larger when compared to the P3-2 nanoparticle (Table 2.3), which is believed to be a function of the PDMS-MA content. Based upon NMR spectroscopic analysis the weight percentage of the poly(PDMS-MA) blocks is smaller for P3-1 than that of P3-2 (Table 2.3), which may result in weaker interactions between the PDMS segments for P3-1. The rigid poly(6FDA-co-TMPD) shell combined with weaker PDMS interactions in the core results in a slightly larger $d_H$ for the P3-1 nanoparticle when compared to P3-2 nanoparticle. The increase in PDMS-MA content also results in more uniform nanoparticle as the polydispersity index (PDI) decreased from 0.20 to 0.17 (Table 2.3). A further increase in PDMS-MA content, from P3-2 (65 wt.%) to P3-3 (74 wt.%), did not result in a further decrease in $d_H$ as stable nanoparticles with longer PDMS-MA blocks were formed. Hence, the increase in $d_H$ observed in going from P3-2 (87 nm) to P3-3 (109 nm) nanoparticle (Table 2.3) is attributed to an increase in PDMS in the core.
Table 2.3 Intensity-average hydrodynamic diameter distributions of polyimide/poly(dimethylsiloxane) triblock copolymers self-assemblies.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Self-assembled</th>
<th>wt.% PDMS&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3-1</td>
<td>96</td>
<td>0.20</td>
</tr>
<tr>
<td>P3-2</td>
<td>87</td>
<td>0.17</td>
</tr>
<tr>
<td>P3-3</td>
<td>109</td>
<td>0.16</td>
</tr>
</tbody>
</table>

<sup>a</sup> Wt.% PDMS calculated from number-average molecular weight measured by GPC based upon the assumption of 100% mass recovery.

2.3.5 Cross-linking of polyimide/poly(dimethylsiloxane) triblock copolymers

Cross-linking of the nanoparticle was conducted to covalently stabilize the structure and prevent disassembly in good solvents for both the PI and PDMS blocks (e.g., THF). In general, there are many possible approaches to prepare cross-linked polysiloxanes, these include (i) the use of multi-functional siloxane comonomers, (ii) the incorporation of a photo or thermal radical initiators that induce radical cross-linking or (iii) exposure to high energy irradiation (e.g., gamma-rays) to generate radicals [41, 42]. For simplicity, benzoyl peroxide (BP), a thermal radical initiator, was used to cross-link both the core and shell through radical dimerization reactions, for which several mechanisms have been proposed for PDMS-based systems (Scheme 2.2) [43].
Both the triblock copolymer and BP were initially dissolved together in a good solvent (THF) for both the PDMS and PI segments before the addition of a PI selective solvent (DMF) to promote the incorporation of BP into the core of the self-assemblies. After dissolution in DMF the samples were analyzed via DLS (Table 2.4), which revealed an increase in the nanoparticle size upon the addition of BP, thus inferring its incorporation into the nanoparticles or reorganization of the self-assemblies to form larger aggregates. The increase in size was accompanied by an increase in PDI (Table 2.4). Before the cross-linking process, samples were bubbled with argon for an hour to minimize the presence of oxygen, which would compete with the desired radical cross-linking mechanism. Previous studies have indicated that polymer radicals, which are generated through hydrogen abstraction from the degradation of thermal initiators, can be converted into their oxidized derivatives in the presence of oxygen and are thus not able to participate in the cross-linking process [45]. These derivatives were identified as carboxylic acid and two peroxides of the type Si-O-OC- [46].
Table 2.4 Intensity-average hydrodynamic diameter distributions of polyimide/poly(dimethylsiloxane) triblock copolymers self-assemblies before and after cross-linking.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Self-assembled</th>
<th>Addition of BP</th>
<th>Cross-linked</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$d_H$ (nm)</td>
<td>PDI</td>
<td>$d_H$ (nm)</td>
</tr>
<tr>
<td>P3-1</td>
<td>96</td>
<td>0.20</td>
<td>176</td>
</tr>
<tr>
<td>P3-2</td>
<td>87</td>
<td>0.17</td>
<td>146</td>
</tr>
<tr>
<td>P3-3</td>
<td>109</td>
<td>0.16</td>
<td>257</td>
</tr>
</tbody>
</table>

The samples were heated at 90 °C for 7 hours for the cross-linking process. After the removal of the solvent, samples were diluted with THF to verify the extent of cross-linking; THF is a good solvent for both blocks. From DLS analysis a single peak was detected, which implied that all of the self-assembled copolymers (P3-1 to P3-3) had been fully cross-linked. Additionally, correlation function plots revealed smooth profiles, verifying no aggregation in the measured samples. For all of the cross-linked nanoparticles, the $d_H$ values were found to decrease from the uncross-linked values recorded in the presence of BP (Table 2.4), which is expected as cross-linking would result in a more compact structure. However, the $d_H$ values of the cross-linked nanoparticles were still larger than those of the corresponding self-assemblies formed in the absence of BP. This difference is attributed to the influence of BP on the self-assembly process, resulting in larger block copolymers aggregation number and therefore, larger self-assembled structures.
2.3.6 Imaging of polyimide/poly(dimethylsiloxane) triblock copolymers

Representative TEM images of the PI/PDMS triblock copolymer nanoparticles are shown in Figure 2.7. Copolymer **P3-2** formed nanoparticles with a spherical morphology and diameters of 70 to 100 nm (**Figure 2.7a**), which is in agreement with the DLS results ($d_H = 87$ nm, PDI = 0.17) (**Table 2.3**). Based on the obtained image (**Figure 2.7c**), the corresponding cross-linked copolymers have a more irregular shape, which is most likely due to the uncontrolled nature of the cross-linking process. The image also revealed that the size of cross-linked nanoparticles ranges from 80 to 150 nm, which is again in agreement with the result obtained from the DLS analysis ($d_H = 125$ nm, PDI = 0.18) (**Table 2.4**). An STEM image of **P3-2** (**Figure 2.7b**) and its cross-linked derivative (**Figure 2.7d**) also revealed similar sizes and morphologies as DLS analysis and TEM. Elemental analysis performed on the corona of the nanoparticles (**Figure 2.7b and 2.7d**) revealed the presence of oxygen and silicon in addition to fluorine, indicating the presence of both PDMS and PI. These results suggest that the core-shell structure of the nanoparticles may consist of a very thin PI shell.
Figure 2.7 (a) TEM image of P3-2, (b) STEM image of P3-2 and its elemental analysis recorded at a single point marked ‘x’, (c) TEM image of cross-linked P3-2 and (d) STEM image of cross-linked P3-2 and its elemental analysis recorded at a single point marked ‘x’.
2.4 Chapter summary

In conclusion, well-defined poly(6FDA-co-TMPD) with a very high degree of α,ω-diamino end-groups, as determined by MALDI ToF MS and 1H NMR spectroscopic analysis, was prepared via step-growth polymerization. The amine end-groups were then quantitatively functionalized with alkyl bromides to afford a telechelic macrorinitiator suitable for ATRP. Subsequently, ATRP with this initiator and a PDMS-MA macromonomer were employed to synthesize PI/PDMS triblock copolymers with different molecular weight poly(PDMS-MA) blocks in high conversions (88-94%). Self-assembly of these block copolymers in DMF resulted in the formation of nanoparticles, which were subsequently cross-linked via hydrogen abstraction through the thermal degradation of BP. TEM and STEM analysis revealed that the self-assembled block copolymers and their cross-linked derivatives had spherical morphologies. The synthetic approach outlined in this study is a viable strategy to fabricate soft polymeric nanoparticles based on block copolymers that combine both step- and chain-growth polymerization.
2.5 References


Soft Polymeric Nanoparticles Based on Linear Poly(ethylene glycol) and Linear Brush Poly(dimethylsiloxane) Diblock Copolymers

3.1 Chapter perspective

It is hard to synthesize well-defined polymers via step-growth polymerization as the process involves a random reaction of two molecules that may be any combination of a monomer, oligomer, or a longer-chain molecule. This chapter presents a simpler way of fabricating soft polymeric nanoparticles utilizing commercially available polymers, poly(ethylene glycol) (PEG) as a substitute for the selective polyimide block that was synthesized via step-growth polymerization previously described in Chapter 2. PEG is a class of soft material that provide selective CO$_2$ separation as the ether group is able to interact with CO$_2$, resulting in a high CO$_2$ solubility. As before, poly(dimethylsiloxane) is the other soft component to be utilized for the fabrication of nanoparticles. This chapter also presents a better approach of nanoparticle stabilization. Photocross-linking, which enables more temporal and positional control, was utilized to stabilize the synthesized nanoparticles. Light-induced cross-linking also provides a stabilization route which avoids unwanted by-products.
3.2 Introduction

Poly(ethylene glycol) (PEG) is a water soluble polymer that has attracted much attention as a result of its biocompatibility and low toxicity [1]. PEG has been widely employed in a variety of biomedical applications including the preparation of biocompatible conjugates, surface modification of drug delivery vectors and as scaffolds for tissue engineering [2]. PEG has also been significant in the development of membranes for CO₂ separation as it possesses a high affinity towards CO₂ [3]. Additionally, PEG is readily available, inexpensive and easily produced on an industrial scale [4]. Several approaches have been reported to combine PEG and PDMS; mainly through covalently linking linear PEG with linear PDMS to form a diblock copolymer [5-7], end-capping linear PEG with linear PDMS to form a triblock copolymer [8, 9], end-capping linear PDMS with linear PEG to form a triblock copolymer [10-12]. Other examples include a random grafted PEG/PDMS copolymer [13] and a commercially available grafted PEG along a PDMS backbone.

The stability of nanoparticles is a crucial condition for applications such as gas separation as the process may occur at high temperature and pressure [14]. Several approaches have been utilized to stabilize polymeric nanoparticles including core [15, 16] and shell cross-linking [17, 18]. There has been a growing interest in stabilizing nanoparticles via photocross-linking as this provides good temporal and spatial control over the process [19]. Light-induced cross-linking also provides a stabilization route which avoids unwanted by-products [20]. Past studies have utilized coumarin [21] and cinnamate groups [22] to incorporate photochromic moieties into the nanoparticles. Limited studies have utilized anthracene moieties to stabilize nanoparticles. Compared to coumarin and cinnamate groups, the [4+4] photodimerization of anthracene groups provides stability at elevated temperatures [23]. Additionally, photodimerization of coumarin and cinnamate groups may be easily reversed under certain conditions [19], which maybe undesirable for certain conditions.
This chapter presents the synthesis of novel soft polymeric nanoparticles assembled from well-defined linear PEG linked with a photocross-linkable PDMS brush. The photocross-linkable diblock copolymers were synthesized by chain extension of functionalized linear PEG with monomethacryloxypropyl terminated PDMS (PDMS-MA) and photoactive 2-(methylacyloyloxy)ethyl anthracene-9-carboxylate (MEAC) under atom transfer radical polymerization (ATRP) conditions in different molar ratios. Self-assembly of the diblock copolymers was investigated in N,N-dimethylformamide (DMF), which is a selective solvent for the PEG block, and resulted in the formation of nanoparticles that were further stabilized by photocross-linking via [4+4] photodimerization. The self-assembled nanoparticles and their cross-linked derivatives were characterized to determine their size, morphology and molecular structure. The self-assembly of well-defined linear-linear brush diblock copolymers displayed various structures, from spherical micelles to large compound micelles, with unique particle sizes.
Scheme 3.1 Synthetic outline for the preparation of soft polymeric nanoparticles based on linear poly(ethylene glycol) and linear brush poly(dimethylsiloxane) diblock copolymers.
3.3 Result and discussion

Atom transfer radical polymerization (ATRP) was employed to synthesize photoresponsive amphiphilic linear poly(ethylene glycol) and linear brush poly(dimethylsiloxane) diblock copolymers (Scheme 3.1). Initially, three different molecular weights of monomethyl ether PEG (MeOPEG) were functionalized to afford α-methyl, ω-bromo functionalized PEG macroinitiators P1 suitable for ATRP. The macroinitiators were characterized via gel permeation chromatography (GPC), nuclear magnetic resonance (NMR) spectroscopic analysis and matrix-assisted laser desorption/ionization time of flight mass spectroscopy (MALDI ToF MS). The PEG macroinitiators P1 were subsequently chain extended with varying amounts of PDMS-MA macromonomer and photoactive 2-(methylacyloyloxy)ethyl anthracene-9-carboxylate (MEAC) to afford a series of novel photoresponsive amphiphilic copolymers with variable degrees of polymerization (DP).

3.3.1 Synthesis of α-methyl, ω-bromo functionalized poly(ethylene glycol) macroinitiators

Functionalization of MeOPEG with initiating moieties was achieved through reaction with 2-bromoisoctyl bromide to afford α-methyl, ω-bromo functionalized PEG macroinitiator P1 in a quantitative yield, as shown in Scheme 3.1. In this study, three different molecular weights of MeOPEG were functionalized and the resulting macroinitiators (P11, P15 and P110) were obtained in moderate yields following a rigorous purification process.
Figure 3.1 ¹H NMR spectra (d₆-DMSO) of macroinitiator P1₅.

¹H NMR spectroscopic analysis of P1₅ revealed a new resonance at δ₁H 1.9 ppm (Figure 3.1) corresponding to the methyl groups of the bromoisobutyrate end-group upon esterification. Spectroscopic analysis also confirmed the formation of the PEG macroinitiators P1₁ and P1₁₀ (Figure A3.4).

Table 3.1 Molecular weight characterization of MeOPEG macroinitiator P1.

<table>
<thead>
<tr>
<th>Macroinitiator</th>
<th>MₙNMR (kDa)ᵃ</th>
<th>MₙMALDIToF (kDa)ᵇ</th>
<th>MₙGPC (kDa)ᶜ</th>
<th>PDIᶜ</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1₁</td>
<td>1.1</td>
<td>1.1</td>
<td>1.6</td>
<td>1.07</td>
</tr>
<tr>
<td>P1₅</td>
<td>5.2</td>
<td>5.1</td>
<td>5.7</td>
<td>1.13</td>
</tr>
<tr>
<td>P1₁₀</td>
<td>10.5</td>
<td>10.8</td>
<td>13.6</td>
<td>1.26</td>
</tr>
</tbody>
</table>

ᵃ Number-average molecular weight calculated from ¹H NMR spectroscopic analysis. ᵇ Number-average molecular weight determined by MALDI ToF MS analysis. ᶜ Number-average molecular weight and polydispersity index (PDI) measured by GPC-UV trace (230nm).
NMR spectroscopy and MALDI ToF MS were used to determine the molecular weights of the MeOPEG macroinitiators P1 (Figure 3.1, Figure 3.2b and Table 3.1). MALDI ToF MS spectra of the functionalized MeOPEG macroinitiators revealed a series of peaks shifted by ca. 150 m/z relative to their precursors (Figure 3.2b), which corresponds to the addition of the bromoisobutyrate end-group. The observed mass values were found to correlate well with the sodium salts of the desired macroinitiator P1₅, resulting from the use of sodium trifluoroacetate (NaTFA) as the cationization agent. MALDI ToF MS spectra of P1₁ and P1₁₀ also showed similar results (Figure A3.5 and A3.6). All of the MALDI ToF MS spectra revealed series of peaks separated by ca. 44 m/z, corresponding to the repeat unit of PEG (Figure 3.2a and 3.2b). Determination of the number-average molecular weights (Mₙ) via MALDI ToF MS analysis provided values that correspond well with those determined by NMR spectroscopy (Table 3.1). GPC analysis was performed on the MeOPEG macroinitiators P1, and their molecular weights and molecular weight distributions were determined relative to a conventional column calibration with poly(ethylene oxide) (PEO) standards. Despite PEG having a strong positive RI signal in chloroform, to be consistent, the UV traces were used for the analysis of all polymers, as the PDMS components in the following section have either a negative RI signal in chloroform or are isorefractive in THF. The Mₙ values determined from GPC analysis were slightly higher than those calculated from MALDI ToF MS and NMR spectroscopy analysis, which possibly results from the inaccuracy of the standard calibration method with PEO standards (Table 3.1).
Figure 3.2 MALDI-ToF mass spectra of (a) 5 kDa MeOPEG and (b) its bromo-functionalized derivate, P1, recorded in linear/positive mode using DCTB and NaTFA as the matrix and cationization agent, respectively. The numbers on the peaks represent the number of EO repeat units (n, 44 m/z).
3.3.2 Synthesis of poly(ethylene glycol)/poly(dimethylsiloxane) diblock copolymers

Photoresponsive amphiphilic copolymers were synthesized via ATRP with α-methyl, ω-bromo functionalized PEG P1 as the macroinitiators, PDMS-MA as the macromonomer and MEAC as the photoactive monomer. Cu(I)/PMDETA was utilized as the catalyst/ligand system for the copolymers based on the 1 kDa macroinitiator P1\textsubscript{1} while Cu(I)/bipyridine was used for copolymers based on the 5 and 10 kDa macroinitiators P1\textsubscript{5} and P1\textsubscript{10}, respectively. ATRP of PDMS-MA and MEAC was initiated with P1\textsubscript{1} using THF as a solvent at various macromonomer to macroinitiator ratios to yield copolymers with high PDMS-MA conversions, up to 95\% (Table 3.2); the reaction was conducted at 60 °C. Longer PEG chain macroinitiators (P1\textsubscript{5} and P1\textsubscript{10}) required a more polar solvent, tert.-BuOH, and higher temperature (90 °C) to yield copolymers with high PDMS-MA conversions, up to 96\% (Table 3.2). MEAC conversions were observed to be greater than 99\% for all the synthesized copolymers as MEAC was a smaller molecule which resulted in less steric constraints. Additionally, MEAC was used in a much lower amount so that it was all consumed. Confirmation of the presence of anthracene moieties within the copolymers was determined using GPC analysis coupled with UV detection at a wavelength of 390 nm due to a strong series of absorbance peaks between 320 and 400 nm.
Table 3.2 Synthesis and characterization of poly(ethylene glycol)/poly(dimethylsiloxane) diblock copolymers.

<table>
<thead>
<tr>
<th>Polymer ( (P_{\text{PEG-MW}}/P_{\text{PDMS-MW}}) )</th>
<th>Macroinitiator</th>
<th>Molar ratio ( ^{b} )</th>
<th>Conversion ( ^{c} )</th>
<th>( M_{n}^{\text{theor}} ) ( ^{d} ) (kDa)</th>
<th>( M_{n}^{\text{NMR}} ) ( ^{e} ) (kDa)</th>
<th>( M_{n}^{\text{GPC}} ) ( ^{f} ) (kDa)</th>
<th>PDI ( ^{f} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>P2(_{1/5})</td>
<td>P1(_{1})</td>
<td>1:5:3</td>
<td>95/&gt;99</td>
<td>5.7</td>
<td>6.0</td>
<td>19.7</td>
<td>2.00</td>
</tr>
<tr>
<td>P2(_{1/8})</td>
<td>P1(_{1})</td>
<td>1:10:3</td>
<td>92/&gt;99</td>
<td>8.6</td>
<td>9.8</td>
<td>29.2</td>
<td>2.28</td>
</tr>
<tr>
<td>P2(_{5/4})</td>
<td>P1(_{5})</td>
<td>1:4:3</td>
<td>94/&gt;99</td>
<td>8.7</td>
<td>9.7</td>
<td>13.0</td>
<td>2.23</td>
</tr>
<tr>
<td>P2(_{5/7})</td>
<td>P1(_{5})</td>
<td>1:8:3</td>
<td>96/&gt;99</td>
<td>11.8</td>
<td>12.3</td>
<td>17.4</td>
<td>2.17</td>
</tr>
<tr>
<td>P2(_{5/9})</td>
<td>P1(_{5})</td>
<td>1:12:4</td>
<td>92/&gt;99</td>
<td>14.1</td>
<td>17.0</td>
<td>22.2</td>
<td>2.06</td>
</tr>
<tr>
<td>P2(_{10/9})</td>
<td>P1(_{10})</td>
<td>1:11:4</td>
<td>92/&gt;99</td>
<td>18.5</td>
<td>19.5</td>
<td>58.9</td>
<td>2.15</td>
</tr>
<tr>
<td>P2(_{10/12})</td>
<td>P1(_{10})</td>
<td>1:16:4</td>
<td>90/&gt;99</td>
<td>21.6</td>
<td>24.0</td>
<td>63.1</td>
<td>2.06</td>
</tr>
<tr>
<td>P2(_{10/15})</td>
<td>P1(_{10})</td>
<td>1:21:5</td>
<td>88/&gt;99</td>
<td>25.1</td>
<td>28.5</td>
<td>64.0</td>
<td>1.90</td>
</tr>
</tbody>
</table>

\( ^{a} \) The first subscript refers to PEG-MW in kDa and the second refers to PDMS-MW in kDa. \( ^{b} \) Molar ratio as [P1]:[PDMS-MA]:[MEAC]. \( ^{c} \) PDMS-MA macromonomer/MEAC conversion was calculated from \( ^{1} \)H NMR spectroscopic analysis. \( ^{d} \) Number-average molecular weight based on macromonomer conversion and initial feed molar ratio. \( ^{e} \) Number-average molecular weight determined by \( ^{1} \)H NMR spectroscopic analysis. \( ^{f} \) Number-average molecular weight and polydispersity index (PDI) measured by GPC-UV trace (230nm).
$^1$H NMR spectroscopic analysis of the copolymers (Figure 3.3), revealed characteristic methylene and methyl proton resonances (ca. δ$_H$ 1.8 and 1.0 ppm) associated with the methacrylate polymer backbone. The peak shifts to lower retention times in the GPC chromatograms (Figure 3.4) and $^1$H NMR spectroscopic analysis confirmed the synthesis of the PEG/PDMS diblock copolymers. The integral ratios of the PEG repeat unit (ca. δ$_H$ 3.6 ppm), PDMS repeat unit (ca. δ$_H$ 0.7 ppm) and the total molecular weight of the anthracene moieties were used to calculate the $M_n^{\text{NMR}}$ values (Table 3.2). The $M_n$ values determined from NMR spectroscopy analysis correspond well to the theoretical values calculated from conversion and molar feed ratios (Table 3.2). $M_n$ values obtained from the GPC UV chromatograms differed significantly from those determined by NMR spectroscopy and theoretical molecular weight calculations. This most likely arises from inaccuracies caused by using a conventional calibration method with PEO standards for copolymers containing both PEG and PDMS moieties. Unfortunately, GPC coupled with multi-angle light scattering detection could not be used as the polymers do not show sufficient peak intensity.
Figure 3.3 $^1$H NMR spectrum (CDCl$_3$) of poly(ethylene glycol)/poly(dimethylsiloxane) diblock copolymers P2$_{5/9}$. The asterisks denote resonances corresponding to the double bond of unreacted PDMS-MA macromonomer.

$^1$H NMR spectroscopic analysis of the copolymers revealed alkene proton resonances that correspond to small amounts (< 8%) of unreacted PDMS-MA macromonomer (Figure 3.3). These trace amounts of unreacted macromonomers were not removed, as previously described in Section 2.3.3, the association of unreacted PDMS-MA with high density brushes made it difficult to completely remove. Closer examination of the GPC chromatograms of copolymers revealed peaks at ca. 31 min, which correspond to a combination of unreacted PDMS-MA and unfunctionalized PDMS (Figure 3.4). The presence of the unfunctionalized PDMS in the PDMS-MA was detected via MALDI ToF MS, although the amount of unfunctionalized PDMS could not be quantified as a result of possible preferential ionization during analysis (Figure A3.7).
Figure 3.4 GPC ultraviolet (UV) chromatograms at 230 (---) and 390 nm (---) of poly(ethylene glycol)/poly(dimethylsiloxane) diblock copolymers and their macroinitiator P1 and PDMS-MA macromonomer. The manufacturer specifies a molecular weight of 600-800 Da for the PDMS-MA macromonomer.
### 3.3.3 Self-assembly of poly(ethylene glycol)/poly(dimethylsiloxane) diblock copolymers

Self-assembly of the diblock copolymers was conducted in DMF, which is a selective solvent for the PEG block. The intensity-average hydrodynamic diameters ($d_H$) of the PEG/PDMS nanoparticles formed from self-assembly in DMF were determined via DLS (Figure 3.5) and ranged from 41 to 268 nm (Table 3.3). Correlation function plots revealed smooth profiles for all samples, implying a continuous distribution in the measured samples (Figure 3.5).

#### Table 3.3 Intensity-average hydrodynamic diameter distributions of poly(ethylene glycol)/poly(dimethylsiloxane) diblock copolymers self-assemblies.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>PDMS wt.%$^a$</th>
<th>Self-assemblies</th>
<th>Photocross-linked assemblies</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$d_H$ (nm)</td>
<td>PDI</td>
</tr>
<tr>
<td>P2$_{1/5}$</td>
<td>63</td>
<td>151</td>
<td>0.17</td>
</tr>
<tr>
<td>P2$_{1/8}$</td>
<td>78</td>
<td>268</td>
<td>0.17</td>
</tr>
<tr>
<td>P2$_{5/4}$</td>
<td>36</td>
<td>72</td>
<td>0.10</td>
</tr>
<tr>
<td>P2$_{5/7}$</td>
<td>50</td>
<td>80</td>
<td>0.14</td>
</tr>
<tr>
<td>P2$_{5/9}$</td>
<td>60</td>
<td>85</td>
<td>0.15</td>
</tr>
<tr>
<td>P2$_{10/9}$</td>
<td>41</td>
<td>41</td>
<td>0.04</td>
</tr>
<tr>
<td>P2$_{10/12}$</td>
<td>52</td>
<td>42</td>
<td>0.04</td>
</tr>
<tr>
<td>P2$_{10/15}$</td>
<td>58</td>
<td>47</td>
<td>0.07</td>
</tr>
</tbody>
</table>

$^a$ Wt.% PDMS calculated from number-average molecular weight measured by $^1$H NMR spectroscopic analysis.
Figure 3.5 (a, c, e) Intensity autocorrelation and (b, d, f) intensity-average hydrodynamic diameter distributions of poly(ethylene glycol)/poly(dimethylsiloxane) diblock copolymers P2 self-assemblies.

Figure 3.6 shows the plot of intensity-average hydrodynamic diameters ($d_{H}$) of assembled particles versus the molecular weight of poly(PDMS-MA) brush block for various PEG block molecular weights. All three series (P21, P25 and P210 series) showed an increasing trend in $d_{H}$ with an increase in poly(PDMS-MA) brush block molecular weight. Interestingly, the P21 series has a much greater increase relative to the other series. Furthermore, the overall $d_{H}$ decreased with an increase in the PEG block molecular weight from the P21 to P210 series, which is not consistent with that normally observed for ordinary block copolymer self-assembly.
Figure 3.6. Intensity-average hydrodynamic radius ($d_H$) of self-assembled nanoparticles as a function of poly(PDMS-MA) number average molecular weight based on $^1$H NMR spectroscopic analysis.

For the P2$_{10}$ series with PEG $M_n$ of 10.5 kDa, the $d_H$ of the self-assemblies increased from 41 to 47 nm as the molecular weight of the poly(PDMS-MA) block increased from 9 to 15 kDa. Judging from the molecular weight of each block and the size of the particles, the assembly structure is likely to be that of spherical micelles with the poly(PDMS-MA) brush block forming the core and PEG block forming the protective coronal shell. In comparison, for the P2$_1$ series with PEG $M_n$ of 1.1 kDa, the assembled particle sizes were significantly larger (e.g., 151 and 268 nm). P2$_{1/5}$ has a poly(PDMS-MA) molecular weight of 5 kDa and PEG molecular weight of only 1.1 kDa, which is not sufficient to form stable spherical micelles. Therefore, it is proposed that different assembled structures are formed in this case.

In amphiphilic block copolymer self-assembly, large compound micelles (LCMs) or crew-cut aggregates are formed when block copolymers with one block that is far shorter than the other blocks are assembled in a selective solvent for the shorter block [24, 25]. For example, Eisenberg observed such aggregates for the assembly of polystyrene-$b$-poly(acrylic acid) (PS$_{200}$-$b$-PAA$_4$) in a selective solvent for PAA. In these LCMs, PAA is located on the surface of the particles as well as within the
particles as isolated domains (Figure 3.7a) [25]. Similarly, the nanoparticles formed from the P21 series of linear-linear brush diblock copolymers observed in this study are likely to form similar LCMs (Figure 3.7b). Interestingly, the particle size increased substantially to 268 nm when the molecular weight of poly(PDMS-MA) was increased from 5 to 8 kDa in the P21 series self-assemblies. This behavior is the first observation of LCMs formed from linear-linear brush block copolymers.

Transmission electron microscopy (TEM) image of P21/5 showed a spherical morphology with a diameter of ca. 185 nm (Figure 3.8a), which is slightly larger than that in solution (dH = 165 nm, PDI = 0.20). The difference is attributed to the flattening of the nanoparticles in the solid state upon deposition on the TEM grid. The spherical morphology of the particles is in agreement with the reported LCMs morphology.

For the P25 series with a PEG block of Mn of 5.2 kDa, a similar trend to that of the P210 series was observed; however, the particle sizes are bigger. Therefore, these particles are likely to represent a transition from spherical micelles to LCMs. Again, particles with spherical morphologies were observed in TEM image (Figure 3.8c).

Figure 3.7 Illustrated structure of large compound micelles formed from (a) PS200-b-PAA4 and (b) P21 series of linear-linear brush diblock copolymers.
Webber et al. observed similar aggregation behavior when a random polystyrene-alt-maleic anhydride-graft-poly(ethylene oxide) (Figure 3.9) was utilized for self-assembly in an aqueous NaCl solution [26]. When the DP of the PEG branch was reduced, a substantial increase in particle size (or aggregation number) was observed (Table 3.4). The reduction in the number of PEG grafted side chains also reduced the stabilization capacity of the particles, resulting in an increase in particle size. This reported trend is similar to the trend observed in this study when the molecular weight of PEG block is reduced.

Figure 3.9 Random polystyrene-alt-maleic anhydride-graft-poly(ethylene oxide).
Table 3.4 Graft copolymers composition and size analysis of graft copolymers micelles [26].

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$N_{PEO}^{(mix)}$</th>
<th>$N_{PEO}^{b}$</th>
<th>Self-assemblies$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>UV-Vis</td>
<td>NMR</td>
<td>$d_H$ (nm)</td>
</tr>
<tr>
<td>G125</td>
<td>20</td>
<td>5.9</td>
<td>10.7</td>
</tr>
<tr>
<td>G105</td>
<td>10</td>
<td>4.2</td>
<td>5.9</td>
</tr>
<tr>
<td>G175</td>
<td>7.5</td>
<td>2.6</td>
<td>5.0</td>
</tr>
<tr>
<td>G155</td>
<td>5</td>
<td>2.1</td>
<td>3.4</td>
</tr>
<tr>
<td>G195</td>
<td>2.5</td>
<td>1.1</td>
<td>1.8</td>
</tr>
</tbody>
</table>

$^a$ The number of PEO branches per graft backbone based on the reaction mixture. $^b$ The number of PEO branches per polymer based on UV-Vis spectrophotometry and NMR spectroscopic analysis. $^c$ Hydrodynamic diameters ($d_H$) and polydispersity index (PDI) based on QELS measurements.

3.3.4 Photocross-linking of poly(ethylene glycol)/poly(dimethylsiloxane) diblock copolymers

Cross-linking of the soft nanoparticles was conducted to covalently stabilize the structure and prevent disassembly in good solvents for both the PEG and PDMS blocks. All of the samples were photocross-linked using UV radiation. The anthracene moieties incorporated into the PDMS segment of the block copolymer are photosensitive and photodimerizes upon exposure to UV radiation at wavelengths greater than 300 nm (Scheme 3.2) [27]. The [4+4] photodimerization of anthracene forms an ortho-substituted benzene molecule. Once dimerized, it does not absorb light at wavelengths greater than 300 nm making the reaction easy to monitor spectrophotometrically [27]. It is well known that the dimerization predominantly occurs in a “head-to-head” arrangement as illustrated in Scheme 3.2 [23, 27].
Scheme 3.2 Mechanism for photodimerization and photocleavage of anthracene molecules.

Samples containing self-assemblies in DMF were exposed to UV radiation with a wavelength of 365 nm for 4 hours and then were tested for their UV absorbance between 300 and 420 nm to monitor the progress of the photodimerization (Figure 3.10 and Figure A3.8). A decrease in UV absorption is indicative of anthracene moieties losing their conjugated structure due to dimerization. The extent of cross-linking was found to vary between 81 and 91% (Table 3.5 and Figure A3.8). A small fraction of non-dimerized anthracene moieties residing within the dense PDMS core were unable to couple possibly as a result of steric hindrance within the core. However, 100% dimerization is not required to effect successful stabilization of the assemblies.

Table 3.5 Extent of photodimerization of the anthracene groups over 4 hours.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Extent of photodimerization (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P21/5</td>
<td>91</td>
</tr>
<tr>
<td>P21/8</td>
<td>87</td>
</tr>
<tr>
<td>P25/4</td>
<td>81</td>
</tr>
<tr>
<td>P25/7</td>
<td>86</td>
</tr>
<tr>
<td>P25/9</td>
<td>86</td>
</tr>
<tr>
<td>P210/9</td>
<td>86</td>
</tr>
<tr>
<td>P210/12</td>
<td>88</td>
</tr>
<tr>
<td>P210/15</td>
<td>82</td>
</tr>
</tbody>
</table>
Figure 3.10 Ultraviolet-visible spectra of $\text{P2}_{5,4}$ upon exposure to UV radiation (365 nm) for 4 hours.

Samples were concentrated in vacuo to remove DMF, then diluted with chloroform to verify the extent of cross-linking; chloroform is a good solvent for both blocks. From DLS analysis similar single peaks were detected, which implied that all of the self-assembled copolymers had been cross-linked. Additionally, correlation function plots revealed smooth profiles, verifying no aggregation in the measured samples (Figure 3.11). DLS analysis revealed that the $d_{H}$ values were found to increase slightly from the uncross-linked values recorded for all of the cross-linked nanoparticles (Table 3.3). Rearrangement of the anthracene moieties to undergo cross-linking possibly forces the chains into a larger and less well-packed structure leading to a slight increase in particle size. The photocross-linking also led to an increase in polydispersity index (PDI) implying a more dispersed nanoparticle size distribution (Table 3.3).

The reversibility of the cross-linked anthracene moieties was investigated by monitoring the UV absorption of the photocross-linked $\text{P2}$ under irradiation at a lower wavelength of 254 nm for 20 hours. Results indicated that on average only 15% of the dimerized anthracene moieties were converted back to the unimolecular state (Table A3.1 and Figure A3.9). These results are in agreement with previously published results which suggest that the presence of the carbonyl functionality inhibits the complete photocleavage process [29, 30].
TEM images of the cross-linked P2₁/₅ and P2₅/₇ nanoparticles (Figure 3.8b and d, respectively) revealed nanoparticles with spherical morphologies of ca. 200 and 100 nm in diameter, which is again slightly larger than the dₜ values of the particles in solution (165 and 88 nm).

Figure 3.11 (a, c, e) Intensity autocorrelation and (b, d, f) intensity-average hydrodynamic diameter distributions of poly(ethylene glycol)/poly(dimethylsiloxane) diblock copolymers P2 self-assemblies post photocross-linking.
3.4 Chapter summary

Well-defined photo-crosslinkable diblock copolymers based on PEG and PDMS were successfully prepared. A range of molecular weights of monomethyl ether PEG were quantitatively functionalized with alkyl bromides to afford macroinitiators suitable for ATRP. Subsequently, ATRP with these PEG macroinitiators, a PDMS-MA macromonomer and an anthracene-based monomer was employed to synthesize photo-crosslinkable diblock copolymers with different molecular weight poly(PDMS-MA) blocks in high conversions (88-96%). Self-assembly of these diblock copolymers in DMF resulted in the formation of nanoparticles, which were subsequently cross-linked via [4+4] photodimerization of the anthracene moieties. TEM analysis showed that the self-assembled diblock copolymers and their cross-linked derivatives had spherical morphologies. DLS studies revealed that the assembly configuration of the nanoparticles is heavily reliant on the individual block lengths of the linear-linear brush diblock copolymers, and is likely to vary from spherical micelles to large compound micelles. The synthetic approach outlined in this chapter is a viable strategy to synthesize stable soft nanoparticles that can be used for different applications such as additives for polymeric gas separation membranes.
3.5 References

Soft Polymeric Nanoparticles Based on Poly(ethylene glycol) and Poly(ethylene glycol)-\textit{b}-poly(dimethylsiloxane) Grafted Star Polymers

4.1 Chapter perspective

The preparation of soft polymeric nanoparticles that has been described in Chapter 2 and 3 requires the need of self-assembly of block copolymer which is generally carried out in low concentration to avoid aggregation of nanoparticles. This hinders the preparation of soft polymeric nanoparticles at large scale. Chapter 4 details a robust approach to synthesize soft polymeric nanoparticles suitable for large scale applications such as gas separation membranes. Soft polymeric nanoparticles based on poly(ethylene glycol) and poly(ethylene glycol)-\textit{b}-poly(dimethylsiloxane) grafted star polymers were synthesized \textit{via} the ‘core-first’ approach. This method also allows the preparation of nanoparticles in high yields as crude reaction mixture only requires separation from unreacted monomers.
4.2 Introduction

Star polymers are a class of globular polymers that comprised of multiple arms or branches radiating from a central point or core. They have attracted scientific interest since they were first prepared sixty years ago as a result of their unique properties which facilitate their application to advanced materials [1, 2]. There are three ways to prepare star polymers via controlled polymerization techniques which have been elaborated in Chapter 1, Section 1.3.2.2.

Star polymers synthesized via the ‘core-first’ approach allow the preparation of well-defined star polymers with a precise number of arms that can be controlled by the number of initiating sites preset in the multifunctional initiator. In addition, star polymers can be prepared in high yield as the crude reaction mixture only requires separation from unreacted monomers. This approach allows the preparation of nanoparticles without the need for self-assembly of block copolymers (BCPs) which is normally conducted at low concentration to avoid the aggregation of nanoparticles [2].

This chapter presents the synthesis of novel soft polymeric nanoparticles based on poly(ethylene glycol) (PEG) and poly(ethylene glycol)-b-poly(dimethylsiloxane) (PEG-b-PDMS) grafted star polymers. The grafted star polymers were synthesized through functionalization of pentaerythritol to afford an initiator suitable for atom transfer radical polymerization (ATRP) and chain extension with methacrylate terminated monomethyl ether poly(ethylene glycol) (MeOPEG-MA) macromonomer to afford PEG grafted star polymers. The PEG-b-PDMS grafted star polymers were synthesized using the same initiator, chain extended with monomethacryloxypropyl terminated poly(dimethylsiloxane) (PDMS-MA) macromonomer and then further chain extended with MeOPEG-MA macromonomer.
Scheme 4.1 Synthetic outline for the preparation of poly(ethylene glycol) and poly(ethylene glycol)-\textit{b}-poly(dimethylsiloxane) grafted star polymers.
4.3 Result and discussion

Atom transfer radical polymerization (ATRP) was employed to synthesize PEG and PEG-\textit{b}-PDMS grafted star polymers (\textbf{Scheme 4.1}). All of the synthesized polymerized were characterized \textit{via} gel permeation chromatography (GPC) and $^1$H nuclear magnetic resonance (NMR) spectroscopic analysis.

\section*{4.3.1 Synthesis of poly(ethylene glycol) grafted star polymers}

PEG grafted star polymers \textbf{P0} were synthesized \textit{via} ATRP and the ‘core-first’ approach (\textbf{Scheme 4.1, step ii}) [2]. Initially, a tetra-functional bromoester initiator with 4 initiating sites was prepared by reacting pentaerythritol with 2-bromoisonobutyryl bromide (\textbf{Scheme 4.1, Figure 4.1} and \textbf{Figure A4.1}).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure41.png}
\caption{$^1$H NMR spectra (CDCl$_3$) of the tetra-functional initiator \textbf{I}.}
\end{figure}

Using this initiator, ATRP reactions using Cu(I)/PMDETA as the catalyst/ligand system were performed with MeOPEG-MA as macromonomer to form star polymers (\textbf{P0$_{24/0}$}). $^1$H NMR spectroscopic analysis revealed high MeOPEG-MA conversions, 96\% (\textbf{Table 4.1}). The number-average molecular weight ($M_n$) and polydispersity index (PDI) values (\textbf{Table 4.1}) were determined by GPC calibrated using poly(ethylene oxide) (PEO) standards. Molecular weights could not be
determined using a light scattering technique as no signals were observed. This is possibly as a result of the isorefractive nature of the synthesized polymers and the GPC eluent. The $M_n$ values were found to be marginally lower when compared to the theoretically determined molecular weight (Table 4.1). The discrepancy could be attributed to the difference in structure between the linear PEO standards and the synthesized globular grafted star polymers. It is known that globular polymers have a more dense structure when compared to linear polymers with the same molecular weights, and therefore they would be eluted at a longer retention time resulting in relatively lower molecular weights (Table 4.1).

![Figure 4.2](image)

**Figure 4.2** GPC differential refractive index chromatograms of poly(ethylene glycol) grafted star polymers $P0$ and MeOPEG-MA macromonomer. The macromonomer has a molecular weight of 300 Da, as specified by the manufacturer.

Closer examination of the GPC refractive index chromatograms of $P0$ revealed a minor trace at $ca. 28$ min, which corresponds to unreacted MeOPEG-MA macromonomers (Figure 4.2). $^1$H NMR spectroscopic analysis also revealed methacrylate characteristics of unreacted MeOPEG-MA macromonomers ($ca. \delta_H 5.5$ and $6.1$) (Figure 4.3). Additionally, $^1$H NMR spectroscopic analysis of the grafted star polymers $P0_{24/0}$ revealed characteristic methyl and methylene proton resonances ($\delta_H 0.85 – 1.01$ and $1.79 – 1.92$ ppm) associated with the methacrylate.
polymer backbone which confirmed the successful synthesis of the poly(ethylene glycol) grafted star polymers P0\textsubscript{24/0}.

**Figure 4.3** \textsuperscript{1}H NMR spectra (CDCl\textsubscript{3}) of poly(ethylene glycol) grafted star polymers P0\textsubscript{24/0}. An insert of 10 times magnification shows the methacrylate characteristics of unreacted MeOPEG-MA macromonomers which is marked by asterisks.
Table 4.1 Synthesis and characterization of grafted star polymers.

<table>
<thead>
<tr>
<th>Polymer (PXMeOPEG/PDMS)</th>
<th>Initiator</th>
<th>Molar ratio&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Conversion&lt;sup&gt;b&lt;/sup&gt; (%)</th>
<th>( M_n^{\text{theor}} ) (kDa)&lt;sup&gt;c&lt;/sup&gt;</th>
<th>( M_n^{\text{GPC}} ) (kDa)&lt;sup&gt;d&lt;/sup&gt;</th>
<th>PDI&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>P0&lt;sub&gt;24/0&lt;/sub&gt;</td>
<td>I</td>
<td>24:1</td>
<td>-</td>
<td>96</td>
<td>29.5</td>
<td>26.6</td>
</tr>
<tr>
<td>P1&lt;sub&gt;0/9&lt;/sub&gt;</td>
<td>I</td>
<td>-</td>
<td>10:1</td>
<td>91</td>
<td>26.2</td>
<td>10.1</td>
</tr>
<tr>
<td>P1&lt;sub&gt;0/27&lt;/sub&gt;</td>
<td>I</td>
<td>-</td>
<td>30:1</td>
<td>91</td>
<td>77.1</td>
<td>37.5</td>
</tr>
<tr>
<td>P2&lt;sub&gt;24/10&lt;/sub&gt;</td>
<td>P1&lt;sub&gt;0/9&lt;/sub&gt;</td>
<td>24:1</td>
<td>-</td>
<td>&gt; 99</td>
<td>57.5</td>
<td>25.9</td>
</tr>
<tr>
<td>P2&lt;sub&gt;72/10&lt;/sub&gt;</td>
<td>P1&lt;sub&gt;0/9&lt;/sub&gt;</td>
<td>72:1</td>
<td>-</td>
<td>&gt; 99</td>
<td>115.1</td>
<td>70.9</td>
</tr>
<tr>
<td>P2&lt;sub&gt;24/30&lt;/sub&gt;</td>
<td>P1&lt;sub&gt;0/27&lt;/sub&gt;</td>
<td>24:1</td>
<td>-</td>
<td>&gt; 99</td>
<td>115.6</td>
<td>49.9</td>
</tr>
</tbody>
</table>

<sup>a</sup> Molar ratio as [macromonomer]:[initiator/macroinitiator].  
<sup>b</sup> Macromonomer conversion was calculated from <sup>1</sup>H NMR spectroscopic analysis.  
<sup>c</sup> Number-average molecular weight based on macromonomer conversion and initial feed ratio.  
<sup>d</sup> Number-average molecular weight and polydispersity (PDI) measured by GPC-RI trace determined based on PEO calibration.
4.3.2 Synthesis of poly(dimethylsiloxane) grafted star polymers

PDMS grafted star polymers P1 were synthesized via ATRP and the 'core-first' approach (Scheme 4.1, step iii) [2]. Using the previously described initiator, ATRP reactions using Cu(I)/PMDETA as the catalyst/ligand system were performed with PDMS-MA as macromonomer to form star polymers with two different arm lengths (P10/9 and P10/27). 1H NMR spectroscopic analysis revealed high PDMS-MA conversions, 91% (Table 4.1). As before, the Mₙ and PDI values (Table 4.1) were determined by GPC, calibrated using PEO standards. The Mₙ values were found to be much lower than the theoretically determined molecular weights. In addition to the inaccuracy of the standard calibration using linear PEO standards discussed previously, further inaccuracy arises from comparing linear PEO moieties to polymers containing PDMS moieties, resulting in a difference in the calculated molecular weight.

Closer examination of the GPC refractive index chromatograms of P1 revealed a trace at ca. 27 min, which corresponds to unreacted PDMS-MA macromonomers (Figure 4.4). Unreacted macromonomers were not removed as the association of unreacted PDMS-MA macromonomers with the high density brushes made it difficult to completely remove (Section 2.3.3). 1H NMR spectroscopic analysis of the grafted star polymers P10/9 also revealed resonances (δH 1.95, 5.54 and 6.10 ppm) associated with the methacrylate moieties of the unreacted PDMS-MA macromonomers (Figure 4.5). Additionally, 1H NMR spectroscopic analysis revealed characteristic methyl and methylene proton resonances (δH 1.04, 1.81 and 1.91 ppm) associated with the methacrylate polymer backbone which confirmed the successful synthesis of the PDMS grafted star polymers P1.
**Figure 4.4** GPC differential refractive index chromatograms of poly(ethylene glycol)-b-poly(dimethysiloxane) grafted star polymers P2 and their precursors, macroinitiator poly(dimethysiloxane) grafted star polymers P1 and PDMS-MA macromonomer. The macromonomer has a molecular weight of 600 – 800 Da, as specified by the manufacturer.

**4.3.3 Synthesis of poly(ethylene glycol)-b-poly(dimethysiloxane) grafted star polymers**

PEG-b-PDMS grafted star polymers were also synthesized via ATRP using Cu(I)/PMDETA as the catalyst/ligand system (Scheme 4.1, step iii), PDMS grafted star polymers P1 as the macroinitiator and MeOPEG-MA as the macromonomer. $^1$H NMR spectroscopic analysis revealed high MeOPEG-MA conversions, > 99% (Table 4.1). It was observed that the unreacted PDMS-MA macromonomers further reacted during the polymerization of the MeOPEG-MA block with the disappearance of the resonances associated with the methacrylate moieties of the unreacted PDMS-MA macromonomers (ca. $\delta H$ 1.95, 5.54 and 6.10 ppm) as shown in Figure 4.5b. This is clearly illustrated by the disappearance of the trace at ca. 27
min which is associated with the unreacted PDMS-MA macromonomers (Figure 4.4). Thus, the second block contained a small number of PDMS-MA repeat units.

As before, GPC analysis of P2 provided $M_n$ values that were lower than those predicted theoretically (Table 4.1). GPC analysis of P2 shows traces skewed towards lower retention time (i.e., higher molecular weight). This is possibly due to the termination of the macromonomer at high conversion which contributed to the large PDI in the synthesized products (Table 4.1). $^1$H NMR spectroscopic analysis of the copolymers P272/10 (Figure 4.5b) revealed characteristic methyl and methylene proton resonance ($\delta_H$ 1.02, 1.79 and 1.89 ppm) associated with the methacrylate polymer backbone, which in combination with the GPC results (Figure 4.4) confirmed the successful synthesis of the PEG-b-PDMS grafted star polymers.
Figure 4.5 $^1$H NMR spectra (CDCl$_3$) of (a) poly(dimethylsiloxane) grafted star polymers P$_{10/9}$ and (b) poly(ethylene glycol)-$b$-poly(dimethylsiloxane) grafted star polymers P$_{272/10}$. The asterisk denotes unreacted PDMS-MA macromonomer.
4.4 Chapter summary

Soft polymeric nanoparticles based on PEG and PEG-\textit{b}-PDMS grafted star polymers were successfully prepared. A tetra-functional initiator suitable for ATRP was prepared by functionalizing pentaerythritol with alkyl bromides. The initiator was subsequently chain extended with MeOPEG-MA macromonomer to afford PEG grafted star polymers in high yield of 96%. The initiator was also chain extended with varying amounts of PDMS-MA macromonomer to afford two sets of PDMS grafted star polymers. The synthesized PDMS grafted star polymers were then further chain extended with varying amounts of MeOPEG-MA macromonomer to afford PEG-\textit{b}-PDMS grafted star polymers with a high yield of 99%.
4.5 References


Soft Polymeric Nanoparticles as Additives for CO\textsubscript{2} Separation Membranes

5.1 Chapter perspective

In the previous Chapters 2-4, soft polymeric nanoparticles with various architectures have been successfully synthesized. The well-defined grafted star polymers that were previously described in Chapter 4 were prepared in a high yielding robust synthetic approach. Thus, they were identified as the best candidates for large scale applications. This chapter presents the utilization of the grafted star polymers as additives for CO\textsubscript{2} separation membranes. Thin film composite membranes with selective layers were prepared from commercially available poly(amide-\textit{b}-ether) (Pebax\textsuperscript{®} 2533) blended with a series of poly(ethylene glycol) and poly(ethylene glycol)-\textit{b}-poly(dimethylsiloxane) grafted star polymers. Their ability to selectively separate CO\textsubscript{2} from N\textsubscript{2} was studied.
5.2 Introduction

The use of polymeric membranes for gas separation applications has experienced a major expansion in the past few decades with current applications ranging from hydrogen recovery to the separation of CO₂ from flue gas [1-3]. It is desirable to develop membranes with high flux and selectivity, but the performance of current polymeric membranes have been constrained to an upper performance limit, referred to as Robeson’s upper bound (Section 1.4) [4, 5]. Various approaches have been explored to fabricate membranes which can exceed this limitation. These include the incorporation of hard inorganic nanoparticles into polymers to form mixed-matrix membrane (MMM) [6-8]. An ideal MMM possesses a morphology that ensures preferential gas transport through the particulate inorganic phase, with the polymer matrix providing mechanical support (Section 1.4.2) [7].

MMMs can be fabricated in symmetric or asymmetric formats. A symmetric dense MMM is the most studied geometry due to the simplicity of the fabrication process [6, 7]. However, the fabrication of an asymmetric membrane in the form of a thin film composite (TFC) structure is more commercially viable due to the increased flux and reduced consumption of expensive nanoparticles [9, 10]. TFC membranes are typically composed of a porous support coated with a highly permeable gutter layer, which is in turn coated with a thin active layer. However, the development of effective asymmetric MMMS has been limited. This is due to the difficulty in fabricating nanoparticles in a size that does not exceed the thickness of the active layer [7] and in avoiding defects in the resulting composite structure [11].

Many MMMS lack processability as it is difficult to ensure a defect-free polymer/inorganic particle interface and thus to guarantee membrane integrity and separation performance [6]. Alternatively, the same concept can be applied through the utilization of soft polymeric nanoparticles. In this case, compatibility between the particle and the polymer matrix can be engineered through the synthesis of particles that are more compatible with the polymer matrix. The requirements for these polymeric nanoparticles include: (i) a soft and CO₂
permeable core and (ii) a corona which is compatible with the polymer matrix. The addition of such soft polymeric nanoparticles into the thin active layer of TFC membranes can further improve gas separation performance. It is envisaged that the incorporation of such nanoparticles may form localized, high flux, CO$_2$ permeable domains within the selective matrix. The size of the soft polymeric nanoparticles are significantly smaller than the thickness of the active layer and this overcomes the problem of blending larger inorganic nanoparticles to form asymmetric MMMs.

Poly(dimethylsiloxane) (PDMS) has been extensively studied for CO$_2$ permeable gas separation membranes as it possesses high intrinsic permeability. The high permeability results from the flexible siloxane (-SiO-) backbone of the polymer [12]. Hence, PDMS is a potential candidate for the fabrication of soft polymeric nanoparticles. In fact, PDMS is often used as the CO$_2$ permeable gutter later in the fabrication of a TFC membrane [9, 13]. Pebax® is a commercially available poly(amide-b-ether) copolymer which has received significant attention as a membrane material, in particular for CO$_2$ separation applications [14-17]. Pebax® is a thermoplastic polymer with two separated microphases; an aliphatic polyamide (PA) “hard” block and an amorphous polyether (PE) “soft” block [18]. Various grades of Pebax® are available which comprise a varying number and length of PA and PE segments. The gas transport occurs mainly through the PE phase, while the PA phase provides the structural stability required for gas separation which often occurs at high temperatures and pressures [15]. Previous dense membrane studies have reported that the CO$_2$ separation performance of Pebax® copolymers can be further enhanced by physical blending with low molecular weight poly(ethylene glycol) (PEG), as the ether oxygen groups interact with CO$_2$, resulting in a high CO$_2$ solubility [19-21]. One study has also reported that the blending of commercially available PDMS grafted with low molecular weight PEG into Pebax® 1657 can result in an improvement in gas separation performance [22].
This chapter describes the utilization of soft polymeric nanoparticles as additives for CO₂ separation membranes. Pebax® 2533/grafted star polymer TFC membranes were prepared by blending PEG and PEG-b-PDMS grafted star polymers into Pebax® 2533, forming a thin film on microporous polyacrylonitrile (PAN) substrates which had been pre-coated with PDMS gutter layer; the synthesis of PEG and PEG-b-PDMS grafted star polymers have been previously detailed in Chapter 4. The separation performance of CO₂ from N₂ was then studied at 35 °C with an upstream pressure of 3.4 bar.

Figure 5.1 Thin composite Pebax® membranes blended with soft polymeric nanoparticles in the form of grafted star polymers.
5.3 Membrane preparation

Commercially available PAN microporous substrate was chosen as the support material for the TFC membranes as this material is resistant to many organic solvents. The solution of amino-terminated PDMS and trimesoyl chloride (TMC) was spin-coated onto the PAN substrate to form a cross-linked CO$_2$ permeable gutter layer (Scheme 5.1, step i). This PDMS intermediate layer prevents the penetration of diluted polymer solution into the PAN microporous substrate as well as rendering the entire membrane surface smoother. Thereafter, the grafted star polymers synthesized in Chapter 4 was blended into the Pebax® 2533 matrix and the mixture was then spin-coated onto the PDMS gutter layer to form the TFC blend membranes (Scheme 5.1, step ii).

Scheme 5.1 The fabrication of TFC blend membrane. (i) The PDMS gutter layer was formed by cross-linking amino-terminated PDMS and trimesoyl chloride. (ii) The TFC blend membrane was prepared by spin-coating the mixture of Pebax® 2533 and grafted star polymers onto the PDMS gutter layer.
5.3.1 Preparation and characterization of cross-linked PDMS gutter layers

The PDMS gutter layer was prepared by spin-coating the cross-linkable PDMS solution onto the PAN substrate. In order to estimate the thickness of the PDMS layer, SEM analysis was carried out on a number of different samples and one image example is presented in Figure 5.2. The average thickness of the gutter layer was determined to be 170 ± 20 nm. The gas transport properties of the PDMS gutter layer were tested using the constant pressure variable volume (CPVV) apparatus (Section 7.5.3). The average CO₂ permeance reached 1900 ± 200 GPU, which suggests that there was a significant degree of penetration of the PDMS into the substrate. However, the average CO₂/N₂ selectivity is 9.1, which is in agreement with previously published data [12].

![Figure 5.2 Cross-section of (a) PAN substrate pre-coated with PDMS gutter layer and (b) Pebax® 2533/PEG-b-PDMS grafted star polymers TFC blend membranes.](image)

5.3.2 Preparation and characterization of active layers

Pebax® 2533 and Pebax® 2533/grafted star polymers TFC blend membranes were prepared by spin-coating the respective polymer solutions onto PAN substrates which were pre-coated with the PDMS gutter layer. The cross-sectional morphology of the TFC blend membranes observed by SEM analysis is illustrated in Figure 5.2b. The thickness of the active layer was calculated by subtracting the thickness of the PDMS gutter layer and it was estimated to be approximately 580 ± 50 nm in all cases.
5.4 Result and discussion

5.4.1 Pure gas permeation characteristics of thin film composite membranes

The trends in $\text{CO}_2$ and $\text{N}_2$ permeance, and selectivity of $\text{CO}_2/\text{N}_2$, for TFC membranes containing from 0 to 40 wt.% of grafted star polymers are shown in Figure 5.3 and Figure 5.4, respectively. The gas transport properties of the fabricated TFC membranes were plotted against the grafted star polymers content in weight percentages. An increase in gas flux was observed with increasing blend percentages which show that the utilization of soft polymeric nanoparticles as additives is able to increase the flux through the membrane (Figure 5.3). More specifically, the TFC blend membranes containing pure PEG grafted star polymers ($\text{P0}_{24/0}$) showed the lowest $\text{CO}_2$ permeance. Increase in gas flux was observed upon introducing PDMS moieties into the grafted star polymers. This was observed upon blending $\text{P2}_{24/10}$ which has a PDMS weight fraction of 39% and a PEG weight fraction of 61% (Figure 5.3 and Table A5.1). Further increasing the weight fraction of PDMS moieties from 39 to 67 wt.% as for $\text{P2}_{24/30}$, further increased the gas flux. Conversely, changing the PEG content from 61 to 86 wt.% as for $\text{P2}_{72/10}$ did not alter the gas permeance results (Figure 5.3). Hence, the gas transport properties are strongly affected by the weight fraction of PDMS in the synthesized grafted star polymers.
Figure 5.3 CO₂ and N₂ permeance of Pebax® 2533 and Pebax® 2533/grafted star polymers TFC blend membranes as a function of grafted star polymers (P₀ and P₂) content tested at 35 °C and 3.4 bar.
TFC blend membranes of $P2_{24/30}$ were found to have the best CO$_2$ permeance with similar CO$_2$/N$_2$ selectivities to other TFC polymer blends. The TFC blend membranes containing between 0 and 40 wt.% of $P2_{24/30}$ exhibited more than a four-fold increase in CO$_2$ permeance, from 326 to 1374 GPU, with an overall decreasing trend of CO$_2$/N$_2$ selectivity from 24 to 12 (Figure 5.4), which approaches the selectivity of the PDMS gutter layer (Table 5.1). The TFC blend membranes containing pure PEG grafted star polymers, $P0_{24/0}$, exhibited the smallest increase in CO$_2$ permeance, from 326 to 564 GPU, with an overall decreasing trend in CO$_2$/N$_2$ selectivity from 24 to 14 (Table 5.1). These results are in agreement with previously published data which shows that dense membranes blended with commercially available linear PDMS-\textit{g}-PEG exhibit higher flux when compared to membranes blended with solely amorphous PEG moieties [22]. This is due to PDMS having a much higher permeability relative to amorphous PEG; PDMS has a permeability of \textit{ca.} 3800 Barrer in comparison to amorphous PEG with a permeability of 143 Barrer [12, 23].

![Figure 5.4 CO$_2$/N$_2$ selectivity of Pebax® 2533 and Pebax® 2533/grafted star polymers TFC blend membranes as a function of grafted star polymers (P0 and P2) content tested at 35 °C and 3.4 bar.](image-url)
### Table 5.1 Gas separation performance of TFC blend membranes and the corresponding active layers tested at 35 °C and 3.4 bar.

<table>
<thead>
<tr>
<th>Sample</th>
<th><strong>P2</strong> (wt.%)</th>
<th><strong>TFC Blend Membrane</strong></th>
<th><strong>Active Layer</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td><strong>CO(_2)</strong> Permeance (GPU)</td>
<td><strong>CO(_2)/N(_2)</strong> selectivity</td>
</tr>
<tr>
<td>Pebax® 2533</td>
<td>0</td>
<td>326</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>378</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>458</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>485</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>564</td>
<td>14</td>
</tr>
<tr>
<td>Pebax® 2533/P2(_{024/0})</td>
<td>10</td>
<td>367</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>440</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>507</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>831</td>
<td>11</td>
</tr>
<tr>
<td>Pebax® 2533/P2(_{24/10})</td>
<td>10</td>
<td>389</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>458</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>488</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>808</td>
<td>13</td>
</tr>
<tr>
<td>Pebax® 2533/P2(_{72/10})</td>
<td>10</td>
<td>408</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>539</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>728</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>1374</td>
<td>12</td>
</tr>
</tbody>
</table>
5.4.2 Pure gas permeation characteristics of active layers

The calculation of permeance through the active layer alone is important as it reveals the true potential of the membrane materials. The CO$_2$ and N$_2$ permeance and permeability through the active layer can be determined by deducting the transport resistances through the porous substrate and the gutter layer (detailed calculation shown in Appendix 5). The CO$_2$/N$_2$ selectivity of the pure Pebax® 2533 active layer calculated using this approach agrees with previously reported studies [24, 25]. The CO$_2$ and N$_2$ permeance and the CO$_2$/N$_2$ selectivity, for the active layer are shown in Figure 5.5. The trends in permeance and selectivity through the active layer for the blend membranes follow closely the trends through the composite structure discussed previously. However, the CO$_2$ permeance through the active layer (P$_{24/30}$ blends at 30 wt.%0) is approximately 170% higher when compared to the permeance through the composites (Table 5.1). This is attributed to the absence of flow resistance through the PDMS gutter layer. The CO$_2$/N$_2$ selectivity through the active layer is higher than the CO$_2$/N$_2$ selectivity through the composite membranes, as the impact of the PDMS layer disappears. The permeance and selectivity trends for the P$_{24/0}$ active layer are also again more modest, reflecting greater permeance achieved when PDMS moieties are introduced.

Merkel et al. (2010) have identified a target range of permeance and selectivity values that would make membrane processes cost-competitive for post combustion capture [10]. Two of the best performing TFC blend membranes and their corresponding active layers, 30 and 40 wt.% blends of P$_{24/30}$, were plotted in Figure 5.6. The TFC membrane with pure Pebax® 2533 as the active layer is at least three times more permeable with slightly lower CO$_2$/N$_2$ selectivity than that indicated by Merkel et al. (2010) as being typical of commercial natural gas membranes, while the performance of the active layer itself is at least four times more permeable with similar CO$_2$/N$_2$ selectivity. The active layers of the P$_{24/30}$ blends at 30 wt.% lie within the target region. This suggests that the approach of blending soft polymeric nanoparticles such as PEG-§-PDMS grafted star polymers into a selective Pebax® 2533 matrix has great potential if these layers could be fabricated without the presence of the gutter layer.
Figure 5.5 (a) CO₂ and N₂ permeance, (b) CO₂/N₂ selectivity of Pebax® 2533 and Pebax® 2533/grafted star polymers blend active layers as a function of grafted star polymers (P2) content tested at 35 °C and 3.4 bar.
Figure 5.6 The performance of Pebax® 2533 and Pebax® 2533/PEG-b-PDMS grafted star polymers TFC blend membranes and the corresponding active layers developed in this study relative to other membranes reported in the literature.

5.4.3 Effect of PDMS content on CO₂ permeability

The permeability of the active layer was calculated as the product of its permeance and thickness (detailed calculation shown in Appendix 5). An increase in star polymer (P2) percentage results in an increase in CO₂ permeability (Figure 5.7). In addition, the CO₂ permeability increases with an increase in the PDMS content of the star polymers (Figure 5.7, green region). The best separation performance was achieved by blending the grafted star polymers with the highest PDMS content, P2_{24/30}. For all three star polymers the highest CO₂ permeabilities were achieved at the highest blend percentages (Figure 5.7, yellow region). This may be a result of the formation of connected PDMS clusters/domains allowing for higher CO₂ permeance through the membrane.
Figure 5.7 The effect of PDMS content in the active layer on CO$_2$ permeability.

The results determined from this study may be further explained by the previous attempts to model the passage of gas through a polymeric membrane *via* a solution-diffusion mechanism [26-30]. At low blend percentages, gas molecules are able to "jump" from one domain to another. In this case, gas molecules are able to effectively diffuse across the membrane through this jumping motion. At high blend percentages, connected domains may be formed which allow for faster diffusion of gases at the expense of lower selectivity.
5.5 Chapter summary

Pebax® 2533/grafted star polymer TFC membranes were prepared by blending up to 40 wt.% PEG and PEG-b-PDMS grafted star polymers as additives relative to Pebax® 2533, and coating these blends onto PAN porous substrates that have been pre-coated with a PDMS gutter layer. The gas separation performance of the fabricated TFC membranes is strongly affected by the weight fraction of PDMS in the synthesized grafted star polymers. The best performing membranes are achieved by blending grafted star polymers with the highest PDMS content. The CO₂/N₂ selectivity generally decreases with increasing blend percentages. These results demonstrate the ability for soft polymeric nanoparticles to form localized, high flux, soft domains within a selective matrix, which in turn leads to an increase in gas separation performance. All together, these results create an interesting route to further develop and utilize soft polymeric nanoparticles as additives for membrane separation systems.
5.6 References


Conclusions and Future Perspective

6.1 Conclusions

This thesis presents a novel way of improving the separation performance of existing gas separation membranes through the addition of soft polymeric nanoparticles. Soft polymeric nanoparticles with well-defined architectures were synthesized mainly via chain-growth polymerization. The proof of concept was studied by blending the best candidate soft polymeric nanoparticles into commercially available poly(amide-\text{-}b\text{-}ether) (Pebax® 2533), forming the active layer of thin film composite (TFC) membranes.

Chapter 2 outlined the synthesis of novel soft polymeric nanoparticles based on linear polyimide (PI) and linear brush poly(dimethysiloxane) (PDMS) triblock copolymers. The triblock copolymers were synthesized via a combination of step- and chain-growth polymerization. Step-growth polymerization was utilized to synthesize the rigid PI middle block through precise control of diamine to dianhydride ratio. Subsequent functionalization of the well-defined diamino PI and chain extension with various molar ratio of poly(dimethysiloxane) monomethacrylate (PDMS-MA) via chain-growth polymerization (atom transfer radical polymerization or commonly abbreviated as ATRP) afforded a series of block copolymers with variable degrees of polymerization (DP) in high conversions (88-94%). Self-assembly of the triblock copolymers in N,N-dimethylformamide (DMF) afforded nanoparticles with hydrodynamic diameters ($d_{\text{H}}$) ranging from 87 to 109 nm. The nanoparticles were further stabilized via hydrogen abstraction through the thermal degradation of benzoyl peroxide. Imaging analysis revealed that the self-assemblies and their cross-linked derivatives had spherical morphologies. Given that the self-assembly is conducted in a selective solvent for the PI block, DMF, it is proposed that the resulting nanoparticles could consist of a rigid PI shell, and a soft PDMS core.
Chapter 3 presented a simpler way of synthesizing soft polymeric nanoparticles as the middle PI block, which was synthesized via step-growth polymerization, was replaced by commercially available, poly(ethylene glycol) (PEG); step-growth polymerization involves a random reaction of two molecules that may be any combination of a monomer, oligomer, or a longer-chain molecule. In addition, the synthetic approach outlined in Chapter 3 presented a better approach of nanoparticle stabilization through photocross-linking. Light-induced photocross-linking provides a stabilization route which avoids unwanted by-products. It also enables more temporal and positional control. Initially, three different molecular weights of linear monomethyl ether PEG (MeOPEG) were functionalized to afford MeOPEG-based macroinitiators suitable for ATRP. The macroinitiators were subsequently chain extended with varying amounts of PDMS-MA macromonomer and 2-(methylacyloyloxy)ethyl anthracene-9-carboxylate, as the photochromic moieties, to afford a series of novel photoresponsive diblock copolymers with variable DP in high conversions (88-96% for the PDMS-MA macromonomers and > 99% for the anthracene moieties). Self-assembly of the diblock copolymers in a selective solvent for the linear PEG block, DMF, afforded nanoparticles with $d_H$ ranging from 41 to 268 nm. Various structures, from spherical to crew-cut type or large compound micelles, with unique particle sizes were displayed. The stabilization of the nanoparticles was achieved via [4+4] photodimerization of the anthracene moieties. Imaging analysis revealed that the self-assemblies and their cross-linked derivatives had spherical morphologies.

Chapter 4 detailed a robust approach to synthesize soft polymeric nanoparticles suitable for large scale applications such as gas separation processes. Soft polymeric nanoparticles based on PEG and PEG-b-PDMS grafted star polymers were synthesized via the ‘core-first’ approach. This method allows the preparation of well-defined soft polymeric nanoparticles without the need for block copolymer self-assembly which is generally carried in low concentration to avoid aggregation of nanoparticles. Additionally, nanoparticles can be synthesized in high yields as the crude reaction mixture only requires separation from unreacted monomers. Initially, pentaerythritol was functionalized to afford tetra-functional initiator suitable for ATRP. The tetra-functional initiator was subsequently chain extended
with poly(ethylene glycol) methyl ether methacrylates (MeOPEG-MA) macromonomer to afford PEG grafted star polymers in high conversions of 96%. The tetra-functional initiator was also chain extended with varying amounts of PDMS-MA macromonomer to afford PDMS grafted star polymers. The synthesized PDMS grafted star polymers were then further chain extended with varying amounts of MeOPEG-MA macromonomer to afford PEG-b-PDMS grafted star polymers in high conversions of > 99%.

Chapter 5 highlighted the utilization of soft polymeric nanoparticles as additives for CO₂ separation membranes. TFC membranes with selective layers prepared from commercially available Pebax® 2533 blended with a series of PEG and PEG-b-PDMS, described in Chapter 4, were prepared. The blends were coated onto polyacrylonitrile porous substrates that have been pre-coated with a PDMS gutter layer. Their ability to selectively separate CO₂ from N₂ was studied at 35 °C with an upstream pressure of 3.4 bar. The gas separation performance of the fabricated TFC membranes is strongly affected by the weight fraction of PDMS in the synthesized grafted star polymers. The best performing membranes are achieved by blending grafted star polymers with the highest PDMS content while the CO₂/N₂ selectivity generally decreases with increasing blend percentages.

All together, these results create an interesting route to further develop and utilize soft polymeric nanoparticles as additives for existing gas separation membrane systems.
6.2 Future perspective

6.2.1 High performance polyimide-based thin film composite membranes

Chapter 1 detailed the synthesis of soft polymeric nanoparticles based on linear PI and linear brush PDMS triblock copolymers. These soft polymeric nanoparticles can be added into TFC membranes with PI as the polymer matrix. In future work, three candidates of PIs may be utilized to fabricate the thin active layer; these include poly(6FDA-co-TMPD), poly(6FDA-co-ODA) and poly(6FDA-co-BAFL). Poly(6FDA-co-TMPD) is a class of high performance PI and it is the linear component of the synthesized soft polymeric nanoparticles described in Chapter 2. Poly(6FDA-co-ODA) and poly(6FDA-co-BAFL) are more selective polymer matrices, when compared to poly(6FDA-co-TMPD), for CO$_2$/N$_2$ separation. The gas transport properties of previously mentioned PIs are summarized in Table 6.1.

<table>
<thead>
<tr>
<th>Polyimide</th>
<th>CO$_2$ Permeability (Barrer)</th>
<th>CO$_2$/N$_2$ selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(6FDA-co-TMPD)</td>
<td>456 – 512</td>
<td>8 – 17</td>
</tr>
<tr>
<td>Poly(6FDA-co-ODA)</td>
<td>23</td>
<td>28</td>
</tr>
<tr>
<td>Poly(6FDA-co-BAFL)</td>
<td>98</td>
<td>30</td>
</tr>
</tbody>
</table>

![Chemical structures of various high performance polyimides](image)

**Figure 6.1** Chemical structures of various high performance polyimides.
6.2.2 Soft polymeric nanoparticles blended dense membranes

As shown in Chapter 5, TFC membranes blended with soft polymeric nanoparticles showed enhanced separation performance. Future work would include fabricating dense Pebax® 2533 blend membranes to measure the solubility and diffusivity parameters which further detail the permeation characteristics of these membranes.

6.2.3 The effect of water vapour and mixed gases on the performance of soft polymeric nanoparticles blended thin film composite membranes

Understanding the permeation behaviour of water vapour and mixed gas would provide critical information for commercial post-combustion CO$_2$ capture. Future work would include testing the performance of blended TFC membranes with the presence of water vapour and under various mixed gases conditions.

6.2.4 Thin film composite membranes with highly selective active layer

Future work could also involve the utilization of a more selective polymer matrix as the addition of soft polymeric nanoparticles resulted in declining selectivity. Selective polymer matrices such as Pebax® 1657 and cross-linked PEG are good candidates.

<table>
<thead>
<tr>
<th></th>
<th>Polyimide</th>
<th>CO$_2$ Permeability (Barrer)</th>
<th>CO$_2$/N$_2$ selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pebax® 1657</td>
<td>78</td>
<td>49</td>
<td></td>
</tr>
<tr>
<td>Cross-linked PEG</td>
<td>112</td>
<td>52</td>
<td></td>
</tr>
</tbody>
</table>

6.2.5 Hard and soft nanoparticles for next generation gas separation membranes

Blending both hard inorganic nanoparticles and soft polymeric nanoparticles may lead to interesting results and a new approach in improving the performance of current gas separation membranes. However, this approach will involve designing
inorganic particles that are in the nanoscale domains if they were to be incorporated to TFC membranes as the current hard inorganic particles are in the micron size range, which exceed the thickness of TFC’s active layer.
6.3 References

Experimental

This chapter describes various characterization methods and detailed experimental procedures utilized in all the work presented in this thesis.
7.1 Characterization methods

7.1.1 Dynamic light scattering

Dynamic light scattering (DLS) was utilized to measure the size of the synthesized nanoparticles. For experiments conducted in Chapter 2, DLS measurements were performed on a Malvern Zetasizer Nano ZS with 4.0 mW He-Ne laser operating at 632.8 nm. Analysis was performed at an angle of 173° and a constant temperature of 25 ± 0.1 °C. For experiments conducted in Chapter 3, DLS measurements were performed on Wyatt DynaPro NanoStar fitted with a 120 mW Ga-As laser operating at 658 nm and 100 mW was delivered to the sample cell. Analysis was performed at an angle of 90° and a constant temperature of 25 ± 0.01 °C.

7.1.2 Gel permeation chromatography

Polymer molecular weight and polydispersity index (PDI) characterization was carried out via gel permeation chromatography (GPC) using HPLC grade THF (RCI Labscan) or chloroform (Chem-Supply) as the mobile phase. For experiments conducted in Chapter 2, GPC analysis was performed on a Shimadzu Liquid Chromatography system fitted with a miniDAWN TREOS detector (658 nm, 30 mW) and a Shimadzu RID-10A refractive index detector (633 nm), using three Phenomenex Phenogel columns (500, 10⁴, 10⁶ Å porosity; 5 μm bead size) maintained at 40 °C. THF was used as the eluent at a flow rate of 1 mL/min. Astra software (Wyatt Technology Corp.) was used to process the data and determine the molecular weight characteristics using either known dn/dc values or based upon the assumption of 100% mass recovery of the polymer where the dn/dc value was unknown. For experiments conducted in Chapter 3, GPC analysis was performed on a Shimadzu Liquid Chromatography system fitted with a Shimadzu RID-10A refractive index detector (633 nm) and a Shimadzu SPD-10A UV-Vis detector (230 and 390 nm), using three Phenomenex Phenogel columns (500, 10⁴, 10⁶ Å porosity; 5 μm bead size) maintained at 50 °C. Chloroform was used as the eluent at a flow rate of 1 mL/min. Astra software (Wyatt Technology Corp.) was used to process the data and determine the molecular weight characteristics based upon a conventional column calibration using PEO standards. For experiments conducted in Chapter 4, GPC analysis was performed on a Shimadzu Liquid
Chromatography system fitted with a Shimadzu RID-10A refractive index detector (633 nm), using three PLgel columns (5 μm, MIXED-C) maintained at 45 °C. THF was used as the eluent at a flow rate of 1 mL/min. Astra software (Wyatt Technology Corp.) was used to process the data and determine the molecular weight characteristics based upon a conventional column calibration using PEO standards.

### 7.1.3 Matrix-assisted laser desorption/ionization time of flight

Matrix-Assisted laser desorption/ionization time of flight (MALDI ToF) mass spectroscopy allows the determination of molecular weight and its distributions. In addition, it permits the identification of end groups and determination of composition homogeneity [1]. All of the MALDI ToF MS was performed on a Bruker Autoflex III Mass Spectrometer operating in positive/linear mode. For experiments conducted in **Chapter 2**, the analyte, matrix and cationization agent were dissolved in THF at concentrations of 10, 10 and 1 mg/mL, respectively, and then mixed in a ratio of 10:1:1. 0.3 μL of this solution was then spotted onto a ground steel target plate, and the solvent was allowed to evaporate prior to analysis. For experiments conducted in **Chapter 3**, the analyte was dissolved in DCM at concentrations of 10 mg/mL while the matrix and cationization agent were dissolved in MeOH at concentrations of 10 and 1 mg/mL, respectively, and then mixed in a ratio of 10:1:1. 0.3 μL of this solution was then spotted onto a ground steel target plate, and the solvent was allowed to evaporate prior to analysis. FlexAnalysis (Bruker) was used to analyze all of the data.

### 7.1.4 Nuclear magnetic resonance

$^1$H and $^{13}$C nuclear magnetic resonance (NMR) spectroscopy allows the determination of molecular structure. $^1$H and $^{13}$C NMR distinguish between different magnetic proton and carbon environments in order to deduce molecular framework [2]. For experiments conducted in **Chapter 2**, $^1$H and $^{13}$C NMR spectroscopic analysis were performed on a Varian Unity Plus 500 MHz spectrometer operating at 500 and 150 MHz, respectively, using deuterated solvent resonance as reference. For experiments conducted in **Chapter 3** and **4**, $^1$H
and $^{13}\text{C}$ NMR spectroscopic analysis were performed on a Varian Unity Plus 400 MHz spectrometer operating at 400 and 100 MHz, respectively, using deuterated solvent resonance as reference.

### 7.1.5 Scanning electron microscopy

The thickness of PDMS gutter layers and active layers of the TFC membranes was measured by scanning electron microscopy (SEM) using FEI Quanta 200 ESEM FEG. Samples were pre-coated with gold using a Dynavac Mini Sputter Coater prior to imaging. The thickness of PDMS gutter layers and the active layers were determined by taking an average value at eight different measurement points.

### 7.1.6 Scanning transmission electron microscopy

Elemental analysis of the synthesized nanoparticles was performed using scanning transmission electron microscopy (STEM) with an EDAX X-ray detector. STEM imaging was conducted using a high angle, annular dark field detector (HAADF) to generate dark field STEM images. Spectrum line profiles were recorded across nanoparticles using a dwell time of 5 s and profile size of 30 points.

### 7.1.7 Transmission electron microscopy

Transmission electron microscopy (TEM) was utilized to analyze the morphology of the synthesized nanoparticles. TEM images were taken using a Tecnai TF30 transmission electron microscopy (FEI Co., Eindhoven, The Netherlands) operating at 200 kV. Images were acquired digitally with a Gatan US1000 2k × 2k CCD Camera (Pleasanton, CA).

### 7.1.8 Ultraviolet-visible spectrophotometry

The activity of photochromic moieties was monitored spectrophotometrically using ultraviolet-visible (UV-Vis) spectrophotometry. UV-Vis analysis was performed on a Shimadzu UV-Vis Scanning Spectrophotometer (UV-2101 PC) using quartz cuvette.
7.2 Experiments for chapter 2

7.2.1 Materials

2,3,5,6-Tetramethyl-1,4-phenylenediamine (TMPD, 99%), 2-bromoisoobutyryl bromide (BIBB, 98%), copper(I) bromide (CuBr, 98%), potassium trifluoroacetate (KTFA, 98%), silver trifluoroacetate (AgTFA, 98%), sodium trifluoroacetate (NaTFA, 98%), tris[2-(dimethylamino)ethyl]amine (Me₆TREN) and benzoyl peroxide (BP, 70%, remainder water) were purchased from Aldrich and used as received. Poly(dimethylsiloxane) monomethacryloxypropyl terminated (Mₘ = 600-800 Da) (PDMS-MA, 95%, Gelest) was stirred with basic alumina (99%, Merck) for 16 h and filtered prior to use. Acetone (AR), dichloromethane (DCM, AR), diethyl ether (Et₂O, AR), methanol (MeOH, AR) and N,N-dimethylformamide (DMF, AR) were purchased from Chem-Supply and used as received. 4,4’-Hexafluoroisopropylidene (6FDA, 99%, Alfa Aesar), trans-2-[3-(4-tert-butyl-phenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB, Santa Cruz Biotechnology) and N,N-dimethylacetamide (DMAc, 99.5%, extra dry, Acros Organics) were used as received. Tetrahydrofuran (THF, HPLC grade, RCI Labscan) was distilled from sodium benzophenone ketyl under argon. Triethylamine (TEA, 99%, Ajax) was distilled from calcium hydride (95%, Aldrich) under argon. Deuterated chloroform (CDCl₃, 99.9%) was purchased from Cambridge Isotope Laboratories. Strong carbon-coated Formvar films mounted on 300 mesh copper grids were purchased from ProSciTech. Teflon syringe filters with a pore size of 0.45 µm were purchased from Labquip Technologies.

7.2.2 Synthesis of α,ω-diamino poly(6FDA-co-TMPD)

6FDA (2.40 g, 5.40 mmol, 5 equiv.) and TMPD (1.09 g, 6.61 mmol, 6 equiv.) were dissolved in DMAc (20 mL) under argon. After stirring for 24 h at room temperature, the mixture was refluxed for 24 h and then precipitated into cold (-18 °C) 1:1 MeOH:Et₂O (200 mL). The precipitate was collected by centrifugation, dried in vacuo (2 mbar) for 16 h, re-dissolved in DCM (15 mL) and re-precipitated into cold (-18 °C) 1:1 MeOH:Et₂O (200 mL). The precipitate was collected by centrifugation and dried in vacuo (0.1 mbar) at 60 °C for 16 h to yield P₁ as a faint yellow solid, 2.95 g (isolated yield: 85%). GPC: Mₙ = 5.2 kDa, PDI = 1.5. MALDI ToF
MS: $M_n = 2.8$ kDa, PDI = 1.1. $^1$H NMR (500 MHz, CDCl$_3$): $\delta_h$ 2.06 (br s, ArH, $H_b$ end-group), 2.14 (br s, CH$_3$, $H_a$), 7.91 – 8.02 (m, ArH, $H_d$ & $H_c$), 8.04 – 8.12 (m, ArH, $H_e$) ppm (Figure A2.1). $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta_c$ 13.7, 15.4, 15.7, 118.7, 119.6, 122.4, 124.0, 124.2 – 124.4 (m), 125.4, 125.5, 130.8, 132.2, 132.4, 132.5, 132.7, 132.8, 132.9, 134.0, 135.7, 136.0, 138.9, 139.2, 139.3, 144.2, 165.7 – 165.8 (m), 166.0, 166.8, 167.1 ppm (Figure A2.2).

7.2.3 Synthesis of $\alpha,\omega$-dibromo poly(functionalized 6FDA-co-TMPD) macroinitiator

Poly(6FDA-co-TMPD) P1 (2.80 g, 0.48 mmol, 1 equiv.) was dissolved in THF (15 mL) under argon. TEA (0.75 mL, 5.38 mmol, 10 equiv.) was added, followed by the dropwise addition of BIBB (1.24 g, 5.38 mmol, 10 equiv.). The mixture was stirred at room temperature for 4 h and precipitated into cold (-18 °C) MeOH thrice (3 × 150 mL). The precipitate was isolated via filtration and dried in vacuo (0.1 mbar) at 60 °C for 16 h to yield P2 as a white solid, 2.93 g (isolated yield: 89%). GPC: $M_n = 5.9$ kDa, PDI = 1.5. MALDI ToF MS: $M_n = 3.1$ kDa, PDI = 1.1. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$H 2.09 (br s, CH$_3$, $H_c$ end-group), 2.11 (br s, CH$_3$, $H_b$ end-group), 2.14 (br s, CH$_3$, $H_a$), 2.21 (br s, CH$_3$, $H_f$ end-group), 7.93 – 8.02 (m, ArH, $H_d$ & $H_c$), 8.05 – 8.11 (m, ArH, $H_e$) ppm (Figure A2.3). $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta_c$ 15.3, 15.4, 15.5, 15.7, 15.8, 15.9, 32.6, 32.7, 120.5, 122.4, 124.2 – 124.4 (m), 125.4, 125.5, 128.8, 130.8, 132.4, 132.8, 132.9, 133.4, 134.0, 134.8, 135.9 – 136.1 (m), 139.2, 165.7 – 165.8 (m), 166.0, 170.2 ppm (Figure A2.4).

7.2.4 Synthesis of polyimide/poly(dimethylsiloxane) triblock copolymers

Poly(6FDA-co-TMPD) macroinitiator P2 (0.25 g, 42.4 µmol, 1 equiv.), Me$_6$TREN (22.7 µL, 84.8 µmol, 2 equiv.) and PDMS-MA macromonomer (5-15 equiv., refer to Table 2.2) were dissolved in THF in a Schlenk tube (oven-dried at 110 °C for 24 h) to afford a macromonomer concentration of 0.2 M. An aliquot (0.2 mL) was taken ($t_0$) to monitor macromonomer conversion. The mixture was then subjected to three freeze-pump-thaw cycles and the Schlenk tube was then immersed again in liquid N$_2$. Once the solution was frozen CuBr (12.2 mg, 84.8 µmol, 2 equiv.) was
added and another three freeze-pump-thaw cycles were performed. The Schlenk tube was allowed to equilibrate at room temperature for 5 min with stirring to ensure homogeneity and then heated at 50 °C for 24 h. After cooling to room temperature an aliquot (0.2 mL) was taken ($t_{24}$) to determine the macromonomer conversion. The reaction mixture was then diluted with THF (3 mL) and passed through a plug of basic alumina to remove the copper catalyst. The filtrate was concentrated in vacuo (2 mbar) and then dried in vacuo (0.1 mbar) at 120 °C for 16 h to yield $P_3$-1, $P_3$-2 and $P_3$-3 as pale yellow tacky solids (isolated yield of $P_3$-1: 94%; isolated yield of $P_3$-2: 92%; isolated yield of $P_3$-3: 87%). The polymer composition was varied by changing the macromonomer:initiator ratio (Table 2.2). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$H -0.1 - 0.30 (m, SiCH$_3$, $H_b$), 0.45 - 0.60 (m, SiCH$_2$, $H_g$), 0.77 - 1.15 (m, CH$_3$, $H_d$, $H_j$), 1.24 - 1.38 (m, CH$_2$, $H_l$), 1.49 - 1.67 (m, CH$_2$, $H_l$), 1.78 (br s, CH$_2$C, $H_c$), 2.15 (br s, ArCH$_3$, $H_b$), 3.87 (br s, CH$_2$O, $H_e$), 7.90 - 8.12 (m, ArH, $H_a$) ppm (Figure 2.4).

7.2.5 Self-assembly of polyimide/poly(dimethylsiloxane) triblock copolymers

THF and DMF for self assembly studies were pre-filtered through 0.45 µm PTFE filters (Labquip Technologies). Copolymers were dissolved in THF (30 mg/mL) and then treated dropwise with DMF to effect dissolution (1.0 mg/mL). Samples were left for 16 h prior to analysis. DLS and TEM were used to analyze the structure and morphology of the copolymers.

7.2.6 Cross-linking of polyimide/poly(dimethylsiloxane) triblock copolymers

5.0 mg of $P_3$-1 and 0.5 g of benzoyl peroxide were dissolved in THF ($P_3$-1: 30 mg/mL) and then treated dropwise with DMF to effect dissolution ($P_3$-1: 1.0 mg/mL). The sample was analyzed by DLS and then bubbled with argon for 1 h. An aliquot (1.5 mL) was quickly added to a 4 mL vial (backpurged with argon) by removing and recapping the plastic cap. The solution was stirred at 90 °C for 7 h and the solvent was removed in vacuo (0.1 mbar) to yield a faint yellow solid. The dried product was then dissolved in pre-filtered THF (1.5 mL) for post cross-
linking DLS analysis. An equivalent amount of polymer and BP were also used to cross-link P3-2 and P3-3.

**7.2.7 Imaging of uncross-linked polyimide/poly(dimethylsiloxane) triblock copolymers**

The TEM and STEM samples were prepared by dissolving P3-2 in THF (30 mg/mL), treated dropwise with DMF to effect dissolution (0.5 mg/mL), drop-coated onto copper TEM grids (5 µL), blotted and negatively stained by uranyl acetate aqueous solution (2 wt.%) before imaging was conducted.

**7.2.8 Imaging of cross-linked polyimide/poly(dimethylsiloxane) triblock copolymers**

The TEM and STEM samples were prepared by drop-coating cross-linked P3-2 in THF (0.1 mg/mL) onto copper TEM grids (5 µL), blotted and negatively stained by uranyl acetate aqueous solution (2 wt.%) before imaging was conducted.

**7.3 Experiments for chapter 3**

**7.3.1 Materials**

2-Bromoisoobutyryl bromide (BIBB, 98%), 2,2’-bipyridyl (bpy, 99%), benzene (AR, 99%), copper(I) bromide (CuBr, 98%), sodium trifluoroacetate (NaTFA, 98%), anhydrous tert.-butanol (tert.-BuOH, 99.5%), anthracene-9-carboxylic acid (99%), N,N,N’,N’,N”-pentamethyldiethylenetriamine (PMDETA, 99%), 1 kDa poly(ethylene glycol) monomethyl ether (MeOPEG<sub>1</sub>) and 5 kDa poly(ethylene glycol) monomethyl ether (MeOPEG<sub>5</sub>) were purchased from Aldrich and used as received. Monomethacryloxypropyl terminated poly(dimethylsiloxane) (M<sub>ω</sub> = 600-800 Da) (PDMS-MA, 95%, Gelest) was stirred with basic alumina (99%, Scharlau) for 16 h and filtered prior to use. 2-Hydroxyethyl methacrylate (HEMA, 98%, Aldrich) was also stirred for 16 h with inhibitor remover (Aldrich) and filtered prior to use. Dichloromethane (DCM, AR), methanol (MeOH, AR), N,N-dimethylformamide (DMF, AR), chloroform (AR), sodium hydroxide (NaOH, 97%) and sodium chloride (NaCl, 97%) were purchased from Chem-Supply and used as received. Tetrahydrofuran (THF, HPLC grade, RCI Labscan) was distilled from sodium
benzophenone ketyl under argon. Triethylamine (TEA, 99%, Ajax) was distilled from calcium hydride (95%, Aldrich) under argon. Deuterated chloroform (CDCl₃, 99.9%) and deuterated dimethyl sulfoxide (d₆-DMSO, 99.9%) were purchased from Cambridge Isotope Laboratories. *Trans*-2-[3-(4-tert-butyl-phenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB, Santa Cruz Biotechnology), 10 kDa poly(ethylene glycol) monomethyl ether (MeOPEG₁₀, Creative PEGWorks), thionyl chloride (SOCl₂, AR, Merck), hydrogen chloride (HCl, 37%, Scharlau) and anhydrous magnesium sulphate (MgSO₄, 98%, Scharlau) were used as received.

7.3.2 Synthesis of α-methyl, ω-bromo functionalized poly(ethylene glycol) macroinitiators

MeOPEG₅ (10.0 g, 2.0 mmol, 1 equiv.) was dissolved in anhydrous DCM (80 mL) under argon. The solution was cooled to 0 °C followed by the dropwise addition of TEA (4.50 mL, 32.3 mmol, 16 equiv.) and BIBB (6.88 g, 30.0 mmol, 15 equiv.). The mixture was stirred for 1 h at 0 °C. The crude product was then washed with 1 M HCl (2 × 80 mL), 1 M NaOH (4 × 80 mL), saturated NaCl (1 × 80 mL), dried (MgSO₄), filtered and concentrated *in vacuo* (2 mbar). The dried product was redissolved in chloroform (80 mL), flushed through basic alumina and concentrated *in vacuo* (2 mbar). The desired product was then dried *in vacuo* (0.1 mbar) at 25 °C for 16 h to yield P₁-2 as a white solid, 5.76 g (isolated yield: 34.1%). Synthesis procedure was repeated for the functionalization MeOPEG₁ and MeOPEG₁₀. ¹H NMR (400 MHz, CDCl₃): δ H 1.89 (s, CH₃, H₁ end-group), 3.24 (s, CH₃, H₆ end-group), 3.41 – 3.69 (m, CH₂CH₂O, H₅, H₆, H₇ & H₈), 4.23 – 4.25 (m, CH₂CH₂OCO, Hₑ) ppm (Figure 3.1). ¹³C NMR (100 MHz, CDCl₃): δ C 30.2, 57.0, 57.9, 64.9, 67.9, 69.5, 69.7, 71.2, 170.7 ppm (Figure A3.1).

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

Anthracene-9-carboxylic acid (2.22 g, 10.0 mmol) and SOCl₂ (30 mL) were added to a dried flask under argon. The reaction mixture was refluxed under argon for 90 minutes and the excess SOCl₂ was removed *in vacuo* (0.1 mbar). The resulting residue was azeotroped with benzene (3 × 10 mL), redissolved in anhydrous THF
(40 mL) and cooled to 0 °C. TEA (2.4 mL, 32.7 mmol) was added, followed by the dropwise addition of HEMA (1.15 mL, 9.5 mmol) in anhydrous THF (30 mL). The reaction solution was stirred at 0 °C for 1 h, warmed to 25 °C and stirred for 20 h, and then filtered and concentrated. The crude product was redissolved in DCM (100 mL), washed with 2 M HCl (2 × 100 mL), 2 M NaOH (4 × 100 mL), saturated NaCl (1 × 100 mL) and distilled water (2 × 100 mL), dried (MgSO₄), filtered, and concentrated in vacuo (2 mbar). The product was then dried in vacuo (0.1 mbar) at 30 °C for 16 h to yield 2-(methacryloyloxy)ethyl anthracene-9-carboxylate (MEAC) as a pale yellow solid, 2.88 g (isolated yield: 83.3%) with a purity of 95.6%.

1H NMR (400 MHz, CDCl₃): δH 1.99 – 2.00 (t, J = 1.2 Hz, CH₃, Hc), 4.60 – 4.62 (m, CH₂, Hd), 4.87 – 4.90 (m, CH₂, Hc), 5.64 – 5.65 (quin, J = 1.6 Hz, J = 3.2 Hz, CH, H₃), 6.20 – 6.25 (quin, J = 1.2 Hz, J = 2.4 Hz, CH, Hf), 7.47 – 7.54 (m, ArH, H₆), 8.02 – 8.10 (m, ArH, H₆), 8.55 (s, ArH, Hf) (Figure A3.2). 13C NMR (100 MHz, CDCl₃, δ): δC 18.3, 62.5, 63.3, 125.0, 125.4, 126.2, 127.0, 128 (d), 129.7, 130.9, 135.9, 167.0, 169.3 ppm (Figure A3.3).

7.3.4 Synthesis of poly(ethylene glycol)/poly(dimethylsiloxane) diblock copolymers

PDMS-MA (0.30 g, 0.429 mmol, 8 equiv.), P1-2 (0.279 g, 0.054 mmol, 1 equiv.) and MEAC (53.7 mg, 0.161 mmol, 3 equiv.) were dissolved in tert.-BuOH (1.85 mL) at 60 °C to afford a macromonomer concentration of 0.02 M. An aliquot (0.2 mL) was taken (t₀) to monitor macromonomer and MEAC conversion. Bpy (16.7 mg, 0.107 mmol, 2 equiv.) was then added to the mixture and the solution was then transferred to a Schlenk tube (oven-dried at 110 °C for 24 h). The mixture was then subjected to four freeze-pump-thaw cycles (thaw cycles conducted at 60 °C) and the Schlenk tube was then immersed again in liquid N₂. Once the solution was frozen, CuBr (15.4 mg, 0.107 mmol, 2 equiv.) was added and one more freeze-pump-thaw cycle was completed. The Schlenk tube was then equilibrated at room temperature for 10 min with stirring to ensure homogeneity and finally heated at 90 °C for 48 h. After cooling to room temperature an aliquot (0.2 mL) was taken (t₄₈) to determine the macromonomer and MEAC conversion. The reaction mixture was then diluted with DCM and passed through a plug of basic alumina to remove the copper catalyst. The filtrate was concentrated in vacuo (2 mbar) before drying.
in vacuo (0.1 mbar) at 45 °C for 16 h to yield product P2-B1 as an opaque tacky solid, 0.35 g (isolated yield: 65.4%). The polymer composition was varied by changing the macroinitiator, macromonomer and MEAC feed ratio (Table 3.2). 1H NMR (400 MHz, CDCl₃): 0.04 – 0.09 (m, Hₐ), 0.51 – 0.55 (m, H₆), 0.86 – 1.04 (m, H₄, H₅), 1.25 – 1.35 (m, H₁), 1.64 (br s, H₂), 1.78 (br s, H₃), 3.38 (s, H₅), 3.38 – 4.12 (m, H₆), 3.87 (br s, H₈), 7.44 (br s, H₉), 7.99 (br s, H₁₀), 8.43 (br s, Hₘ) ppm (Figure 3.3).

7.3.5 Self-assembly of poly(ethylene glycol)/poly(dimethylsiloxane) diblock copolymers

Chloroform and DMF for self-assembly studies were pre-filtered through 0.45 μm PTFE filters (Labquip Technologies). Copolymers were dissolved in chloroform (30 mg/mL) prior to dropwise addition of DMF to effect dissolution (0.167 mg/mL). DLS was then employed to measure the hydrodynamic diameters of the self-assemblies.

7.3.6 Photocross-linking of poly(ethylene glycol)/poly(dimethylsiloxane) diblock copolymers

Following self-assembly, brush diblock copolymer samples were photocross-linked by exposure to UV radiation with a wavelength of 365 nm over a period of 4 h. UV-Vis spectrophotometer was utilized to monitor the progression of the [4+4] photodimerization process. Samples were concentrated in vacuo (0.1 mbar) to remove DMF and then diluted with chloroform (0.167 mg/mL) for post cross-linking DLS analysis.

7.3.7 Photocleavage of poly(ethylene glycol)/poly(dimethylsiloxane) diblock copolymers

Samples were exposed to UV radiation with a wavelength of 254 nm over a period of 20 h. UV-Vis spectrophotometer was again utilized to monitor the progress of photocleavage process.
7.3.8 Imaging of uncross-linked and photocross-linked poly(ethylene glycol)/poly(dimethylsiloxane) diblock copolymers

TEM samples were prepared by drop-coating the self-assembled nanoparticles in DMF (0.167 mg/ml) and their photocross-linked derivatives in chloroform (0.167 mg/mL) onto copper grids (10 µL). The samples were then blotted and negatively stained by uranyl acetate aqueous solution (2 wt.%) before imaging was conducted.

7.4 Experiments for chapter 4

7.4.1 Materials

2-Bromoisoobutyryl bromide (BIBB, 98%), anhydrous tert-butanol (tert.-BuOH, 99.5%), copper(I) bromide (CuBr, 98%), N,N,N′,N″,N‴-pentamethyldiethylenetriamine (PMDETA, 99%) and pentaerythritol (99%) were purchased from Aldrich and used as received. Poly(ethylene glycol) methyl ether methacrylate ($M_n = 300$ Da) (MeOPEG-MA, Sigma Aldrich) and monomethacryloxypropyl terminated poly(dimethylsiloxane) ($M_w = 600-800$ Da) (PDMS-MA, 95%, Gelest) were stirred with basic alumina (99%, Scharlau) for 16 h and filtered prior to use. Dichloromethane (DCM, AR), ethanol (EtOH, AR) and sodium hydrogen carbonate ($\text{NaHCO}_3$, AR) were purchased from Chem-Supply and used as received. Tetrahydrofuran (THF, HPLC grade, RCI Labscan) was distilled from sodium benzophenone ketyl under argon. Triethylamine (TEA, 99%, Ajax) was distilled from calcium hydride (95%, Aldrich) under argon. Deuterated chloroform ($\text{CDCl}_3$, 99.9%) was purchased from Cambridge Isotope Laboratories, hydrogen chloride (HCl, 37%, Scharlau) and anhydrous magnesium sulphate ($\text{MgSO}_4$, 98%, Scharlau) were each used as received.

7.4.2 Synthesis of tetra-functional initiator

To an aliquot of pentaerythritol (2.00 g, 14.7 mmol, 1 equiv.), TEA (12.3 mL, 88.2 mmol, 6 equiv.) and anhydrous THF (100 mL) were added under argon. The solution was cooled to -18 °C and BIBB (10.9 mL, 88.2 mmol, 6 equiv.) dissolved in anhydrous THF (20 mL) was added dropwise over a period of 1 h. The resulting
mixture was stirred at room temperature for 12 h and then diluted with DCM (400 mL) and stirred for 30 min. The organic solution was washed with 2 M HCl (2 × 250 mL), saturated NaHCO₃ (2 × 250 mL), dried (MgSO₄), filtered and concentrated in vacuo to afford a yellow solid. The solid was recrystallised from hot EtOH, cooled to 0 °C and filtered to afford tetra-functional ATRP initiator, I, as a colourless crystalline solid, 8.82 g (isolated yield: 79%).

$^1$H NMR (CDCl₃, 400 MHz): δ_H 1.94 (s, 24H, 8C₃H₃, H_a), 4.33 (s, 8H, 4C₂H₂, H_b) ppm (Figure 4.1). $^{13}$C NMR (CDCl₃, 100 MHz): δ_H 30.6 (8C₃H₃), 43.6 (C(CH₂)₄), 55.2 (4CBr), 62.9 (4C₂H₂O), 170.9 (4C=O) ppm (Figure A4.1).

7.4.3 Synthesis of poly(ethylene glycol) grafted star polymers

PMDETA (21.8 µL, 0.104 mmol, 2 equiv.) and MeOPEG-MA (1.50 g, 5.00 mmol, 24 equiv.) were dissolved in tert.-BuOH in a Schlenk tube (oven-dried at 110 °C for 24 h) to afford a macromonomer concentration of 0.60 M. An aliquot (0.2 mL) was taken (t₀) to monitor macromonomer conversion. The mixture was bubbled with argon for 30 min and then subjected to four freeze-pump-thaw cycles and the Schlenk tube was then immersed again in liquid N₂. Once the solution was frozen, I (0.038 g, 0.052 mmol, 1 equiv.) and CuBr (14.9 mg, 0.104 mmol, 2 equiv.) were added and another two freeze-pump-thaw cycles were performed. The Schlenk tube was allowed to equilibrate at room temperature for 5 min with stirring to ensure homogeneity and then heated at 60 °C for 48 h. After cooling to room temperature an aliquot (0.2 mL) was taken (t₄₈) to determine the macromonomer conversion. The reaction mixture was then diluted with THF (10 mL) and passed through a plug of basic alumina to remove the copper catalyst. The filtrate was concentrated in vacuo (2 mbar) and then dried in vacuo (0.1 mbar) at 60 °C for 16 h to yield P0₂₄/₀ as an opaque tacky solid, 1.26 g (isolated yield: 82%). $^1$H NMR (CDCl₃, 400 MHz): δ_H 0.85 – 1.01 (m, CH₃, H_b), 1.79 – 1.92 (m, CH₂, H_a), 3.37 (s, CH₃O, Hₐ), 3.54 – 3.66 (m, CH₂CH₂O, H_d), 4.08 (br s, CH₂O, H_c) ppm (Figure 4.3).

7.4.4 Synthesis of poly(dimethylsiloxy) grafted star polymers

PMDETA (22.4 µL, 0.107 mmol, 2 equiv.) and PDMS-MA (10 and 30 equiv. refer to Table 4.1) were dissolved in tert.-BuOH in a Schlenk tube (oven-dried at 110 °C
for 24 h) to afford a macromonomer concentration of 0.25 M. An aliquot (0.2 mL) was taken ($t_0$) to monitor macromonomer conversion. The mixture was bubbled with argon for 30 min and then subjected to four freeze-pump-thaw cycles, and the Schlenk tube was then immersed again in liquid N$_2$. Once the solution was frozen, I (39.2 mg, 0.054 mmol, 1 equiv.) and CuBr (15.4 mg, 0.011 mmol, 2 equiv.) were added and another two freeze-pump-thaw cycles were performed. The Schlenk tube was allowed to equilibrate at room temperature for 5 min with stirring to ensure homogeneity and then heated at 60 °C for 24 h. After cooling to room temperature an aliquot (0.2 mL) was taken ($t_{24}$) to determine the macromonomer conversion. The reaction mixture was then diluted with THF (10 mL) and passed through a plug of basic alumina to remove the copper catalyst. The filtrate was concentrated in vacuo (2 mbar) and then dried in vacuo (0.1 mbar) at 60 °C for 16 h to yield $P_{10/9}$ and $P_{10/27}$ as white liquids (isolated yield of $P_{10/9}$: 90%; isolated yield of $P_{10/27}$: 88%). The polymer composition was varied by changing the macromonomer:initiator ratio (Table 4.1). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta_H$ 0.04 – 0.09 (m, SiCH$_3$, $H_I$), 0.51 – 0.55 (m, SiCH$_2$, $H_e$), 0.86 – 1.04 (m, CH$_3$, $H_b$, $H_h$), 1.30 – 1.32 (m, CH$_2$, $H_g$), 1.57 – 1.62 (m, CH$_2$, $H_d$), 1.80 (br s, CH$_2$C, $H_a$), 1.91 (br s, CH$_2$C, $H_a$), 3.87 (br s, CH$_2$O, $H_e$) ppm (Figure 4.5a).

7.4.5 Synthesis of poly(ethylene glycol)-b-poly(dimethylsiloxane) grafted star polymers

PDMS grafted star polymer $P_{10/9}$ (1.00 g, 3.33 mmol, 1 equiv.), PMDETA (14.5 µL, 0.069 mmol, 2 equiv.) and MeOPEG-MA (24 and 72 equiv. refer to Table 4.1) were dissolved in tert.-BuOH in a Schlenk tube (oven-dried at 110 °C for 24 h) to afford a macromonomer concentration of 0.60 M. An aliquot (0.2 mL) was taken ($t_0$) to monitor macromonomer conversion. The mixture was bubbled with argon for 30 min and then subjected to four freeze-pump-thaw cycles and the Schlenk tube was then immersed again in liquid N$_2$. Once the solution was frozen, CuBr (10.0 mg, 0.069 mmol, 2 equiv.) was added and another two freeze-pump-thaw cycles were performed. The Schlenk tube was allowed to equilibrate at room temperature for 5 min with stirring to ensure homogeneity and then heated at 60 °C for 48 h. After cooling to room temperature an aliquot (0.2 mL) was taken ($t_{48}$) to determine the macromonomer conversion. The reaction mixture was then diluted with THF (10...
mL) and passed through a plug of basic alumina to remove the copper catalyst. The filtrate was concentrated in vacuo (2 mbar) and then dried in vacuo (0.1 mbar) at 60 °C for 16 h to yield P24/10, P272/10 and P224/30 as white liquids (isolated yield of P224/10: 87%; isolated yield of P272/10: 89%; isolated yield of P224/30: 88%). The polymer composition was varied by changing the macromonomer:initiator ratio (Table 4.1). 1H NMR (CDCl3, 400 MHz): δH 0.04 – 0.09 (m, SiCH3, Hf), 0.51 – 0.55 (m, SiCH2, He), 0.86 – 1.03 (m, CH3, Hb, Hh, Hj), 1.30 – 1.32 (m, CH2, Hg), 1.62 – 1.68 (m, CH2, Hd), 1.79 (br s, CH2C, Hh), 1.88 (br s, CH2C, Hd), 3.38 (s, CH3O, Hm), 3.55 – 3.66 (m, CH2CH2O, Hf), 3.86 (br s, CH2O, Hc), 4.08 (br s, CH2O, Hk) ppm (Figure 4.5b).

7.5 Experiments for chapter 5

7.5.1 Materials

Trimesoyl chloride (TMC, 98%) and hexane (AR) were purchased from Aldrich and used as received. Aminopropyl terminated poly(dimethylsiloxane) (Mw = 5000-7000 Da) (NH2-PDMS-NH2, 95%) was purchased from Gelest and used as received. Propan-2-ol (IPA, AR) and n-butyl alcohol (n-BuOH, AR) were purchased from Chem-Supply and used as received. Pebax® 2533 was obtained from Arkema and polyacrylonitrile (PAN) microporous support was purchased from SolSep BV, both were used as received.

7.5.2 Membrane preparation

A cross-linked PDMS gutter layer was spin-coated onto a microporous PAN substrate as shown in Scheme 5.1. To prepare the PDMS gutter layer, TMC (0.020 g, 0.077 mmol) was dissolved in hexane (1.05 mL) and NH2-PDMS-NH2 (0.6 g, 0.12 mmol, 1 equiv.) was dissolved in hexane (30 mL). The two solutions were then mixed for 1 min and 1 mL of the solution was spin coated (1000 rpm, 10 s) onto each microporous PAN substrate. The coated PAN substrates were dried in vacuo (0.1 mbar) at 25 °C for 16 h and tested for their gas transport properties to ensure the integrity of each substrate prior to addition of the active layer. Coated PAN
substrates with similar gas transport properties were chosen to eliminate batch to batch variations.

To prepare the active layer, Pebax® 2533 was dissolved in a mixture of IPA/n-BuOH (3:1 vol.%) at 80 °C for 2 h to prepare a stock polymer solution (2 wt.% of Pebax® 2533). After cooling to room temperature, different amounts of \( P_0 \) and \( P_2 \) were added (10 to 40 wt.% relative to the amount of Pebax® 2533) and stirred at 50 °C for 1 h. IPA/n-BuOH is a binary solvent which dissolves Pebax® 2533, \( P_0 \) and \( P_2 \), and does not damage the microporous substrate. 1.5 mL of Pebax® 2533/\( P_0 \) and Pebax® 2533/\( P_2 \) mixture was then spin coated (1200 rpm, 20 s) onto the substrates that were pre-coated with PDMS gutter layers. The TFC membranes were then dried \textit{in vacuo} (0.1 mbar) at 25 °C for 16 h and tested for their gas transport properties. All membranes were macroscopically homogeneous and mechanically robust.

\textit{7.5.3 Gas permeation experiments}

A constant pressure variable volume (CPVV) apparatus designed and built in-house (\textit{Figure 7.1}) was used to measure the flow rate of individual gases (CO\(_2\) and N\(_2\)). The permeate flowrate was measured with a digital flowmeter (Agilent Technologies). In all cases, three samples of the TFC membranes were tested at 35 °C and an upstream pressure of 3.4 gauge bar. The detailed calculation of permeance, permeability and selectivity of the active layer is shown in Appendix 5.
7.5.4 Imaging of thin film composite membranes cross-section

The thickness of the TFC membranes was analysed by SEM using a FEI Quanta 200 ESEM FEG. Samples were pre-coated with gold using a Dynavac Mini Sputter Coater prior to imaging. The thickness of the PDMS gutter layer and the active layer were determined by taking an average value at eight different measurement points.
7.6 References


Appendices

Chapter 2 Appendix

Figure A2.1 $^1$H NMR spectrum (CDCl$_3$) of $\alpha,\omega$-diamino poly(6FDA-co-TMPD) P1. The asterisk denotes CDCl$_3$. An inset of 10 times magnification is included to show the absence of resonances corresponding to carboxylic protons (typically in the $\delta_H$ 10.5 - 13 ppm region).
Figure A2.2 $^{13}$C NMR spectrum (CDCl$_3$) of $\alpha,\omega$-diamino poly(6FDA-co-TMPD) P1. The asterisk denotes CDCl$_3$.

Figure A2.3 $^1$H NMR spectrum (CDCl$_3$) of $\alpha,\omega$-dibromo poly(6FDA-co-TMPD) P2. The asterisk denotes CDCl$_3$. An inset of 10 times magnification is included to show the absence of resonances corresponding to carboxylic protons (typically in the $\delta_H$ 10.5 - 13 ppm region).
Figure A2.4 $^{13}$C NMR spectrum (CDCl$_3$) of $\alpha,\omega$-dibromo poly(6FDA-co-TMPD) P2. The asterisk denotes CDCl$_3$. 
Figure A2.5 MALDI ToF mass spectra of $\alpha,\omega$-amino poly(6FDA-co-TMPD) recorded in linear/positive using (a) DCTB/KTFA and (b) DCTB/NaTFA. The numbers on the mass spectra denote the number of repeat units ($n$, 573 m/z) and the mass values.
Figure A2.6 MALDI ToF mass spectra of functionalized \(\alpha,\omega\)-amino poly(6FDA-co-TMPD) recorded in linear/positive using (a) DCTB/KTFA and (b) DCTB/NaTFA. The numbers on the mass spectra denote the number of repeat units (n, 573 m/z) and the mass values.
Chapter 3 Appendix

Figure A3.1 $^{13}$C NMR spectra ($d_6$-DMSO) of bromo-functionalized 5 kDa MeOPEG macroinitiator $\text{P}15$.

Figure A3.2 $^1$H NMR spectra (CDCl$_3$) of 2-(methacryloyloxy)ethyl anthracene-9-carboxylate.
Figure A3.3 $^{13}$C NMR spectra (CDCl$_3$) of 2-(methacryloyloxy)ethyl anthracene-9-carboxylate.
**Figure A3.4** $^1$H NMR spectra ($d_6$-DMSO) of (a) bromo-functionalized 1 kDa MeOPEG macroinitiator $\text{P1}_1$, and (b) bromo-functionalized 10 kDa MeOPEG macroinitiator $\text{P1}_{10}$.
Figure A3.5 MALDI ToF mass spectra of (a) 1 kDa MeOPEG and (b) its bromo-functionalized derivative, P11, recorded in linear/positive mode using DCTB and NaTFA as the matrix and cationization agent, respectively. The numbers on the mass spectra denote the number of EO repeat units \( n \), 44 \( m/z \).
**Figure A3.6** MALDI ToF mass spectra of (a) 10 kDa MeOPEG and (b) its bromo-functionalized derivative, $\text{P1}_{10}$, recorded in linear/positive mode using DCTB and NaTFA as the matrix and cationization agent, respectively. The numbers on the mass spectra denote the number of EO repeat units ($n$, 44 m/z).
Figure A3.7 MALDI ToF mass spectra of PDMS-MA macromonomer recorded in linear/positive mode using no matrix and KTFA as the cationization agent. Series a refers to the PDMS-MA while series b refers to the unfunctionalized PDMS. Each peak in both series is separated by 74 m/z which are indicative of PDMS repeat unit.
Figure A3.8 Ultraviolet-visible spectra of P2’s self-assemblies upon exposure to UV radiation (365 nm) for 4 hours.
Figure A3.9 Ultraviolet-visible spectra of various photocross-linked nanoparticles upon exposure to UV radiation (254 nm) for 20 hours.
Table A3.1 Extent of photocleavage of the anthracene moieties over 20 hours.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Extent of photocleavage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P$_{21/5}$</td>
<td>8</td>
</tr>
<tr>
<td>P$_{21/8}$</td>
<td>7</td>
</tr>
<tr>
<td>P$_{25/4}$</td>
<td>15</td>
</tr>
<tr>
<td>P$_{25/7}$</td>
<td>19</td>
</tr>
<tr>
<td>P$_{25/9}$</td>
<td>16</td>
</tr>
<tr>
<td>P$_{210/9}$</td>
<td>17</td>
</tr>
<tr>
<td>P$_{210/12}$</td>
<td>19</td>
</tr>
<tr>
<td>P$_{210/15}$</td>
<td>15</td>
</tr>
</tbody>
</table>
Chapter 4 Appendix

Figure A4.1 $^{13}$C NMR spectra of tetra-functional initiator I.
Chapter 5 Appendix

Table A5.1 PDMS and PEG weight fraction of the synthesized grafted star polymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>wt.% PDMS</th>
<th>wt.% PEG</th>
</tr>
</thead>
<tbody>
<tr>
<td>P0\textsubscript{24/0}</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>P2\textsubscript{72/10}</td>
<td>14</td>
<td>86</td>
</tr>
<tr>
<td>P2\textsubscript{24/10}</td>
<td>39</td>
<td>61</td>
</tr>
<tr>
<td>P2\textsubscript{24/30}</td>
<td>67</td>
<td>33</td>
</tr>
</tbody>
</table>

Sample calculation

The following sub-section provides a sample calculation to determine the gas transport properties of the fabricated TFC membranes.

The measured data for 30 wt.% blends of Pebax\textsuperscript{®} 2533/P2\textsubscript{10/72} at 340 kPa of upstream pressure is as follows:

Table A5.2 \(\text{CO}_2\) and \(\text{N}_2\) flux of PDMS-coated support and fabricated TFC membrane.

<table>
<thead>
<tr>
<th>Flux (mL/min)</th>
<th>PDMS-coated support(^#)</th>
<th>TFC(^\wedge)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{N}_2)</td>
<td>39.6</td>
<td>2.0</td>
</tr>
<tr>
<td>(\text{CO}_2)</td>
<td>358</td>
<td>42.8</td>
</tr>
</tbody>
</table>

\(^\#\) Flux of PDMS-coated support was measured on a large membrane area of 13.85 cm\textsuperscript{2}.

\(^\wedge\) Flux of TFC blend membrane was measured on a small membrane area of 5.722 cm\textsuperscript{2}.

Total resistance through PDMS-coated support

\[
R_{N_2,PDMS\text{-coated support}} = \frac{\Delta P \cdot A}{J_{N_2}} = \frac{340 \times 13.85}{39.6} = 118.9 \text{ kPa} \cdot \text{cm}^2 \cdot \text{min/mL}
\]
\[ R_{\text{CO}_2,\text{PDMS-coated support}} = \frac{\Delta P \cdot A}{J_{\text{CO}_2}} = \frac{340 \times 13.85}{358} = 13.2 \text{ kPa} \cdot \text{cm}^2 \cdot \text{min/mL} \]

**Total resistance through TFC blend membrane**

\[ R_{\text{N}_2,\text{TFC}} = \frac{\Delta P \cdot A}{J_{\text{N}_2}} = \frac{340 \times 5.722}{2.0} = 972.7 \text{ kPa} \cdot \text{cm}^2 \cdot \text{min/mL} \]

\[ R_{\text{CO}_2,\text{TFC}} = \frac{\Delta P \cdot A}{J_{\text{CO}_2}} = \frac{340 \times 5.722}{42.8} = 45.5 \text{ kPa} \cdot \text{cm}^2 \cdot \text{min/mL} \]

**Resistance through the active layer**

\[ R_{\text{N}_2,\text{AL}} = R_{\text{N}_2,\text{TFC}} - R_{\text{N}_2,\text{PDMS-coated support}} = 972.7 - 118.9 = 853.8 \text{ kPa} \cdot \text{cm}^2 \cdot \text{min/mL} \]

\[ R_{\text{CO}_2,\text{AL}} = R_{\text{CO}_2,\text{TFC}} - R_{\text{CO}_2,\text{PDMS-coated support}} = 45.5 - 13.2 = 32.3 \text{ kPa} \cdot \text{cm}^2 \cdot \text{min/mL} \]

**Flux through the active layer**

\[ J_{\text{N}_2,\text{AL}} = \frac{\Delta P \cdot A}{R_{\text{N}_2,\text{SL}}} = \frac{340 \times 5.722}{853.8} = 2.27 \text{ mL/min} \]

\[ J_{\text{CO}_2,\text{AL}} = \frac{\Delta P \cdot A}{R_{\text{CO}_2,\text{SL}}} = \frac{340 \times 5.722}{32.3} = 60.2 \text{ mL/min} \]

**Permeance of the active layer**

\[
\text{Permeance}_{\text{N}_2,\text{AL}} = \frac{2.27 \text{ cm}^3}{60 \text{ s}} \cdot \frac{101.325 \text{ kPa}}{340 \text{ kPa} \times 76 \text{ cm Hg}} \cdot \frac{1}{5.722 \text{ cm}^2} \cdot \frac{10^6 \text{GPU} \cdot \text{cm}^2 \cdot \text{cm Hg} \cdot \text{s}}{1 \text{ cm}^3} = 26 \text{ GPU}
\]
The calculation of permeance, in GPU, was not corrected to STP condition (0 °C, 100 kPa) and all the permeance data shown in this thesis is out by a factor of 0.898, i.e.

\[
(\frac{100.325}{100}) \times \left( \frac{273}{273 + 35} \right) = 0.898
\]

**CO₂/N₂ selective of the active layer**

\[
\alpha_{CO₂/N₂} = \frac{\text{Permeance}_{CO₂, AL}}{\text{Permeance}_{N₂, AL}} = \frac{687}{26} = 26.4
\]

**Permeability of the active layer with a thickness of 580 nm**

\[
P_{N₂, AL} = 26 \text{ GPU} \times \frac{5.8 \times 10^{-5} \text{cm}}{10^{-4} \text{ GPU} \cdot \text{cm}} = 15 \text{ Barrer}
\]

\[
P_{CO₂, AL} = 687 \text{ GPU} \times \frac{5.8 \times 10^{-5} \text{cm}}{10^{-4} \text{ GPU} \cdot \text{cm}} = 398 \text{ Barrer}
\]
Minerva Access is the Institutional Repository of The University of Melbourne

Author/s:
Halim, Andri

Title:
Soft polymeric nanoparticles as additives for CO2 separation membranes

Date:
2014

Citation:

Persistent Link:
http://hdl.handle.net/11343/38663

File Description:
Soft polymeric nanoparticles as additives for CO2 separation membranes

Terms and Conditions:
Terms and Conditions: Copyright in works deposited in Minerva Access is retained by the copyright owner. The work may not be altered without permission from the copyright owner. Readers may only download, print and save electronic copies of whole works for their own personal non-commercial use. Any use that exceeds these limits requires permission from the copyright owner. Attribution is essential when quoting or paraphrasing from these works.