Poly(Pentafluorostyrene)-b-Poly(Methacrylic acid) Amphiphilic Block Copolymers via Nitroxide Mediated Polymerization

By

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Thesis submitted to the Faculty of Graduate and Postdoctoral Studies in partial fulfilment of the requirements for the M.A.Sc. degree in Chemical Engineering.

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October 2016

ABSTRACT:

Fluoropolymers are a versatile and attractive group of compounds having an interesting mix of properties that make them highly useful for various applications. Because of strong bonding between the carbon and fluorine atom, they exhibit unique physical and chemical properties such as high thermal stability, increased chemical resistance, low refractive index, enhanced inertness towards many solvents and hydro-compounds. These characteristics have led them to be widely used in aerospace, aeronautics, optics, microelectronics, paints and coatings, and engineering structures and as biomaterials.

Amphiphilic copolymers possess unique solution and solid-state properties due to their well-defined molecular architecture. These properties arise as the result of covalently combining two thermodynamically different polymer blocks that phase separate on the nanoscale. Amphiphilic copolymers based on a fluoro-monomer will combine the favourable physiochemical properties of the desired fluorine segment in combination with complementary hydrophilic segments. Such fluorinated amphiphilic copolymers are potentially useful for drug delivery vehicles and membrane applications.

This project is aimed at making fluorinated amphiphilic block copolymers of hydrophobic 2, 3, 4, 5, 6 –pentafluorostyrene (PFS) and hydrophilic methacrylic acid (MAA). A controlled radical polymerization mechanism, nitroxide mediated polymerization (NMP) using NHS-BlocBuilder as the initiator was employed. The advantage of using NMP is that it facilitates the synthesis of copolymers with well-controlled narrow molecular weight distribution. However, methacrylate homopolymerization by NMP is challenging due to the high dissociation equilibrium constant therefore, the use of PFS as a controlling comonomer was explored. We established that to obtain a controlled copolymerization, a minimum of 70 mol% PFS was required, which is significantly greater than other copolymerization systems

such as using as little as 4.5-8 mol% styrene to control the copolymerization of MAA. We surmise that this lack of control is due to the unfavourable reactivity ratios (Appendix I) which favour the addition of MAA rather than PFS ($r_{PFS} = 0.012$, $r_{MAA} = 8.12$). However, these unique reactivity ratios suggest that a semi-batch approach can be utilized to synthesize almost pure block copolymers in one pot. Therefore, poly(PFS)–*b*-(PFS-*ran*-MAA) block copolymers were synthesized and characterized by a semi batch addition of MAA. While successful, the concentration of irreversibly terminated chains was evident and greater care in reducing these unwanted reactions needs to be addressed.

RÉSUMÉ:

Les fluoro=polymères sont un groupe polyvalent et attractif de composés ayant un mélange intéressant de propriétés qui les rendent très utiles pour diverses applications. À la suite d'une forte liaison entre le carbone et un atome de fluor, ils présentent des propriétés physiques et chimiques uniques telles que la stabilité thermique élevée, une résistance accrue aux produits chimiques, à faible indice de réfraction, une inertie accrue vers de nombreux solvants et hydro-composés. Ces caractéristiques ont conduit leur être largement utilisés dans l'aérospatiale, l'aéronautique, l'optique, la microélectronique, les peintures et revêtements, et des structures d'ingénierie et de biomatériaux.

Les copolymères amphiphiles possèdent une solution unique et propriétés de l'état solide en raison de leur architecture moléculaire unique et bien définie. Ces propriétés se présentent comme résultat de la combinaison covalente de deux séquences de polymère différentes qui thermodynamiquement phase distincte à l'échelle nanométrique. Les copolymères amphiphiles à base d'un monomère fluoré va combiner les propriétés physico-chimiques favorables du segment de fluor désiré en combinaison avec des segments complémentaires hydrophiles. Ces copolymères amphiphiles fluorés sont potentiellement utiles pour des véhicules de délivrance de médicaments et les applications de la membrane.

Ce projet vise à rendre les copolymères séquencés amphiphiles fluorés de hydrophobe 2, 3, 4, 5, 6 -pentafluorostyrene (PFS) et de l'acide méthacrylique hydrophile (MAA). Le mécanisme de polymérisation radicalaire contrôlée a été adopté nitroxyde polymérisation à médiation (NMP) en utilisant NHS BlocBuilder comme initiateur. L'avantage d'utiliser de la NMP est qu'elle facilite la synthèse de copolymères à distribution contrôlée et de masse moléculaire étroite. Cependant, l'homopolymérisation du méthacrylate par NMP est difficile en raison de la forte dissociation constante d'équilibre donc l'utilisation de PFS comme comonomère de

contrôle a été explorée. Nous avons établi que pour obtenir une copolymérisation contrôlée d'au moins 70% en moles de survie sans progression était nécessaire, ce qui est nettement plus grande que les autres systèmes de copolymérisation par exemple en utilisant aussi peu que 4.5 à 8% en moles de styrène pour contrôler la copolymérisation de MAA. Nous supposons que ce manque de contrôle est due aux rapports de réactivité défavorables qui favorisent l'ajout de MAA plutôt que PFS ($r_{PFS} = 0.012$, $r_{MAA} = 8.12$). Cependant, ce rapport unique suggère que la réactivité d'une approche semi-discontinue peut être utilisée pour synthétiser des copolymères à blocs presque purs dans une casserole. Par conséquent, le poly (PFS)-*b*-(PFS-*ran*-MAA), les copolymères à blocs ont été synthétisés et caractérisés par une addition semi-discontinue de MAA. Bien que la réussite, la concentration des chaînes irréversiblement terminés était évidente et le plus grand soin dans la réduction de ces réactions indésirables doit être abordée.

STATEMENT OF CONTRIBUTION OF COLLABORATORS

I hereby declare that I am the sole author of this thesis. I have performed all the experiments and the data analysis. I have written all the chapters contained in this thesis.

Dr. Benoit Lessard supervised this thesis project and provided continual guidance and support. He also made editorial comments and corrections to the written work presented.

SIGNATURE: **DATE:**

ACKNOWLEDGEMENT:

I would like to express my deepest gratitude to my supervisor Dr Benoit Lessard for his extensive support and guidance, invaluable suggestions and profound discussions throughout the period of this thesis. I would also like to thank my colleagues in the Lessard Research Group for their encouragement and enthusiasm doing scientific research.

I would like to thank Louis. G. Tremblay, Franco Ziroldo and Gerard Nina for their technical assistance, Dr. Xudong Cao for allowing me to use the DSC apparatus and Dr. Milan Maric, Department of Chemical Engineering, McGill University, Montreal for performing the GPC characterizations.

I would like to thank the Natural Sciences and Engineering Research Council of Canada (NSERC) for the Discovery Grant Scholarship Funding provided toward my research work.

Finally, I would like to convey my sincere gratitude to all my friends and family for the unwavering moral support provided throughout my Master's degree.

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NOMENCLATURE AND ACRONYMS:

$<K>$	Average activation-deactivation equilibrium constant (mol.L^{-1})
$<k_p>$	Average propagation rate constant (L. mol^{-1}.s^{-1})
ATRP	Atom transfer radical polymerization
BLOCBUILDER-MA	(N-(2-methylpropyl)-N-(1-diethylphosphono-2,2-dimethylpropyl)-O-(2-carboxylprop-2-yl)
CRP	Controlled radical polymerization
DSC	Differential scanning calorimetry
$f_{PFS,0}$	Initial mole fraction of PFS in the feed based on total monomers (excluding solvent).
F_{PFS}	Final mole fraction of PFS in the product determined from FT-IR spectroscopy.
$f_{MAA,0}$	Initial mole fraction of MAA in the feed based on total monomers (excluding solvent).
F_{MAA}	Final mole fraction of MAA in the product determined from FT-IR spectroscopy.
FT-IR	Fourier transform infrared spectroscopy
GPC	Gel permeation chromatography
K	Activation-deactivation equilibrium constant (mol.L^{-1})

k_P	Propagation rate constant (L. mol^{-1}.s^{-1})
MAA	Methacrylic acid
MMA	Methyl methacrylate
M_n	Number average molecular weight (kg.mol^{-1})
M_w	Weight average molecular weight (kg.mol^{-1})
M_w/M_n	Polydispersity index
NHS-BLOCBUILDER	N-hydroxysuccinimide BlocBuilder
NMP	Nitroxide mediated polymerization
PFS	2,3,4,5,6-pentafluorostyrene
RAFT	Reversible addition fragmentation chain transfer polymerization
RDRP	Reversible deactivation radical polymerization
r_{MAA}	Reactivity ratio of MAA
r_{MMA}	Reactivity ratio of MMA
r_{PFS}	Reactivity ratio of PFS
r_S	Reactivity ratio of S
r_{VBK}	Reactivity ratio of VBK
S	Styrene

SG1	tert-butyl (1-(diethoxyphosphoryl)-2,2-dimethylpropyl) amino) nitroxide
TEMPO	2, 2, 6, 6-tetramethylpiperidine 1-oxyl
T_g	Glass transition temperature (°C)
TIPNO	2,2,5-trimethyl-4-phenyl-3-azahexane-*N*-oxyl
VBK	9-(4-vinylbenzenyl)-9H-carbazole
X	Monomer conversion determined by gravimetry.
$X_{PFS,inject}$	Conversion of PFS at the point of injection of MAA solution

Chapter 1

Introduction

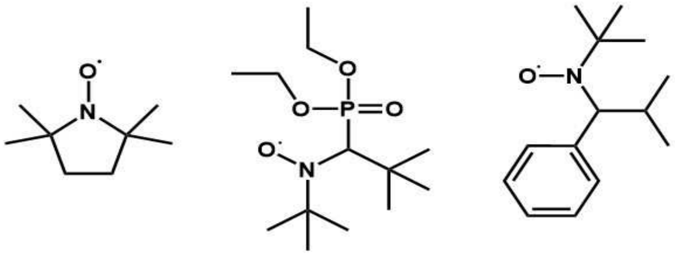
Block copolymers are polymers which contain more than one segment of different monomer units. Essentially they are two or more different homopolymers that are covalently bound. Many interesting applications are possible as each block imparts its own physiochemical property to the final material. Amphiphilic block copolymers result when a hydrophobic and a hydrophilic segment are combined. They have unique solution properties as a result of immiscibility between the distinct blocks and varying thermodynamic effects that are present at a molecular level.[1] Depending on the block composition, molecular weight of the respective block copolymers and the nature of the monomers themselves various molecular architectures like spherical, gyroid and lamellar can be obtained in both bulk and in aqueous solution.[2] These complex architectures play a significant role in defining the final material properties in solution and in bulk. Modern advancements in free radical polymerizations have enabled us to better engineer these architectures to meet specific needs.[1] Micelle formation of amphiphilic block copolymers in some selected solvents have been extensively studied and their capability to perform as a nano reservoir has resulted in the study of their use in drug delivery, gene therapy, phase transfer catalysis and in fabrication of nanostructured hybrids.[3–7]

Fluoropolymers are a versatile and attractive group of compounds which exhibit unique physical and chemical properties such as high thermal stability, increased chemical resistance, low refractive index, enhanced inertness to many solvents and hydrocompounds.[8–10] Fluorinated polymers containing 2,3,4,5,6-pentafluorostyrene (PFS) find application in several new materials in the optical electronic industry due to their excellent optical wave guiding properties[11] and low permittivity or low dielectric constant.[12] PFS is highly hydrophobic and can be copolymerized with hydrophilic monomers such as methacrylic acid (MAA) resulting in amphiphilic copolymers.

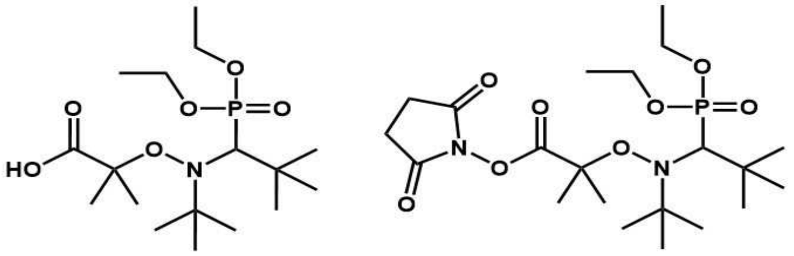
Polymer membranes fabricated using well-defined fluoropolymers has given rise to three dimensionally ordered porous structures which can potentially be used as substrates or reservoirs for biocatalyst[13], templates for preparing nanoparticles[14], and media or substrates for cell culture[15,16]. However to obtain these desired microstructures, block copolymers with well-defined molecular characteristics are necessary. Block copolymers are traditionally synthesized from living polymerization techniques such as anionic polymerization[17,18] cationic polymerization[19] and other coupling reactions.[20] Recent advancements in reversible deactivation radical polymerization (RDRP)[21], also known as controlled radical polymerization (CRP), has provided routes to synthesize well defined polymers having narrow molecular weight distribution, with the industrial ease of free radical chemistry.

Nitroxide mediated polymerization (NMP)[22,23], a type of RDRP, has long been an excellent method to obtain polymers with narrow molecular weight distribution. Other commonly studied RDRP techniques are reversible addition-fragmentation chain transfer polymerization (RAFT)[24] and atom transfer radical polymerization (ATRP).[25] Moreover, NMP is also advantageous as it is a relatively simple technique and produces pure products without the need to remove sulphur based chain transfer agents necessary in RAFT polymerization or metallic ligands used in atom transfer radical polymerization ATRP.[26,27] Therefore, with as little as a simple precipitation and filtration, NMP can be used to synthesize well defined polymers for use in sensitive biological and electronic applications.[26,27]

Traditionally, NMP was restricted to the controlled polymerization of styrene based monomers[22,28–34] especially with the use of TEMPO (2, 2, 6, 6-tetramethylpiperidine 1-oxyl, Figure 1.1) as the stable free radical mediator. Second generation mediator systems are now being used including SG1[35] (tert-butyl (1-(diethoxyphosphoryl)-2,2-dimethylpropyl) amino) nitroxide, Figure 1.1) and TIPNO[36] (2,2,5-trimethyl-4-phenyl-3-azahexane-*N*-oxyl, Figure 1.1) and have enabled the controlled homopolymerization of a wider selection of monomers including acrylates[37–40] and acrylamides.[41,42] In the majority of these examples, commercially available unimolecular initiators based on SG1, BlocBuilder-MA[43] (N-(2-methylpropyl)-N-(1-diethylphosphono-2,2-dimethylpropyl)-O-(2-carboxylprop-2-yl) hydroxyl amine, Figure 1.1), was employed, resulting in controlled polymerization (defined as a linear increase in number average molecular weight, M_n and monomer conversion, X) and low polymer dispersity.



(a) TEMPO (b) SG1 (c) TIPNO



(d) BlocBuilder - MA (e) NHS-BlocBuilder

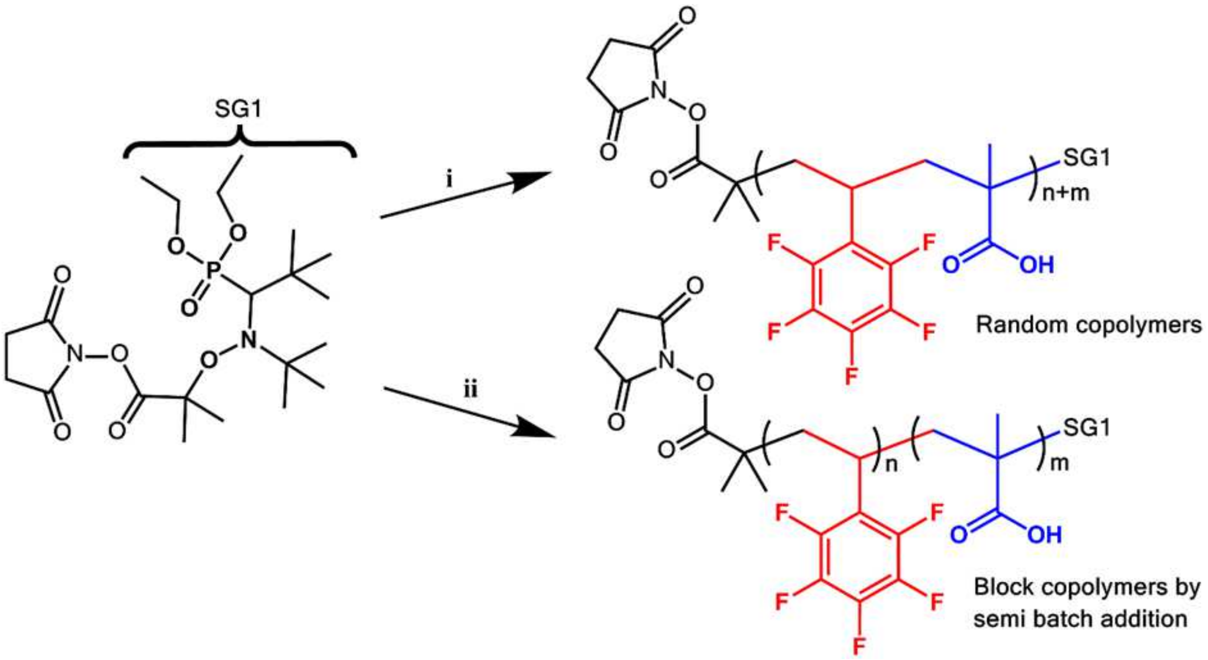
Figure 1.1: Structures of various mediators used in Nitroxide Mediated Polymerization (NMP)

The controlled homopolymerization of methacrylates continues to be a challenge for NMP as they have a very high activation-deactivation equilibrium constant (*K*) and produce a large amount of propagating radicals which favour self-termination reaction pathways instead of reversible termination by SG1.[44,45] Charleux et.al[44] suggested that with the help of a comonomer, such as styrene that has a lower *K*, the average value of the equilibrium constant <*K*> can be reduced resulting in a controlled polymerization and making controlled copolymerization of methyl methacrylate (MMA) and styrene possible.[44,46 47,48] Others have recently developed new alkoxyamine-based initiators[49,50] that have afforded moderate success in the homopolymerization of methacrylates, however eclipsed by the simplicity of employing an industrially available initiator and a small addition of controlling comonomer.

Recently, researchers have explored the use of a dual function controlling comonomer to impart secondary functionality to the final material while controlling the methacrylate rich copolymerization. For example, substituting the use of styrene for biocompatible acrylonitrile,[51] boronic acid functional monomers,[52] biodegradable 2-methylene-4-phenyl-1,3-dioxolane[53,54] and fluorescent 9-(4-vinylbenzenyl)-9H-carbazole (VBK)[55–57] have all been successfully employed as controlling comonomers for methacrylates by NMP. This controlling comonomer strategy has therefore been used to synthesize various methacrylic monomers including, methyl, ethyl, tert-butyl, benzyl, glycidyl, and several others.[48,58–63]

In this work, we aim to produce fluorinated amphiphilic block copolymers via NMP using methacrylic acid (MAA) as the monomer to impart the required hydrophilic component to the final polymers. MAA has been previously polymerized by NMP using styrene[60] and other styrene based monomers like VBK[64] and sodium 4-styrenesulfonate[65,66] as the controlling comonomers. We explore the possibility of using another styrene-based compound 2, 3, 4, 5, 6 - pentafluorostyrene (PFS) as the controlling comonomer. Therefore, PFS could potentially be used to incorporate hydrophobicity into the methacrylate polymer while controlling its copolymerization.

We report the synthesis of both random and block copolymers of PFS and MAA by nitroxide mediated polymerization (NMP). The initiator used was N-hydroxysuccinimide BlocBuilder (NHS-BB, Scheme 1) and xylene was used as the solvent. Though studies have been done previously with PFS as the controlling comonomer for methacrylate polymerization by NMP,[11,43] to the best of our knowledge, the synthesis of poly(PFS-ran-MAA) has not yet been reported. These polymerization reactions demonstrate the ability of PFS to be a controlling comonomer for MAA polymerization and the amphiphilic polymers obtained, Future studies could look into potential applications of these novel materials such as in drug delivery.



Scheme 1: Chemical reaction scheme used to obtain amphiphilic random and block copolymers by NMP where i) Monomers PFS (red) and MAA (blue) are added at 90°C and xylene as solvent and ii)Semi batch reaction with PFS (red) added initially and MAA (blue) is added at a later stage. Reaction was carried out at 90°C and xylene as solvent.

1.1. THESIS OUTLINE:

The thesis is organized into six different chapters. The first chapter is the introduction where the need and motivation of this work are discussed. The introduction also presents the objective of the thesis work.

The second chapter is the literature review. The chapter highlights the various challenges associated with methacrylate polymerization by NMP. The reasons for the difficulty in obtaining a controlled polymerization and the routes to overcome those difficulties are discussed in detail. This chapter also explores the various possible applications for amphiphilic fluoropolymers and goes into detail for two applications, namely, in drug delivery and in membranes.

The third chapter lists the various materials used in this project and where they were obtained. The characterization techniques used for both the random and block copolymers are explained with the equipment specifications.

The fourth chapter is the synthesis and characterization of poly (PFS-*ran*-MAA) copolymers by NMP section. Here, the experimental information regarding the concentrations of monomers used, the reaction conditions and various characterization techniques employed to identify the properties of the poly (PFS-*ran*-MAA) copolymers are written. The characterization results obtained from the final random copolymers are also discussed.

The fifth chapter of the thesis is synthesis and characterization of poly(PFS)-*b*-poly (PFS-*ran*-MAA) block copolymers by NMP. This chapter outlines the experimental information and the reaction conditions for the synthesis of amphiphilic block copolymers. Similar characterization methods as for the random copolymers were used for the block copolymers as well and the results and data obtained are presented in this section.

The final chapter summarizes all the results and data obtained throughout the thesis and proposes the possible future work that could be pursued to exploit the various positive outcomes from this project.

Chapter 2

Literature Review

2.1. PHYSIOCHEMICAL PROPERTIES OF FLUOROPOLYMERS:

Fluorinated homopolymers and copolymers have a unique combination of properties making them attractive for a variety of applications. High thermal stability, chemical resistance, weather and aging resistance, low refractive indices, flammability, very good inertness to acids, hydrocarbons and alkalis, low dielectric constant, low surface energy and moisture absorption (hydrophobic) are among some of these desired material properties. It is believed that these unique characteristics are due to the low polarizability, strong electronegativity and small van der Waals radius (1.32 Å) of the fluorine atom and to the strong C-F bond (the energy dissociation of which is 485 kJ mol^{-1}) which also enables the polymers with high fluorine content to resist oxidation and hydrolytic decomposition.[8,9,67–69]

Fluorinated polymers are therefore ideal for a variety of products such as paints and coatings that are UV and weather resistant (e.g. coatings for culturally significant old temple carvings and relics), transmission fluids used in the automotive industry, extreme temperature-resistant O-rings for space shuttle booster seals in the aerospace and aeronautical industry, as high performance separation membranes and in textile treatment among others.[8,9,67–70] In the majority of these applications, control over the molecular weight distribution and composition is either crucial or beneficial to the final material application.

Reversible-deactivation radical polymerization (RDRP),[21] has enabled the synthesis of polymeric materials with controlled molecular architectures. It can also be used to combine other monomers with fluorinated monomers resulting in copolymers with added functionality to the final material. Well-defined fluoropolymers obtained by these RDRP techniques can be used for making high performance elastomers, dispersants, lubricants and also for further development of novel advanced materials for optical,[71] electrical[72] and biomedical applications.[73,74]

2.2. CONTROLLED POLYMERIZATION VIA NMP:

"Livingness" in a polymerization reaction is defined as the formation of a final polymer with no irreversible termination and therefore can be used to re-initiate a new batch of monomer. In NMP, a pseudo-"living" polymerization is achieved by using stable free radicals in the form of nitroxides. The nitroxide radicals are used to reversibly terminate the polymer chain ends thus resulting in a low concentration of propagating chains and therefore a low probability for irreversible termination (due to combination and disproportionation). Above the activation temperature the nitroxide bond cleavage occurs thus providing means to perform monomer propagation between cycles of reversible termination.

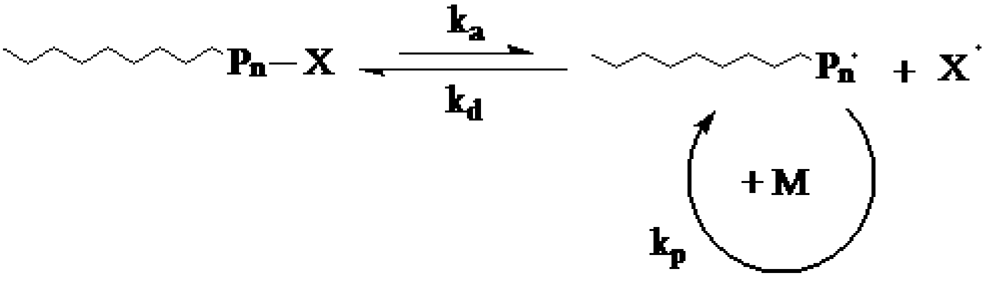


Figure 2.1: Basic schematic of an NMP reaction. Here k_a is the activation rate constant, k_d is the deactivation rate constant, k_p is the propagation rate constant, $X^{\cdot}$ is a stable free radical and M is the monomer.

This activation-deactivation cycle is referred to the persistent radical effect and is responsible for the controlled and pseudo-“living” behaviour of NMP.[75,76] Figure 2.1 represents the basic schematic of an NMP reaction. Here k_a, k_d and k_p represent the activation, deactivation and propagation rate constants respectively. M is the monomer repeat unit and X is the stable nitroxide free radical. The activation deactivation equilibrium constant K is given by,

$$K = \frac{k_a}{k_d}$$

The K defines how often the propagating chains are reversibly terminated by the stable nitroxide and how often they are actively propagating. Hence to have a controlled pseudo-“living” reaction the value of K needs to sufficiently low. As mentioned in the previous chapter, a controlled polymerization is identified by a linear increase in number average molecular weight (M_n) vs. conversion (X).

2.3. METHACRYLATES AND NITROXIDE MEDIATED POLYMERIZATION:

Nitroxide mediated polymerization (NMP), despite being a highly efficient RDRP method for producing polymers with narrow molecular weight distributions is limited to a few families of monomers. Historically, nitroxide mediators such as TEMPO (2, 2, 6, 6-tetramethylpiperidine 1-oxyl) were not only restricted to styrenic monomers but also needed high temperatures (>120°C) to activate the polymerization. Development of new nitroxide mediators such as SG1[35] became vital for two reasons: 1- to extend the bracket of monomers that can be homopolymerized in a controlled fashion and 2- to allow for reduced reaction temperatures. The reduced polymerization temperature facilitates the polymerization of acrylates, which are known to have an elevated, temperature dependent propagation rate constant (k_P, Figure 2.2). In addition to the drop in temperature (drop in k_P), the controlled homopolymerization of acrylates was successful with the addition of a slight excess of SG1, which favours the reversibly terminated state, reducing the probability for irreversible termination.[59,77] Finally, the reduction in temperature to as low as 75-90°C enabled the NMP to be carried out in aqueous dispersion media such as emulsion, microemulsion and miniemulsion under atmospheric pressure.[78,79,79]

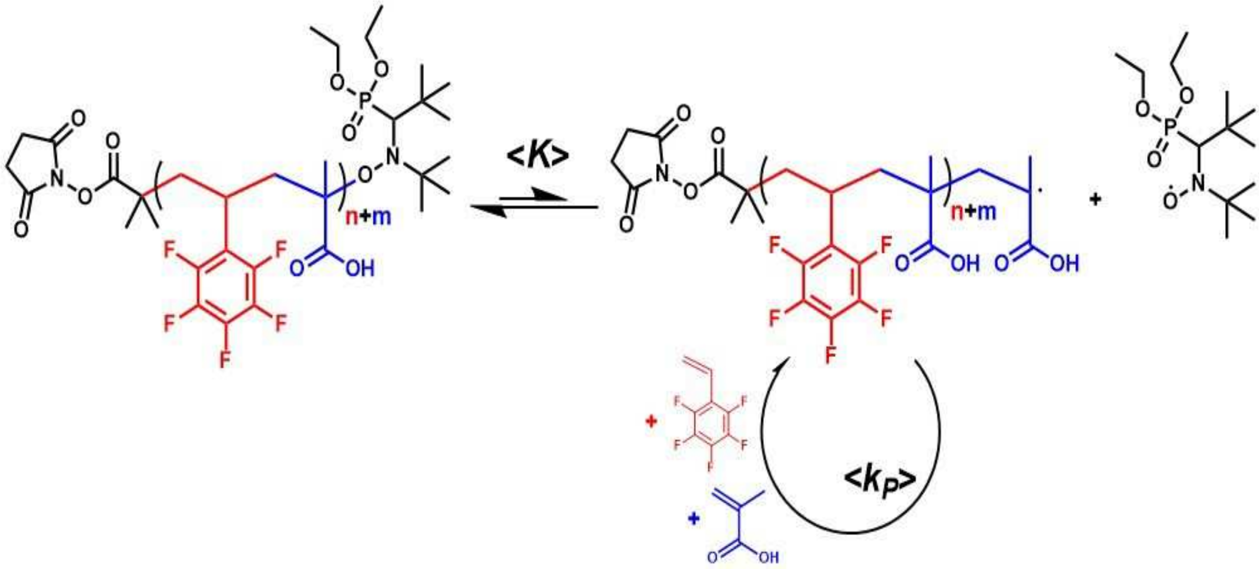


Figure 2.2: Mechanism of nitroxide mediated polymerization of poly (PFS-*ran*-MAA) random copolymerization reaction used in this thesis. PFS = 2, 3, 4, 5, 6 – pentafluorostyrene, MAA = methacrylic acid, NHS = N – hydroxysuccinimide, k_p = average propagation rate constant and <*K*> = average equilibrium rate constant.

Though the modern stable free radical initiators enabled the use of various monomers like dienes, acrylates and acrylamides[27] they had a limitation when it came to performing an effectively controlled reaction with methacrylic monomers. Since methacrylates have a high activation deactivation equilibrium constant (K), they strongly favour the irreversible termination reaction between the large number of propagating radicals generated instead of the preferred reversible nitroxide termination. Unlike acrylates, additional SG1 is insufficient to control the homopolymerization of methacrylates. At elevated SG1 concentrations irreversible termination also occurred due to ß- hydrogen transfer from the propagating radical to the SG1.[80] This drawback has led to extensive study, especially with methyl methacrylate (MMA). Various solutions were developed to address this problem; one of the most effective being the introduction of a suitable comonomer with a lower K value thus reducing the average $<K>$ and achieving a controlled reaction.[44,45] Charleux et al.[44] identified styrene (S) to be a good comonomer and established a theoretical expression for the activation deactivation constant K. This expression illustrated that with only 4-5 mol% of styrene in the feed a low $<K>$ could be obtained resulting in a controlled, pseudo-living copolymerization of mostly methacrylic feed. This has since offered better understanding of the concept which was then applied to many methacrylates beyond MMA to many other methacrylates such as biologically relevant monomers. These monomers include (dimethylamino) ethyl methacrylate (DMAEMA),[43,81,82] poly (ethylene glycol) methyl ether methacrylate (MePEGMA)[63,83–86] and glucose-functionalized methacryloyl galactose (AcGalEMA)[87]. The same technique was also extended successfully to ionic liquids and aqueous dispersion media, namely emulsion and microemulsion. These results proved the versatility of the strategy employed.

Other than S, derivatives of styrene such as 4–styrene sulphonate (SS)[65,88], PFS[43] and 9-(4-vinylbenzenyl)-9H-carbazole (VBK)[47,57,81,85] which is a styrenic monomer with a carbazole group having hole transport and fluorescent properties, have also been successfully employed as the controlling comonomer. PFS used in the above case was modified with thiols using a click reaction. VBK as a controlling comonomer was particularly effective even when used in concentrations as low as 1 mol% relative to MMA resulting in a significant drop in $<K>$. The concentration of VBK was significant enough to have a controlled polymerization reaction with $M_w/M_n \approx 1.3$.[57] The effectiveness of VBK over styrene was attributed to its high reactivity ratio (the definition of reactivity ratios can be found in the appendix). The VBK/MMA system had a difference in monomer reactivity ratios ($r_{VBK} = 2.7$, $r_{MMA} = 0.24$)[57] that was significantly higher compared to the S/MMA system ($r_S = 0.489$, $r_{MMA} = 0.492$).[89] This high difference in the monomer reactivity ratios led to favourable addition of VBK to the terminal positions which in turn reduced the value of $<K>$ even though $K_{VBK} \approx K_{Styrene}$.[47] Thus, the reactivity ratios can play a vital role in determining the effectiveness of a particular controlling comonomer.

PFS being a fluoromonomer exhibits many desirable properties in itself and when combined with the likes of MAA, the hydrophobic PFS and the highly hydrophilic MAA result in the formation of amphiphilic copolymers. Many interests, in varied applications, lie in the quest for identifying a highly efficient method for making well-defined and narrow molecular weight distributed amphiphilic copolymers. In this thesis, the effectiveness of PFS as a controlling comonomer for a methacrylate polymerization, namely methacrylic acid (MAA) has been studied and amphiphilic block copolymers of PFS and MAA poly (PFS)-*b*-poly (PFS-*ran*-MAA) with a narrow molecular weight distribution were successfully made. The block copolymers were made using a semi-batch reaction approach adding MAA at a later stage of the reaction.

2.4. ADVANTAGES OF USING NHS–BLOCBUILDER AS THE INITIATOR:

Vinas et al.[90] developed an initiator, known as NHS-BlocBuilder, which is based on the commercially available BlocBuilder-MA alkoxyamine having a succinimidyl ester group instead of the carboxylic acid group.[90] The NHS – BlocBuilder opened up better possibilities for polymerizing methacrylates as it had a dissociation constant that was about 15 times higher when compared to BlocBuilder-MA.[61] This meant that NHS-BlocBuilder can provide significantly higher free SG1 nitroxide which can prevent irreversible termination in methacrylates. Methacrylate copolymerizations (with a controlling comonomer) were identified to typically need about 10% excess SG1 for a controlled polymerization reaction to occur.[80] Thus, NHS-BlocBuilder eliminated the need for additional free SG1 during the reaction.

NHS-BlocBuilder was also of interest when polymerizing monomers with reactive groups, such as glycidyl methacrylic acid (GMA). When using BlocBuilder-MA, the epoxy group tends to react with the carboxylic acid group present in the initiator, forming insoluble side products.[61] The use of NHS-BlocBuilder provides effective control against these side reactions. In the case of polymerizing acrylates, the succinimidyl ester group in the NHS-BlocBuilder can be coupled with amines,[91,92] which is often used in peptide coupling.[83]

2.5. APPLICATIONS OF AMPHIPHILIC BLOCK COPOLYMERS:

Amphiphilic block copolymers are of interest among both academic and industrial researchers as they exhibit a unique set of properties in solution and in the bulk phase. As a result of the combination of two distinct blocks, one being hydrophobic, and the other hydrophilic, they can be tuned to achieve various thermodynamically favoured molecular architectures such as spherical, gyroid and lamellar.[2] They possess the ability to self-assemble into micelles and other morphologies[93–98] which are easily modified by altering the nature and length of the blocks, and each modification can lead to a broader range of properties.

These characteristics of amphiphilic block copolymers have enabled them to find applications in drug and gene delivery, colloidal science and the synthesis of advanced materials.[95,99–104] Incorporation of fluorinated blocks in an amphiphilic block copolymer could introduce desired material properties such as low refractive index, thermal, mechanical and chemical resistances.[12,72,105–109] PFS in particular has excellent optical wave guiding properties and finds application in optoelectronic industries.[108,110] Traditionally, controlled polymerizations containing PFS were carried out by ionic living polymerization however the use of RDRP is desired due to the relative ease of manipulation.[111] Some of the most common applications of amphiphilic block copolymers are discussed below.

2.5.1. Applications in Drug Delivery:

Many of the highly effective therapeutics are rendered with limited potential to reach their full capacity as a result of their poor water solubility.[112] Amphiphilic block copolymers have the ability to form micelles in solutions. The hydrophilic blocks form the shell while the hydrophobic blocks form the core of the micelle respectively (Figure 2.3). Thus, there will be a stabilized hydrophobic core that remains separated from the bulk of the solution by the hydrophilic blocks. This enables the hydrophobic centre to serve as a reservoir to store and effectively carry drugs and therapeutics that are poorly soluble in water and other solvents.

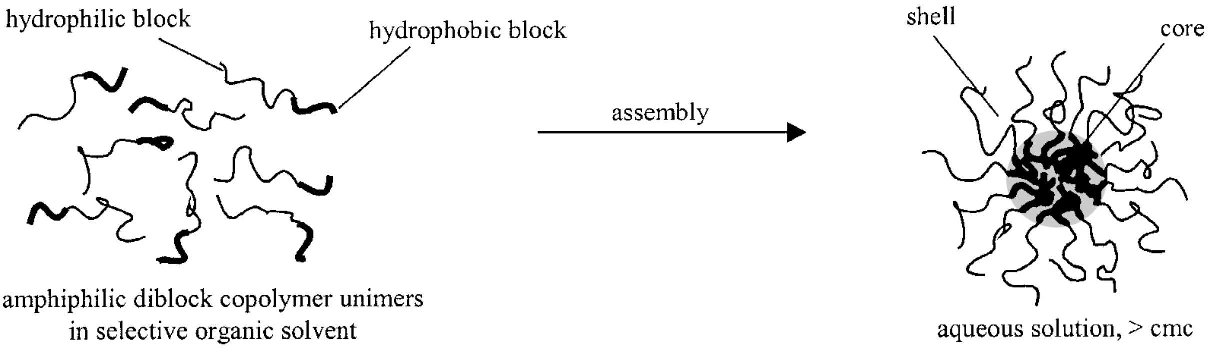


Figure 2.3: Mechanism of micelle formation in an amphiphilic di-block copolymer. [112]

Some of the most studied amphiphilic block copolymer systems for pharmaceutical applications including gene delivery are poly(ethylene oxide)-*b*-poly(*L*-amino acid)s[113–115], poly(ethylene oxide)-*b*-poly(ester)s[116–118] and poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*- poly(ethylene oxide).[119–121]

Apart from offering an increased drug loading capability, amphiphilic block copolymers can also serve as an effective medium for targeted delivery of the drug in a specific part of the body at a desired time. The release characteristics of the copolymers depend on the size of the blocks and surface properties of the hydrophilic end group.[122–126] The advantage is that since the drug is carried in a stable hydrophobic shell, the characteristics of the drug would not have a profound effect on its distribution hence providing the flexibility of application to a variety of drugs.[122] Several studies have targeted at engineering the micellar structure of a particular amphiphilic block copolymer in an attempt to reduce the rate of dissociation of the core. This, in-turn, will result in increasing the drug retention time, which eventually leads to better accumulation of the drug at the targeted delivery site.

2.5.2. Applications in membranes:

Amphiphilic block copolymers have the ability to self-assemble and to be presented in a three dimensionally ordered pore structure. These properties make them well suited for developing membranes with or without a suitable crosslinking material for various applications ranging from biological filtration to green chemistry. Some of the morphologies that are formed by block copolymer assembly make them highly applicable as ultrafiltration membranes for fluid separations. Figure 2.4 represents a particular setup which involves the selective removal of a minority domain having hexagonal cylinder assembly perpendicular to the membrane surface.[127–129]

Amphiphilic block copolymers containing fluoropolymer blocks offer an added advantage in membrane science as many of the properties of fluoromaterials like thermal and chemical resistance complement the properties of the amphiphilic copolymers and their intended applications.

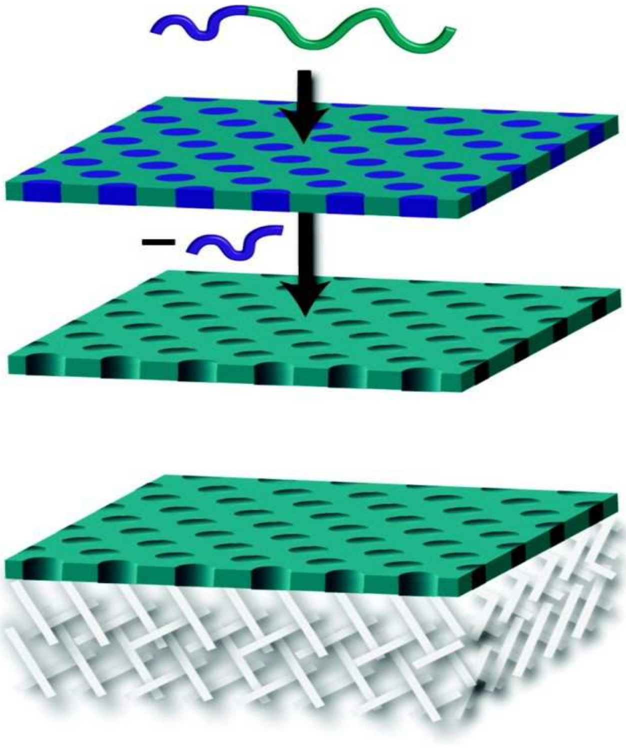


Figure 2.4: Self-assembly of block copolymer membranes used in ultrafiltration.[127] **This figure (top) gives a schematic representation of the cylindrical structure forming membrane of a diblock copolymer and the corresponding nanoporous assembly (green) obtained after the selective removal of the minor component (purple). The bottom figure shows a nanoporous membrane over macro porous support.**

Fluoropolymers like poly(vinyldiene fluoride) (PVDF) and poly(tetrafluoro ethylene) i.e., Teflon (PTFE) are known for their effectiveness as membranes mainly because of their excellent solution processability.[9,130] PVDF and PTFE homopolymer and copolymer membranes find application in ultrafiltration, micro-filtration, wastewater treatment, proton conduction, stimuli responsive and controlled deliveries, and biotechnology.[9,130–134]

2, 3, 4, 5, 6 - Pentafluorostyrene (PFS) has been viewed as a potential candidate to act as a polymer electrolyte membrane (PEM) in fuel cell applications when combined with the right material for enhanced proton conductivity and water transport. Modified PFS membranes (polysulfone (PSU) grafted with phosphonated poly(PFS)) have been studied previously keeping this particular application in mind.[135,136]

Chapter 3

Materials and Characterization

3.1. MATERIALS

2, 3, 4, 5, 6-pentafluorostyrene (PFS) (98%) was purchased from Oakwood Chemicals and methacrylic acid (99%), containing MEHQ as inhibitor was obtained from Sigma-Aldrich and used as received. The initiator, NHS-BlocBuilder was prepared by following the procedure mentioned by Vinas et al.[90] N-hydroxysuccinimide and N, N'-dicyclohexylcarbodiimide were purchased from Oakwood Chemicals while hexanes (95%) and Tetrahydrofuran (Certified, contains about 0.025% butylated hydroxytoluene as a preservative) were obtained from Fisher Scientific for the preparation of NHS-BlocBuilder. The methylation agent (trimethylsilyl) diazomethane, 2M solution in hexanes and nitrogen flushed was obtained from Acros Organics. The solvent used, xylenes (98.5%, ACS reagent grade) was purchased from Anachemia and was used as received.

3.2. CHARACTERIZATION

Monomer conversion was determined using gravimetric analysis and was based on total polymer. The molecular weight distribution was obtained by using gel permeation chromatography (GPC, Water Breeze) with tetrahydrofuran (THF) as the mobile phase. A mobile phase flow rate of 0.3 mL min^{-1} was applied and the GPC was equipped with 3 Waters Styragel® HR columns (HR1 molecular weight measurement range of 10^2 – 5×10^3 g·mol^{-1}, HR2 with molecular weight measurement range of 5×10^2 – 2×10^4 g·mol^{-1} and HR4 with molecular weight measurement range $5x10^3 – 6x10^5$ g·mol^{-1}) and a guard column was used. The columns were heated to 40 °C during the analysis. The GPC was equipped with both ultraviolet (UV 2487) and differential refractive index (2410) detectors. Though fluorine absorption in the column has posed a problem with certain fluoropolymers, there are no reported cases of this occurrence with PFS monomer to the best of our knowledge.[12,108,137,138] A poly(methyl methacrylate) (PMMA) standard was used for calibration and the samples were treated with a methylating agent prior to GPC analysis. PMMA standard was preferred over the polystyrene (PS) standard as the polymers characterized were found to be primarily methacrylic in nature. The Mark-Houwink coefficients for PFS are not known and therefore the values were reported relative to PMMA which we believe is a good assumption due to the relatively low concentration of PFS in the final copolymers.

Fourier Transform Infrared Spectroscopy (FT-IR) (Agilent Cary 630) was used to determine the final composition of the polymer. The carbonyl (C=O) characteristic peak at ~1680 cm^{-1} was used as a marker for concentration of MAA and the (C = C) aromatic carbon bond stretch at ~1502 cm^{-1} was used a marker for the concentration of PFS in the copolymer. Figure 3.1 shows the FT-IR spectra for homopolymers of PFS and MAA with the characteristic peaks used as markers. Differential scanning calorimetry (DSC, Q1000 V9.9 Build 303, TA Instruments) was used to determine the glass transition temperature (T_g) of the copolymer. A cycle of heat/cool/heat was employed using a heating rate of 10 °C min^{-1} and the resulting T_g was determined from the change in slope of the curve observed by inflection method.

Appropriate safety precautions were exercised while handling the monomers and other chemicals involved during the course of this thesis. These include wearing a lab coat, safety glasses and proper nitrile gloves at all times. All the reactions were carried out in a fume hood. Respiratory protection is recommended when handling the methylating agent as its fumes are identified to be extremely toxic.

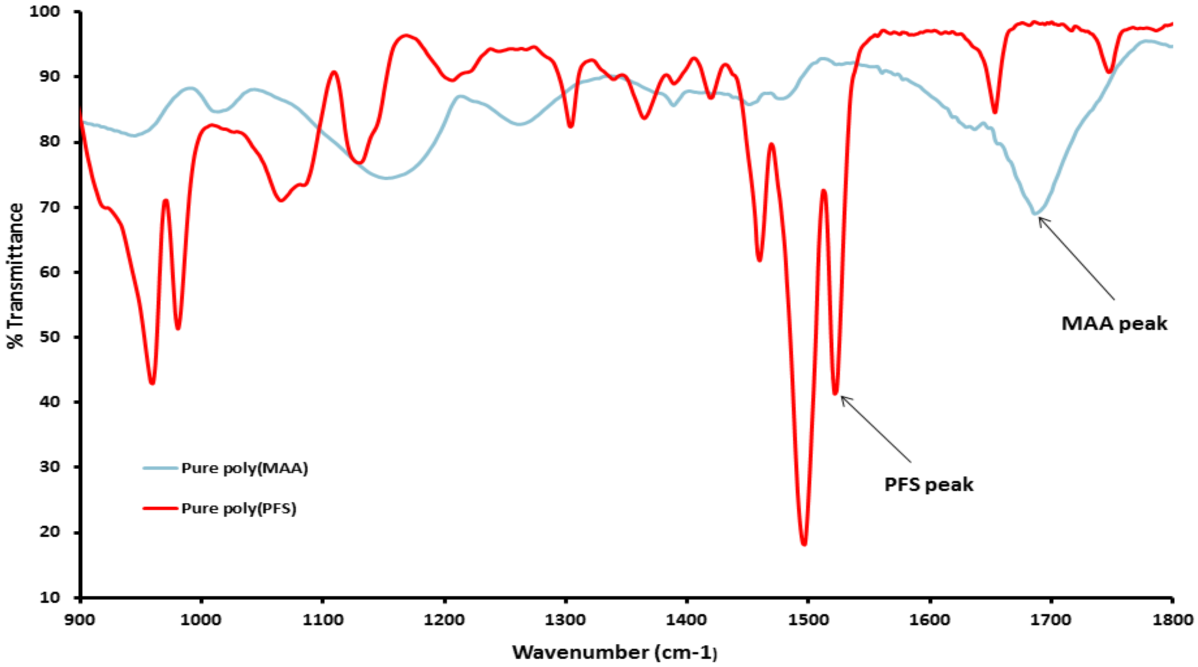


Figure 3.1: FT-IR spectra for 2,3,4,5,6 – pentafluorostyrene (PFS) and methacrylic acid (MAA) homopolymers with the characteristic peaks at ~1680 cm^{-1} for MAA and ~1502 cm^{-1} for PFS respectively.

Chapter 4

Synthesis and Characterization of Poly (PFS-*ran*-MAA) Random Copolymers by Nitroxide Mediated Polymerization

4.1. INTRODUCTION

The main objective of this thesis was to synthesize fluorinated amphiphilic block copolymers of 2, 3, 4, 5, 6 – pentafluorostyrene (PFS) and methacrylic acid (MAA). As this particular system has never been polymerized before it became essential to identify the suitable reaction conditions and understand the kinetics of the polymerization before proceeding further. For this purpose, a series of poly(PFS-*ran*-MAA) random solution copolymerization reactions were carried out at 90 °C using NHS-BlocBuilder as the initiator in xylenes.

The polymers obtained were analysed by gel permeation chromatography (GPC), differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR). This polymerization system was challenging as the reactivity of MAA was greater than that of PFS. This affected the role of PFS as a controlling comonomer as a higher concentration of PFS was required compared to other styrenic comonomers previously studied.

4.2. EXPERIMENTAL

4.2.1. Synthesis of poly (PFS-*ran*-MAA) Copolymers by NMP:

The reactions were carried out in a 50mL three-neck round bottom flask fitted with a thermal well and a condenser. A magnetic stir bar was inserted into the reactor which was placed in a heating mantle over a magnetic stirrer. PFS was loaded at various initial molar feed compositions ($f_{PFS,\ 0}$) from 0.1 to 0.98 and xylenes was used as a solvent (50 wt %). Table 4.1 lists the various experiments and their resulting feed compositions. For example, consider the case $f_{PFS,\ 0} = 0.3$: PFS (1.748 g, 9.002 mmol), MAA (1.838 g, 21.31 mmol), NHS-BlocBuilder initiator (0.1 g, 0.21 mmol) and xylenes (3.5 g, 33.78 mmol) were added to the reactor prior to sealing the openings with rubber septa and mounting the condenser. The target number average molecular weight, M_n was determined to be 17.0 kg·mol^{-1} for $f_{PFS,\ 0} =$ 0.3 by calculating the monomer to initiator feed ratio (Appendix I).

A thermocouple, with thermal well, was inserted into the reactor to monitor and control the temperature. Before applying heat, the contents of the reactor were subjected to nitrogen bubbling for a minimum of 20 min under constant stirring to remove any dissolved oxygen. The reaction setup was then heated and maintained at 90 °C. Using a syringe, the first sample was withdrawn at time t = 0 min, which was arbitrarily identified as the moment when the reactor temperature reached 90 °C. Samples were withdrawn periodically for determining the conversion, which was calculated using gravimetric analysis.

Once the reaction reached the desired conversion, the contents of the reactor were allowed to cool to room temperature and then precipitated in hexanes to recover the polymer. The polymers were then dried in a vacuum oven for a minimum of 8 h, until the samples were dried to constant weight. In this particular example given, the polymerization was carried out for 5h and the resulting polymer sample was characterized at a yield of 1.597 g, for a conversion, $X = 30.5$ % and had $M_n = 5.2$ kg·mol^{-1} , $M_w/M_n = 1.79$ and $F_{PFS} = 0.05$.

Table 4.1: Various compositions of poly (PFS-*ran*-MAA) random copolymerizations initiated by NHS-BlocBuilder carried out at 90°C in xylene solution studied.

Experiment ID [a]	$f_{PFS,0}$ [b]	**NHS-BB (mmol)**	**PFS (mmol)**	**MAA (mmol)**	**xylene (mmol)**
PFS/MAA 10/90	0.1	0.21	2.38	35.3	33.02
PFS/MAA 15/85	0.15	0.21	4.57	30.23	32.91
PFS/MAA 30/70	0.3	0.21	9.002	21.31	33.78
PFS/MAA 40/60	0.4	0.21	10.42	18.17	33.84
PFS/MAA 50/50	0.5	0.21	12.12	13.34	33.02
PFS/MAA 60/40	0.6	0.21	13.73	9.71	33.02
PFS/MAA 70/30	0.7	0.21	15.25	6.28	33.02
PFS/MAA 80/20	0.8	0.21	15.29	4.02	31.23
PFS/MAA 90/10	0.9	0.21	16.95	2.42	33.01
PFS/MAA 95/05	0.95	0.21	17.13	1.21	32.04
PFS/MAA 98/02	0.98	0.21	17.78	0.52	32.99

a) Experimental ID – is the experimental identification used in the format PFS / MAA X / Y where, PFS / MAA = 2, 3, 4, 5, 6 – pentafluorostyrene / methacrylic acid and X / Y = initial molar concentration of PFS / MAA. NHS-BB = NHS-BlocBuilder. Ratio of NHS-BlocBuilder to monomer results in a target number average molecular weight of ≈ 16.7 kg·mol^{-1}

b) $f_{PFS,\ 0}$ = initial mole fraction of PFS in the feed based on total monomers (excluding solvent).

4.3. RESULTS AND DISCUSSION

4.3.1. Copolymerization of poly (PFS-*ran*-MAA) random copolymers:

As discussed earlier, copolymerizations were carried out at 90 °C in a 50 wt% xylene solution while using NHS-BlocBuilder as the initiator. Figure 4.1.A and Figure 4.1.B illustrates the conversion (X) and scaled conversion ln $(1\text{-}X)^{-1}$ versus copolymerization time, respectively. Figure 4.1.C represents the $k_p[P^{\cdot}]$ vs. $f_{PFS,0}$ plot and Table 4.2 summarizes these results. The apparent rate constant $k_p[P^{\cdot}]$, where $[P^{\cdot}]$ is the concentration of propagating radicals and k_p is the propagation rate constant. $k_p[P^{\cdot}]$ was estimated from the slopes of the first 4-5 data points in the ln $(1\text{-}X)^{-1}$ versus copolymerization time when conversion was less than 30 % ($X < 0.3$) and we assumed the concentration of irreversible termination was negligible (Table 4.2).

The average equilibrium constant between the dormant and the active chains for the copolymerization is defined as equation 1.[139]

$$< K > = \frac{[P^{\cdot}][N^{\cdot}]}{[P-N]} \qquad (1)$$

where $<K>$ is the average activation-deactivation equilibrium constant, $[P^{\cdot}]$ is the concentration of propagating radicals, $[N^{\cdot}]$ is the concentration of free nitroxide and [P-N] is the concentration of the reversibly terminated SG1-terminated copolymers.. The overall polymerization rate can be defined by the rate of chain propagation which is defined by eq 2.

$$R_p = \frac{-d[M]}{dt} = k_p[P^{\cdot}][M] \qquad (2)$$

where the propagating radical concentration, $[P^{\cdot}]$, is moderated by eq 1. Early in the polymerization we can assume the initial concentration of free nitroxide $[N^{\cdot}]_0$ is high and does not change significantly at this point so that $[N^{\cdot}] = [N^{\cdot}]_0$. Also, [P-N] is assumed approximately equal to the initial concentration of initiator ([P-N] = [NHS-BlocBuilder]$_0$).

Therefore if we assume no termination at low conversion then $[SG1]_0 = [\text{NHS-BlocBuilder}]_0$, eq 1 can be multiplied by $<k_p>$ to give the following:

$$< k_p >< K > = < k_p > \frac{[P^{\cdot}][SG1^{\cdot}]_0}{[NHS{-}Blocbuilder]_0} = < k_p > [P^{\cdot}] \qquad (3)$$

As previously mentioned, the $k_p[P^{\cdot}]$ is equal to the slope of the scaled conversion $\ln(1-X)^{-1}$ versus copolymerization time, for the various copolymerizations samples were taken during the early stages of polymerization, at low conversion, where a linear growth of M_n versus X was observed (Figure 4.2.A).

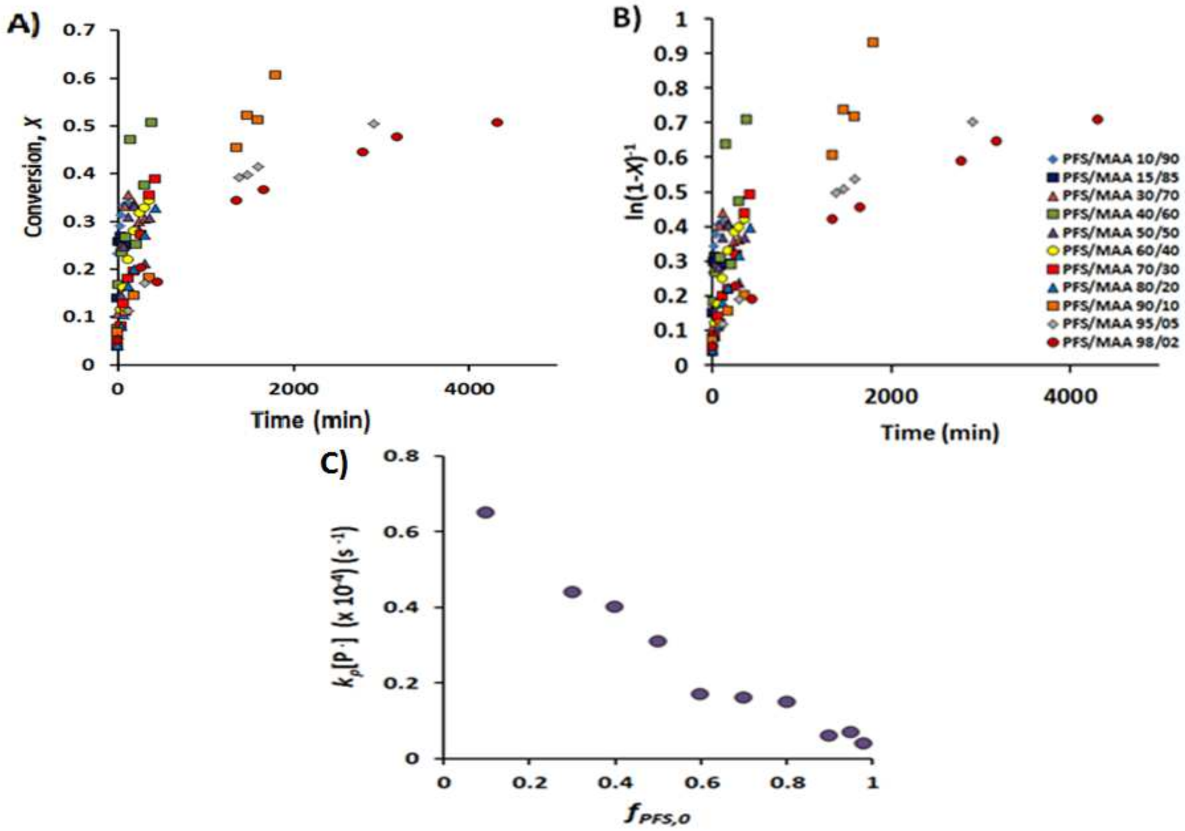


Figure 4.1: A) Conversion (X) vs. time B) Kinetic plot $\ln(1-X)^{-1}$ vs. time and B) Apparent rate constant ($k_p[P^{\cdot}]$) vs. initial molar concentration of PFS ($f_{PFS,0}$) for various poly(PFS-*ran*-MAA) copolymerization reactions carried out in 50 wt% xylene at 90° C with NHS-BlocBuilder as initiator.

Previously Wang et al.[11] reported a $k_p[P^\cdot]$ of (1.0 ± 0.1) x 10 $^{-4}$ s^{-1} for a 10 mol% PFS feed ratio in a PFS/GMA random copolymerization reaction with NHS-BlocBuilder as an initiator and 1, 4-dioxane as the solvent. Similar to Wang et al.[11], $k_p[P^\cdot]$ = 0.65 x 10^{-4} s^{-1} (Table 4.2) when using the same polymerization temperature, a feed ratio 10 mol% PFS and xylenes instead of 1,4-dioxane was obtained. Overall, the general trend was that $k_p[P^\cdot]$ decreased with increasing $f_{PFS,0}$ (Figure 4.1), which is not surprising due to the relative homopolymerization propagating rate constants at 80 °C for styrenics, such as styrene $k_{p,S}$ = 0.628 x 10^3 L $mol^{-1}\cdot s^{-1}$ and for MAA $k_{p,MAA}$ = 4.003 x 10^3 L $mol^{-1}\cdot s^{-1}$.[60] Unfortunately, to the best of our knowledge, no $k_{p,PFS}$ are reported in the literature for direct comparison. However it is interesting to note that the kinetics of the copolymerization reactions tended to follow a linear decrease in $k_p[P^\cdot]$ as $f_{PFS,0}$ increased (Figure 4.1 B, Table 4.2).

Table 4.2: Summary of poly (PFS-*ran*-MAA) copolymerization reactions carried out in 50 wt% xylene at 90°C with NHS-BlocBuilder as initiator.

Experiment ID [a]	f_{PFS} [b]	Time (min)	Conversion (X)	F_{PFS} [c]	$k_p[P^\cdot]$ (*10^{-4}) (s^{-1}) [d]
PFS/MAA 10/90	0.1	120	0.3	0.06	0.65
PFS/MAA 15/85	0.15	150	0.25	0.08	1.64
PFS/MAA 30/70	0.3	300	0.31	0.10	0.44 ± 0.12
PFS/MAA 40/60	0.4	380	0.51	0.11	0.40 ± 0.12
PFS/MAA 50/50	0.5	360	0.31	0.12	0.31 ± 0.06
PFS/MAA 60/40	0.6	360	0.34	0.14	0.17 ± 0.02
PFS/MAA 70/30	0.7	420	0.39	0.14	0.16 ± 0.01
PFS/MAA 80/20	0.8	420	0.40	0.24	0.15 ± 0.01
PFS/MAA 90/10	0.9	1800	0.61	0.26	0.06 ± 0.01
PFS/MAA 95/05	0.95	2910	0.50	0.31	0.06 ± 0.01
PFS/MAA 98/02	0.98	4320	0.51	0.41	0.04 ± 0.03

a) Experimental ID – is the experimental identification used in the format PFS / MAA X / Y where, PFS / MAA = 2, 3, 4, 5, 6 – pentafluorostyrene / methacrylic acid and X / Y = initial molar concentration of PFS / MAA.

b) $f_{PFS,\ 0}$ - initial mole fraction of PFS in the feed based on total monomers (excluding solvent).

c) F_{PFS} - final mole fraction of PFS in the polymer determined by FTIR spectroscopy.

d) $k_p[P^\cdot]$ - apparent rate constant determined from the slope of the ln $(1-X)^{-1}$ versus copolymerization time. X is the conversion determined by gravimetry.

Figure 4.2.A. shows the number average molecular weight (M_n) vs. conversion (X) plot and Figure 4.2.B shows the dispersity (M_w/M_n) vs. X plot for poly(PFS-*ran*-MAA) copolymers. A controlled polymerization is defined by a linear increase in a M_n vs. X plot. Table 4.3 presents the values of final copolymer M_n, M_w/M_n and the theoretical M_n ($M_{n,\ Theoretical}$) values which are calculated based on the ratio of initiator to monomer in the feed. The $M_{n,\ Theoretical}$ has been represented by the solid line in Figure 4.2.A.

Overall, a linear increase in M_n versus X and $M_w/M_n < 1.5$ was observed when $X < 0.30$, regardless of the initial feed composition ($0.10 < f_{PFS,\ 0} < 0.98$). These observations suggest that the copolymerization of MAA is controlled at low conversions. However it was evident that the control over the reaction is difficult when there is high concentration of methacrylate present. This fact can be further inferred from Figure 4.2.B where it can be seen that the reactions with high methacrylate content the M_w/M_n values were greater than 2.0 and the reactions with more than 50% PFS in the feed had lower M_w/M_n values that were in the range of 1.3 to 1.8. When compared to other controlling comonomers, 9-(4-vinylbenzenyl)-9H-carbazole (VBK) which when used at a concentration 20 mol% relative to MAA had M_w/M_n value of 1.3 at 22% conversion.[64] Under slightly different reaction conditions we needed roughly 80% molar concentration of PFS in the feed to have a similar M_w/M_n value of 1.28 (Table 4.3). In contradiction to the poly (PFS-*ran*-MAA) system, VBK has a higher reactivity compared to MAA which results in its preferable addition thus reducing the chances for irreversible termination reactions.[47] This increases its efficiency as the controlling comonomer for methacrylate polymerization by NMP.

Table 4.3: Observations from GPC for poly(PFS-*ran*-MAA) copolymers.

Experiment ID [a]	$f_{PFS,0}$[b]	Conversion (X)	F_{PFS}[c]	Theoretical M_n at conversion X (kg·mol^{-1})	M_n of final polymer(kg·mol^{-1})	Mw/M_n - of the final polymer [d]
PFS/MAA 10/90	0.1	0.3	0.06	5.7	9.4	2.19
PFS/MAA 15/85	0.15	0.25	0.08	4.2	4.1	2.1
PFS/MAA 30/70	0.3	0.31	0.10	5.2	8.0	2.07
PFS/MAA 40/60	0.4	0.51	0.11	8.7	16.1	1.52
PFS/MAA 50/50	0.5	0.31	0.12	5.1	9.9	1.59
PFS/MAA 60/40	0.6	0.34	0.14	5.7	7.1	1.4
PFS/MAA 70/30	0.7	0.39	0.14	6.5	7.4	1.35
PFS/MAA 80/20	0.8	0.40	0.24	5.5	6.0	1.28
PFS/MAA 90/10	0.9	0.61	0.26	10.8	3.9	1.43
PFS/MAA 95/05	0.95	0.50	0.31	8.2	3.5	1.37
PFS/MAA 98/02	0.98	0.51	0.41	8.4	2.5	1.54

a) Experimental ID – is the experimental identification used in the format PFS / MAA X / Y where, PFS / MAA = 2, 3, 4, 5, 6 – pentafluorostyrene / methacrylic acid and X / Y = initial molar concentration of PFS / MAA. The ratio of NHS-BlocBuilder to monomer results in a target number average molecular weight of ≈ 16.7 kg·mol^{-1}.

b) $f_{PFS,0}$ - initial molar concentration of PFS in the feed.

c) F_{PFS} - final molar concentration of PFS in the polymer determined by FTIR spectroscopy.

d) The number average molecular weight (M_n), weight average molecular weight (M_w), dispersity index (M_w/M_n) were determined by using gel permeation chromatography (GPC)

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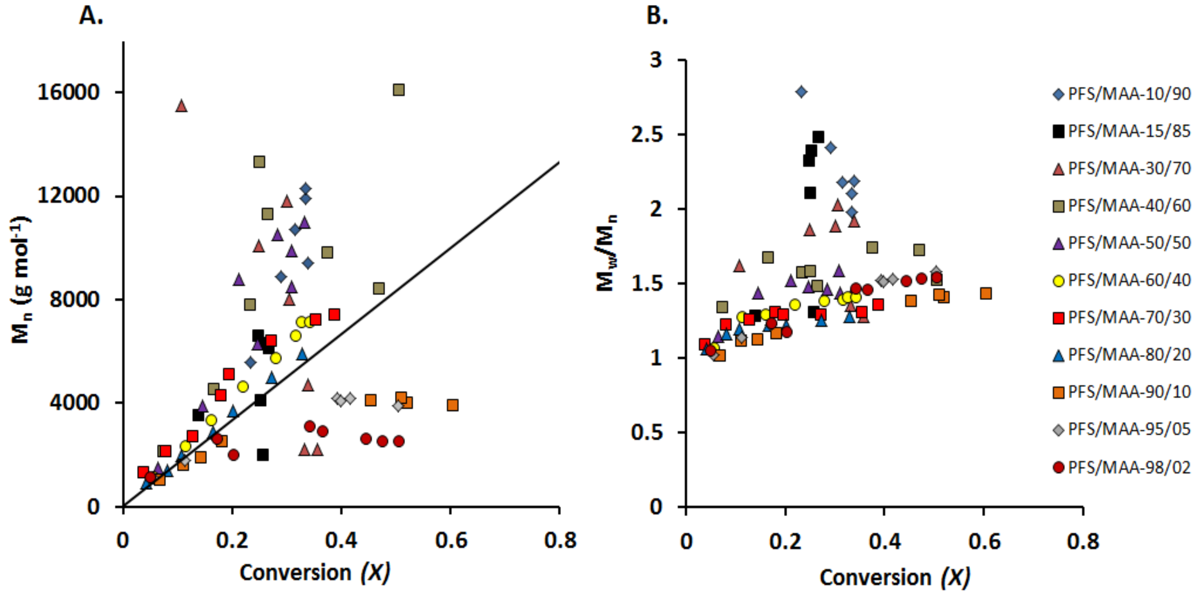

Figure 4.2. Observations from gel permeation chromatography for poly(PFS-*ran*-MAA) copolymers. A) M_n vs. Conversion (X) and B) M_w/M_n vs. Conversion (X). M_n = Number average molecular weight, M_w = Weight average molecular weight, M_w/M_n = Polydispersity index. Conversion (X) was determined by gravimetry. The copolymers were methylated prior to GPC analysis.

4.3.2. Final composition of poly(PFS-*ran*-MAA) copolymers:

The final copolymer composition was determined using Fourier transform infrared spectroscopy (FT-IR). Composition could not be identified by 1H-NMR spectroscopy because the PFS and the MAA did not have easily detectable protons which could be used for calculating the composition (Figure 4.3.B). Both MAA and PFS represent distinct FTIR traces such as the carbonyl peak (C=O) at ~1680 cm^{-1} and (C=C) aromatic carbon bond stretch at ~1502 cm^{-1} which can be used to identify MAA and PFS, respectively. Figure 4.3.A illustrates the characteristic FT-IR spectra for PFS/MAA 90/10 which clearly indicates that the relative peaks associated to PFS and MAA. As a comparison, all poly(PFS-*ran*-MAA) copolymers were characterized by FTIR and their respective spectra can be found in Figure 4.4, illustrating the change in relative peak intensity with change in copolymer composition. The figure shows two distinctive peaks for PFS (at ~1502 cm^{-1}) and for MAA (at ~1680 cm^{-1}) increasing and decreasing with increase in PFS composition in the final copolymer. A calibration curve was therefore formulated by comparing these two respective peaks from precise mixtures of pure poly(PFS) and poly(MAA) that were well blended together (Figure 4.3.B). The ratios were plotted in relative molar % and the resulting calibration curve was used to determine the final poly(PFS-*ran*-MAA) copolymer composition values (F_{PFS}) found in Table 4.2.

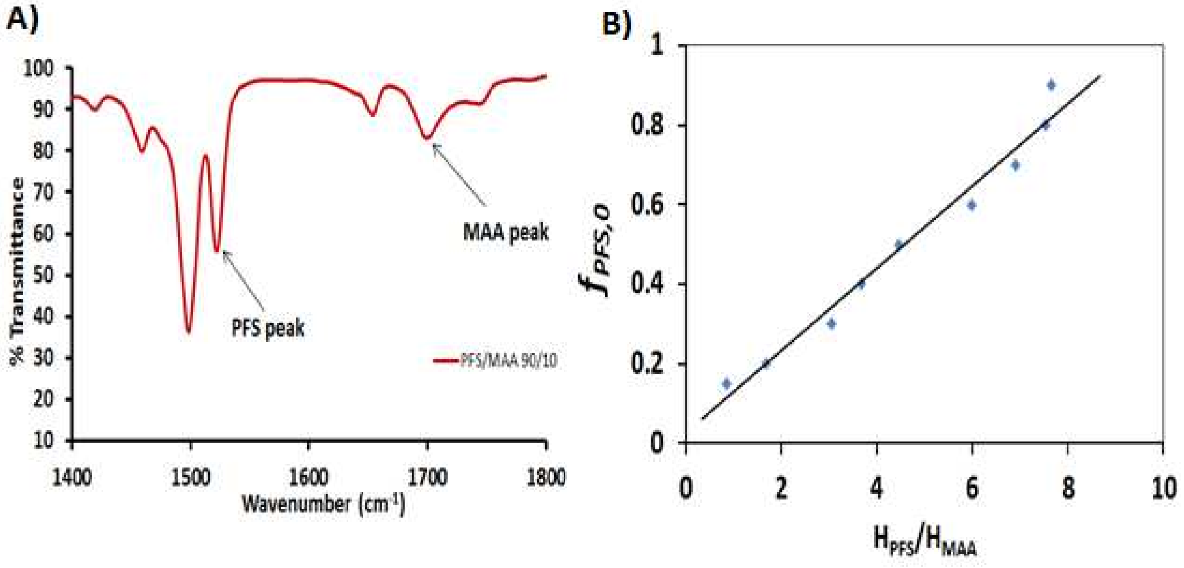

Figure 4.3: A) Characteristic Fourier Transform Infrared (FT-IR) spectra of poly(PFS-*ran*-MAA) random copolymer (PFS/MAA 90/10). B) Calibration plot used to determine F_{PFS} of poly(PFS-*ran*-MAA) random copolymer where H_{PFS}/H_{MAA} is a ratio of the peak heights associated to PFS (~1502 cm^{-1}) and MAA (~1680 cm^{-1}), respectively.

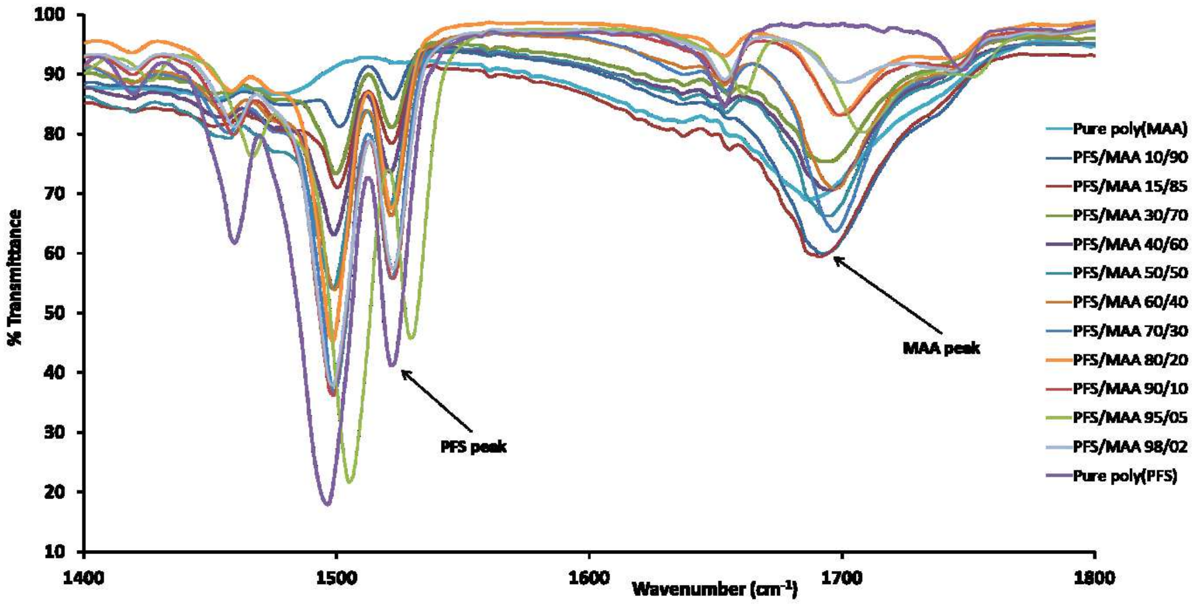

Figure 4.4: Fourier Transform Infrared (FT-IR) spectra for various poly(PFS-*ran*-MAA) random copolymer compositions. The legend corresponds to the poly(PFS-*ran*-MAA) random copolymer found in Table 4.1.

Table 4.4: Molar ratios and the corresponding FT-IR peak heights of pure homopolymer mixtures blended to obtain the calibration curve.

$f_{PFS,0}$[a]	f_{MAA}[b]	H_{PFS}[c]	H_{MAA}[c]	100-H_{PFS}	100-H_{MAA}	H_{PFS}/H_{MAA}[c]
0.15	0.85	86.43	83.97	13.57	16.03	0.85
0.2	0.8	85.06	91.08	14.94	8.92	1.67
0.3	0.7	64.97	88.53	35.03	11.47	3.05
0.4	0.6	74.04	92.93	25.96	7.07	3.67
0.5	0.5	76.12	94.65	23.88	5.35	4.46
0.6	0.4	58.32	93.04	41.68	6.96	5.98
0.7	0.3	63.82	94.76	36.18	5.24	6.90
0.8	0.2	59.75	94.65	40.25	5.35	7.52
0.9	0.1	85.37	98.09	14.63	1.91	7.65

a) $f_{PFS,0}$ = initial molar concentration of 2,3,4,5,6-pentafluorostyrene in the feed.

b) f_{MAA} = initial molar concentration of methacrylic acid in the feed.

c) H_{PFS} = Height of the peak representing PFS (~1502 cm^{-1}) and H_{MAA} = Height of the peak representing MAA (~1680 cm^{-1}) and H_{PFS}/H_{MAA} represents the ratio of the peaks.

4.3.3. Reactivity Ratio Estimation

Reactivity Ratios are defined as the ratio of reaction of species to its own monomer. Consider two monomers M_1 and M_2 and their corresponding reactive species M_1^* and M_2^*. The reactivity ratios of monomer 1 (**r_1**) and monomer 2 (**r_2**) can be expressed as

$$M_1 + M_1^* \xrightarrow{\mathbf{k_{11}}} M_1M_1^* \qquad M_2 + M_2^* \xrightarrow{\mathbf{k_{22}}} M_2M_2^*$$

$$M_1^* + M_2 \xrightarrow{k_{12}} M_1M_2^* \qquad M_2^* + M_1 \xrightarrow{\mathbf{k_{21}}} M_2M_1^*$$

$$\mathbf{r_1} = k_{11}/k_{12} \qquad \mathbf{r_2} = k_{22}/k_{21}$$

where, k_{11}, k_{12}, k_{22}, k_{21} are the rate constants for the corresponding reaction steps.

Low conversion reactions (X<10%) of poly(PFS-*ran*-MAA) copolymers were conducted separately to estimate the reactivity ratios using Kelen-Tudos (KT)[140] method. KT approach linearizes the Mayo-Lewis equation[141] and uses an arbitrary constant α to provide equal weightage to all the molar concentrations. The plot variables used in KT method (Figure 4.5) are defined by the equations below:

$$\eta = \left[r_1 + \frac{r_2}{\alpha}\right]\varepsilon - \frac{r_2}{\alpha};\ \eta = \frac{G}{\alpha + H}, \varepsilon = \frac{H}{\alpha + H}$$

$$\alpha = \sqrt{H_{min}.H_{max}} \tag{4}$$

$$G = \frac{f_1}{f_2}.\frac{2F_1 - 1}{F_1}, \qquad H = \left(\frac{f_1}{f_2}\right)^2.\frac{1 - F_1}{F_1}$$

where, r_1, r_2 are the reactivity ratios of monomers 1 and 2 and G and H are variables defined from an earlier out-dated linearization technique known as Finemann-Ross (FR) method,[142] f_1 and f_2 are the initial molar ratios of monomers 1 and 2 in the feed and F_1 and F_2 are the final molar ratios of monomers 1 and 2 in the product, H_{min} and H_{max} are the minimum and maximum values of H determined from the data. Table 4.5 lists the values of reactivity ratios obtained from the KT technique and Figure 4.6 represents the Mayo-Lewis plot in which the fit with the reactivity ratios obtained is added.

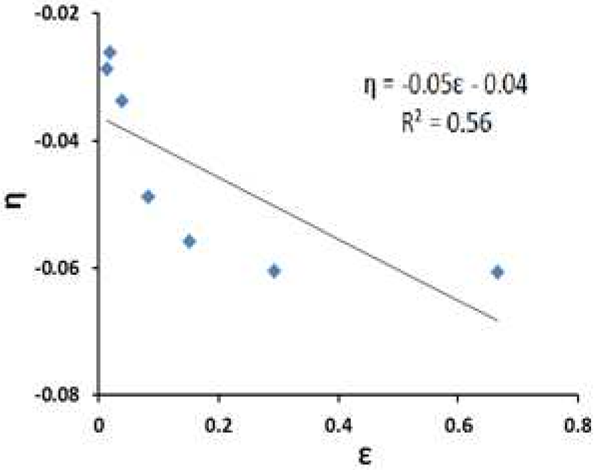

Figure 4.5: Kelen-Tudos plot to determine the reactivity ratios of poly(PFS-*ran*-MAA) copolymerizations carried out in 50 wt% xylene at 90° C with NHS-BlocBuilder as initiator.

Table 4.5: Reactivity ratios obtained from Kelen-Tudos technique:

Estimation Method	r_{PFS}[a]	r_{MAA}[a]	**R^2-value (%)** [b]
Kelen - Tudos (KT)	0.012	8.12	73

a. r_{PFS} and r_{MAA} = reactivity ratio of 2,3,4,5,6-pentafluorostyrene and of methacrylic acid, respectively.

b. R^2-value for the closeness of fit using linearization techniques in the solving of the mayo-lewis equation while seeking the reactivity ratios.

The reactivity ratios obtained by KT method were given by r_{PFS} = 0.012 and r_{MAA} = 8.12 for PFS and MAA respectively (Table 4.5). These values are quite different from literature values for other styrenic and methacrylic copolymerization systems such as S/MAA (r_S = 0.14, r_{MAA} = 0.61)[143], VBK/MMA (r_{VBK} = 2.7, r_{MMA} = 0.24)[64], S/MMA (r_S = 0.48, r_{MMA} = 0.49)[44]. This makes the copolymerization of PFS and MAA unique.

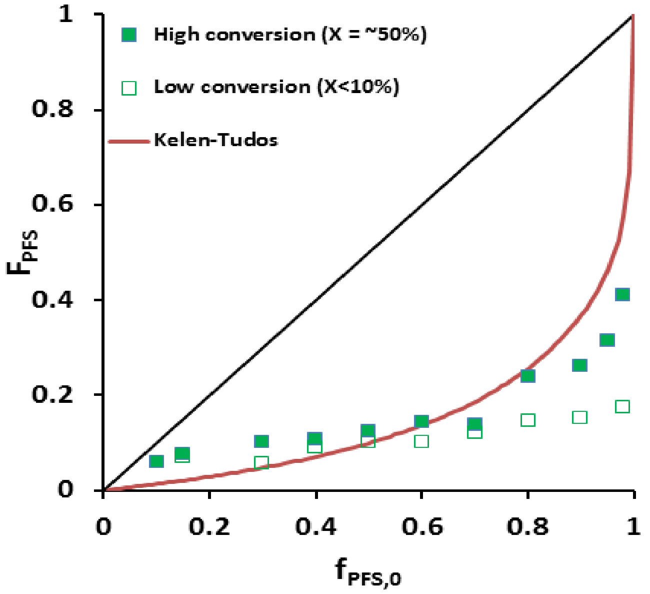

Figure 4.6: Mayo – Lewis Plot for the poly (PFS-ran-MAA) random copolymers synthesised at 90 °C in xylene solution using NHS-BlocBuilder as the initiator. PFS = 2,3,4,5,6 – pentafluorostyrene, MAA = methacrylic acid, $f_{PFS,0}$ = initial molar concentration of PFS in the feed and F_{PFS} = Final molar concentration of PFS in the polymer.

Figure 4.7.A. compares the S/MAA and PFS/MAA systems under similar reaction conditions. The $<k_p><K>$ values were obtained for the plot by using theoretical expression proposed by Charleux et al.[44] , given by:

$$< k_p >< K > = \frac{r_1.f_1^2 + 2.f_1.f_2 + r_2.f_2^2}{\frac{r_1.f_1}{k_{p_1}.K_1} + \frac{r_2.f_2}{k_{p_2}.K_2}} \tag{5}$$

where, r_1, r_2 are the reactivity ratios of monomer 1 and 2; f_1, f_2 are the initial molar ratios in the feed for monomers 1 and 2; k_{p1}, k_{p2} are the propagation rate constants for monomer 1 and 2 and K_1, K_2 are the average equilibrium rate constants for monomer 1 and 2. The values required for the calculation were obtained from literature[143] and are presented in Table 4.6. Dire et al.[143] identified that 8.8 mol% styrene in the feed was sufficient to enable a well-controlled polymerization of S/MAA system at a temperature of 80° C. Under similar conditions, with only the difference in reactivity ratios, Figure 4.7.B illustrates that theoretically about 80 mol% of PFS will be required to offer the same control for the PFS/MAA system. This statement is supported by experimental data from GPC where we noted that about 70% PFS was required to have good control (Figure 4.2.A).

Table 4.6: Kinetic parameters used for the calculation of $<k_p>< K>$.

Kinetic Parameter [a]	**Value**	**Reference**
$k_{p,S} \approx k_{p,PFS}$ ($L \cdot mol^{-1} \cdot s^{-1}$)	628	144
$K_S \approx K_{PFS}$ ($mol \cdot L^{-1}$)	1.3 x 10^{-10}	145
$k_{p,MAA}$ ($L \cdot mol^{-1} \cdot s^{-1}$)	4008	146
K_{MAA} ($mol \cdot L^{-1}$)	1 x 10^{-6}	147,148
r_S / r_{MAA}	0.14 / 0.61	149
r_{PFS} / r_{MAA}	0.012 / 8.12	This work

a) $k_{p,S}$, $k_{p,PFS}$, $k_{p,MAA}$ = propagation rate constant for styrene, 2,3,4,5,6–pentafluorostyrene and methacrylic acid, respectively. K_S, K_{PFS} and K_{MAA} = equilibrium constant for styrene, 2,3,4,5,6–pentafluorostyrene and methacrylic acid, respectively. r_s, r_{PFS} , r_{MAA} are the reactivity ratios of styrene, 2,3,4,5,6–pentafluorostyrene and methacrylic acid respectively.

The method of reactivity ratio estimation used in this work does not offer an ideal value of the reactivity ratios for this particular system as it does not take into consideration the composition drift that occurs during the reaction. The high difference between the reactivity of PFS and MAA lowered the efficiency of PFS as the controlling comonomer. This meant more PFS concentration is needed in the mix to have a controlled copolymerization of methacrylates than other styrenic monomers [60,64].

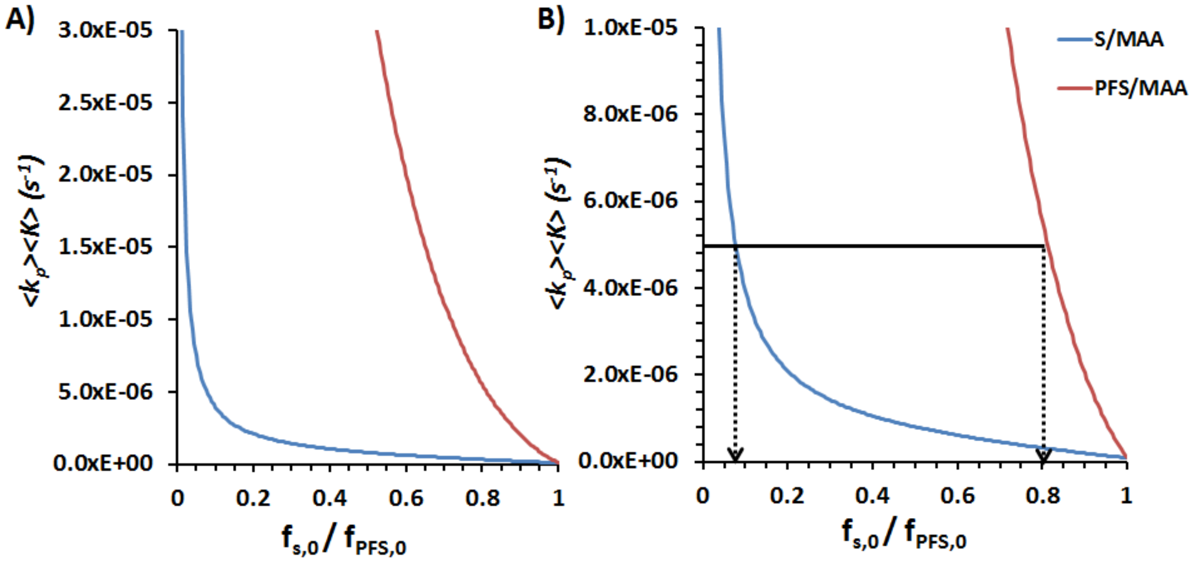

Figure 4.7: A) Comparison of S/MAA and PFS/MAA random copolymerization reactions and B) Effect of reactivity ratios on the control of PFS/MAA random copolymerization. $f_{S,0}$ and $f_{PFS,0}$ denote the initial molar concentrations of styrene and 2,3,4,5,6-pentafluorostyrene relative to MAA in the copolymer feed, $<k_p>$ is the average propagation constant and $<K>$ is average equilibrium constant. The solid horizontal black line in figure b) denotes the necessary minimum of controlling comonomer needed to obtain a controlled copolymerization for both systems.

This huge discrepancy in reactivity ratios between MAA and PFS suggests we should explore a semi batch approach for the synthesis of poly(PFS)-*b*-poly(PFS-*ran*-MAA) copolymers where the second block is mostly methacrylic. The greater PFS concentrations obtained through the semi- batch approach will result in a better controlled copolymerization. The exploration of semi-batch reactions is discussed in detail in Chapter 5.

4.3.4. Differential scanning calorimetry (DSC) characterization of poly (PFS-*ran*-MAA) copolymers:

Copolymer glass transition temperatures (T_g) were determined using differential scanning calorimetry (DSC). The values of T_g (°C) obtained are tabulated in Table 4.7. The theoretical T_g values were calculated by using Fox equation [150,151] which is given by,

$$\frac{1}{T_g} = \frac{w_{PFS}}{T_{g_{PFS}}} + \frac{w_{MAA}}{T_{g_{MAA}}} \tag{6}$$

where, T_g = Final theoretical T_g of the copolymer, $T_{g\,PFS}$ = glass transition temperature for the pure homopolymer of 2,3,4,5,6 – pentafluorostyrene, $T_{g\,MAA}$ = glass transition temperature of the pure homopolymer of methacrylic acid, w_{PFS} = weight fraction of 2,3,4,5,6 – pentafluorostyrene and w_{MAA} = weight fraction of methacrylic Acid.

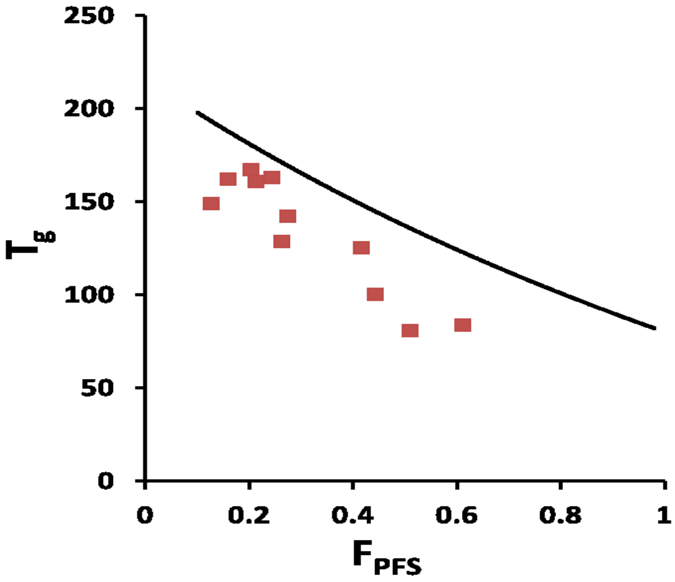

Figure 4.8: Comparison between the theoretical and actual T_g for the poly(PFS-*ran*-MAA) copolymers synthesized at 90° C in xylene. F_{PFS} = final molar concentration of

PFS in the feed determined by FT-IR spectroscopy. The black solid line represents the theoretical T_g values obtained from fox equation and the red points represent the actual T_g. The T_g values are in °C.

Table 4.7: Glass transition temperature values for various poly (PFS-*ran*-MAA) random copolymer compositions synthesized at 90° C in xylene.

Experiment ID [a]	$f_{PFS,0}$ [b]	F_{PFS} [c]	T_g(actual)[d] (°C)	T_g(theoretical)[d] (°C)
PFS/MAA 10/90	0.1	0.06	148	198
PFS/MAA 15/85	0.15	0.08	162	189
PFS/MAA 30/70	0.3	0.10	167	165
PFS/MAA 40/60	0.4	0.11	161	151
PFS/MAA 50/50	0.5	0.12	160	137
PFS/MAA 60/40	0.6	0.14	142	124
PFS/MAA 70/30	0.7	0.14	128	112
PFS/MAA 80/20	0.8	0.24	125	101
PFS/MAA 90/10	0.9	0.26	100	90
PFS/MAA 95/05	0.95	0.31	80	85
PFS/MAA 98/02	0.98	0.41	81	82

a) Experimental ID – is the experimental identification used in the format PFS / MAA X / Y where, PFS / MAA = 2, 3, 4, 5, 6 – pentafluorostyrene / methacrylic acid and X / Y = initial molar concentration of PFS / MAA.

b. $f_{PFS,0}$ = initial molar concentration of PFS in the feed.

c. F_{PFS} = Final molar concentration of PFS in the polymer.

d. T_g(actual) are the values of glass transition temperatures obtained from DSC and T_g(theoretical) were the values obtained from fox equation.

MAA contributed to the high T_g values and hence more the MAA, higher the T_g of the final copolymer and T_g values decreased with the increase in PFS content. Figure 4.8 shows the plot between T_g of the random copolymers and the final copolymer composition. The marker points represent the actual T_g obtained and solid line represents the theoretical T_g values. The theoretical predictions from fox equation tend to be higher than the actual T_g values obtained. This contradiction maybe a result of variations observed in T_g up to a molecular weight (M_n) value of about 20000.[152] The pure homopolymer T_g were determined to be 80°C for PFS and 216°C.

4.4. CONCLUSION

In this chapter, the synthesis and characterization of poly(PFS-*ran*-MAA) copolymers were discussed. Reactions were carried out in various feed concentrations at 90 °C in xylene solution with NHS-Blocbuilder as the initiator. The application of PFS as a successful controlling comonomer for methacrylate polymerization via NMP was demonstrated. It was identified that PFS had better control over the reaction when present at concentrations over 50% (molar) in the feed.

The reason for the need of larger amounts of PFS was identified to be the much higher reactivity of MAA when compared to PFS. The glass transition temperature of the final polymers was measured and the variance in actual and the theoretical T_g calculated by fox equation was discussed.

Chapter 5

Synthesis and Characterization of Poly(PFS)-*b*-PFS-*ran*-MAA) Block Copolymers by Nitroxide Mediated Polymerization

5.1. INTRODUCTION:

In previous sections a better understanding of the kinetics of the system was gained by conducting batch reactions to synthesize poly(PFS-*ran*-MAA) copolymers. An estimate of the reactivity ratios were calculated by using the Kelen-Tudos technique. The mismatched reactivity ratios led us to the hypothesis that a semi-batch reaction could be a useful tool for the synthesis of poly(PFS)-*b*-poly(PFS-*ran*-MAA) block where the second block is mostly MAA.

The semi-batch approach would first facilitate the conversion of a poly(PFS) block followed by the addition of MAA solution. Upon pure MAA injection the presence of the unreacted PFS would act as a controlling comonomer for the MAA. Finally, the measured reactivity ratios indicate that the addition of MAA would trump the addition of the PFS, resulting in the formation of a purely methacrylic second block, hence a one-pot block copolymer synthesis. Three semi-batch reactions were carried out at 90 °C in xylene solution using NHS-BlocBuilder as the initiator. The final block copolymers obtained were characterized using techniques that were similar to the ones employed for characterizing the random copolymers.

5.2. EXPERIMENTAL

5.2.1. Semi Batch Reactions for the Synthesis of poly(PFS)-*b*-poly(PFS-*ran*-MAA) Block Copolymers Through One-pot Semi Batch Addition by NMP:

The semi batch reactions were carried out in a 50 wt% xylene solution using a similar reactor assembly as the one used for the synthesis of random copolymers. Molar feed compositions used for the reactions are listed in Table 5.1 below. PFS, the initiator NHS-BB and half the amount of solvent needed were added in the reactor initially and after carrying out nitrogen bubbling accompanied by constant stirring for about 20 minutes, heat was switched on. The first sample was withdrawn using a syringe when the temperature reached 90 °C and was marked time t = 0 min. MAA and the remaining half of the solvent were added to the reactor at a later stage depending on the reaction being carried out as mentioned in Table 5.1. Nitrogen bubbling was done separately before their addition to remove any dissolved oxygen. After completion of the reaction, the polymers were recovered by precipitation in hexane. Monomer conversion was calculated by gravimetric analysis.

Table 5.1: Experimental conditions for the synthesis of poly(PFS)-*b*-poly(PFS-*ran*-MAA) block copolymers through semi-batch addition initiated by NHS-BlocBuilder carried out at 90°C in xylene solution.

Experiment ID [a]	$f_{PFS,0}$ [b]	NHS-BB (mmol)	PFS (mmol)	MAA (mmol)	xylene (mmol)	t_{inject} [c] (min)	t_{total} [c] (min)
PFS/MAA SB I	0.5	0.21	12.12	13.34	33.02	1440	1740
PFS/MAA SB II	0.5	0.21	12.12	13.34	33.02	2880	3180
PFS/MAA SB III	0.75	0.21	12.12	6.67	24.77	2880	3180

a) Experiment Id = is the experimental identification where PFS = 2,3,4,5,6-pentafluorostyrene, MAA = methacrylic acid, NHS-BB = NHS-BlocBuilder, SB # = semi-batch and the experimental number. The feed composition includes both the initial feed and the semi-batch injection volume.

b) $f_{PFS,0}$ = initial molar concentration of PFS in the feed including the MAA injection.

c) t_{inject} is the time of MAA solution injection; t_{total} is the total time to the polymerization reaction.

5.3. RESULTS AND DISCUSSION

5.3.1. Syntheses of pseudo poly(PFS)-*b*-poly(PFS-*ran*-MAA) block copolymers by one pot semi batch addition:

During the reaction PFS/MAA SB I, MAA was added after 24 hrs, which corresponds to a $X_{PFS,\ Inject}$ = 0.27 (X of PFS at injection = $X_{PFS,\ Inject}$) from the start of the reaction. Therefore at the point of injection 73 % of the initial PFS monomer is present for copolymerization with the incoming MAA. For PFS/MAA SB II and PFS/MAA SB III, MAA was added after 48 hours ($X_{PFS,\ Inject}$ = 0.54) from the start of the reaction, indicating that only 46 % of the PFS is present to copolymerize with the MAA. The amount of MAA and solvent added were halved for the reaction PFS/MAA SB III (Table 5.1).

The one-pot semi batch reactions to obtain pseudo poly(PFS)-*b*-poly(PFS-*ran*-MAA) block copolymers were carried out similar to random copolymerizations at 90 °C with NHS–BlocBuilder as the initiator and 50 wt% xylene solution as the solvent. Table 5.1 shows various data from the reactions including time at which MAA was injected from the start of reaction and PFS monomer conversion before MAA was added and also the total conversion at the end of the reaction. Figure 5.1 represents the ln $(1-X)^{-1}$ vs. time graph which shows clearly a drop in total X marking the time at which MAA was injected to the reaction mixture. It would also appear that the slope increases after the addition of MAA, which is not surprising due to the difference in k_P between PFS (assuming $k_{P,PFS} \approx k_{P,S}$) and MAA.

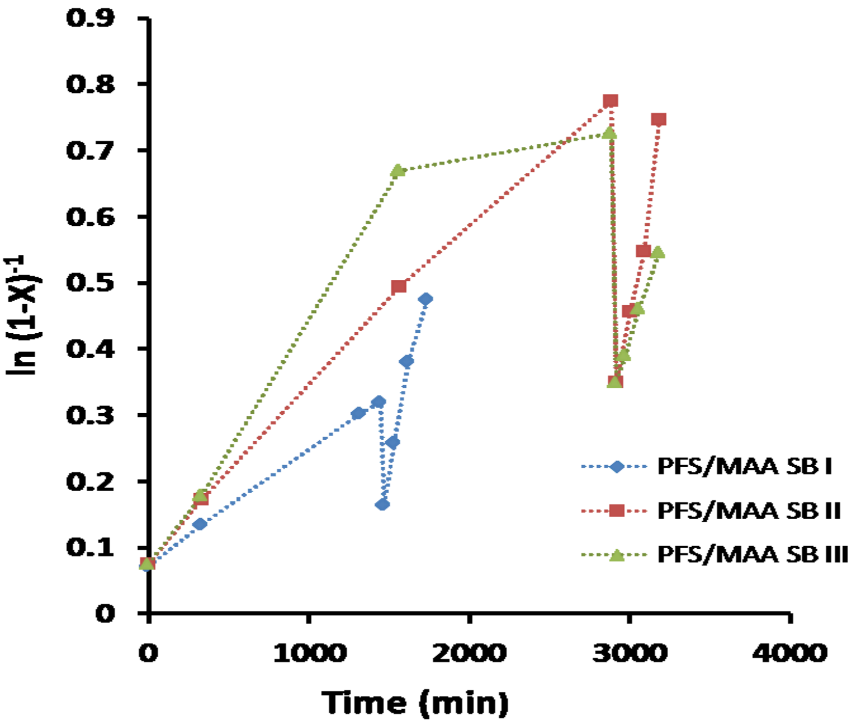

Figure 5.1: **Kinetic plot ln (1-X)$^{-1}$ vs. time for poly(PFS)-*b*-poly(PFS-*ran*-MAA) block copolymerization reactions carried out in 50 wt% xylene at 90°C with NHS-BlocBuilder as initiator. The lines clearly show the drop in conversion after injection of the MAA solution at 1440 mins for PFS/MAA SB I and 2880 mins for PFS/MAA SB II & III.**

Figure 5.2 shows the plot of M_n versus X of the copolymers obtained from the semi batch reactions. In all three cases a steady increase in M_n is observed for the homopolymerization of PFS. For PFS/MAA SB I, upon injection, a clear increase in M_n is observed suggesting incorporation of MAA into a second block. Therefore at the point of injection we can calculate the $f_{PFS,0}$ = 0.37 (73 wt% of 0.5 moles added initially) assuming the unreacted PFS monomer is available for copolymerization. If we examine the Mayo-Lewis plot (Figure 4.6) established in the previous chapter for the copolymerization at this feed ratio, we can expect a second block of mostly MAA copolymer will result. However, for PFS/MAA SB II and PFS/MAA SB III the same behaviour was not observed: the M_n values stayed low and did not vary much before and after the injection. A better understanding of what is taking place is obtained from the GPC traces (Figure 5.3).

Table 5.2: Observations from GPC poly(PFS)-*b*-poly(PFS-*ran*-MAA) for block copolymers.

Experiment Id[a)]	$f_{PFS,0}$[b)]	Before Injection of MAA				Final Polymer			
		$X_{PFS, Inject}$ c)	F_{PFS} d)	M_n (kg·mol^{-1}) e)	M_w/M_n e)	X c)	$F_{PFS,FTIR}$ / $F_{PFS,GPC}$ d)	M_n (kg·mol^{-1}) e)	M_w/M_n e)
PFS/MAA SB I	0.5	0.27	1.0	1.7	1.2	0.39	0.12/0.05	16.6	1.37
PFS/MAA SB II	0.5	0.54	1.0	2.2	1.37	0.53	0.20/0.90	2.3	1.39
PFS/MAA SB III	0.75	0.53	1.0	1.8	1.27	0.42	0.23/0.80	2.0	1.25

a) Experiment Id = is the experimental identification where PFS = 2,3,4,5,6 pentafluorostyrene, MAA = methacrylic acid, SB # = semi-batch and the experimental number. The feed composition includes both the initial feed and the semi-batch injection volume

b) $f_{PFS,0}$ = initial molar concentration of PFS in the feed including the MAA injection.

c) $X_{PFS,\ Inject}$ is the homopolymerization conversion of PFS prior to semi-batch MAA injection; X is the total monomer conversion after injection.

d) F_{PFS} = final molar fraction of PFS in the copolymer determined by FT-IR ($F_{PFS,FTIR}$) or by GPC ($F_{PFS,GPC}$).

e) The number average molecular weight (M_n), weight average molecular weight (M_w), dispersity index (M_w/M_n) were determined by using gel permeation chromatography (GPC). The MAA copolymers were methylated using (trimethylsilyl) diazomethane prior to GPC analysis.

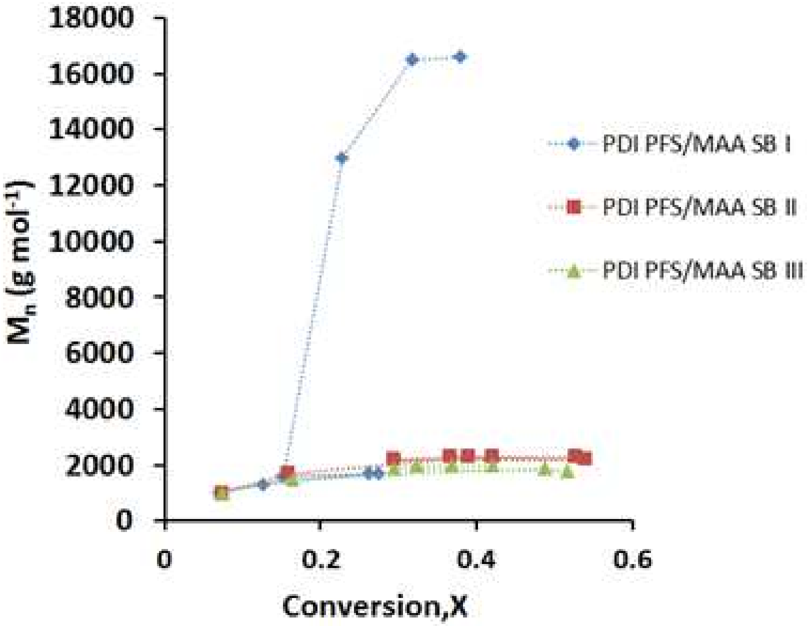

Figure 5.2: Number average molecular weight (*M_n*) plotted against conversion (*X*) and for the various semi-batch reactions carried out at 90°C in xylene by nitroxide mediated polymerization.

It can be observed from the GPC traces in Figure 5.3 that as the polymerization time increases, the elution time decreases, suggesting polymer growth. When further examining PFS/MAA SB I (Figure 5.3.A) it is apparent that at the point of injection (green line) the major peak is at around 31 min and after injection this major peak shifts to 25 min. However it is important to note that a significant amount of polymers eluting at 31 min are still present in the final sample (light red line), indicating that only a portion of the poly(PFS) chains were living at the point of injection.

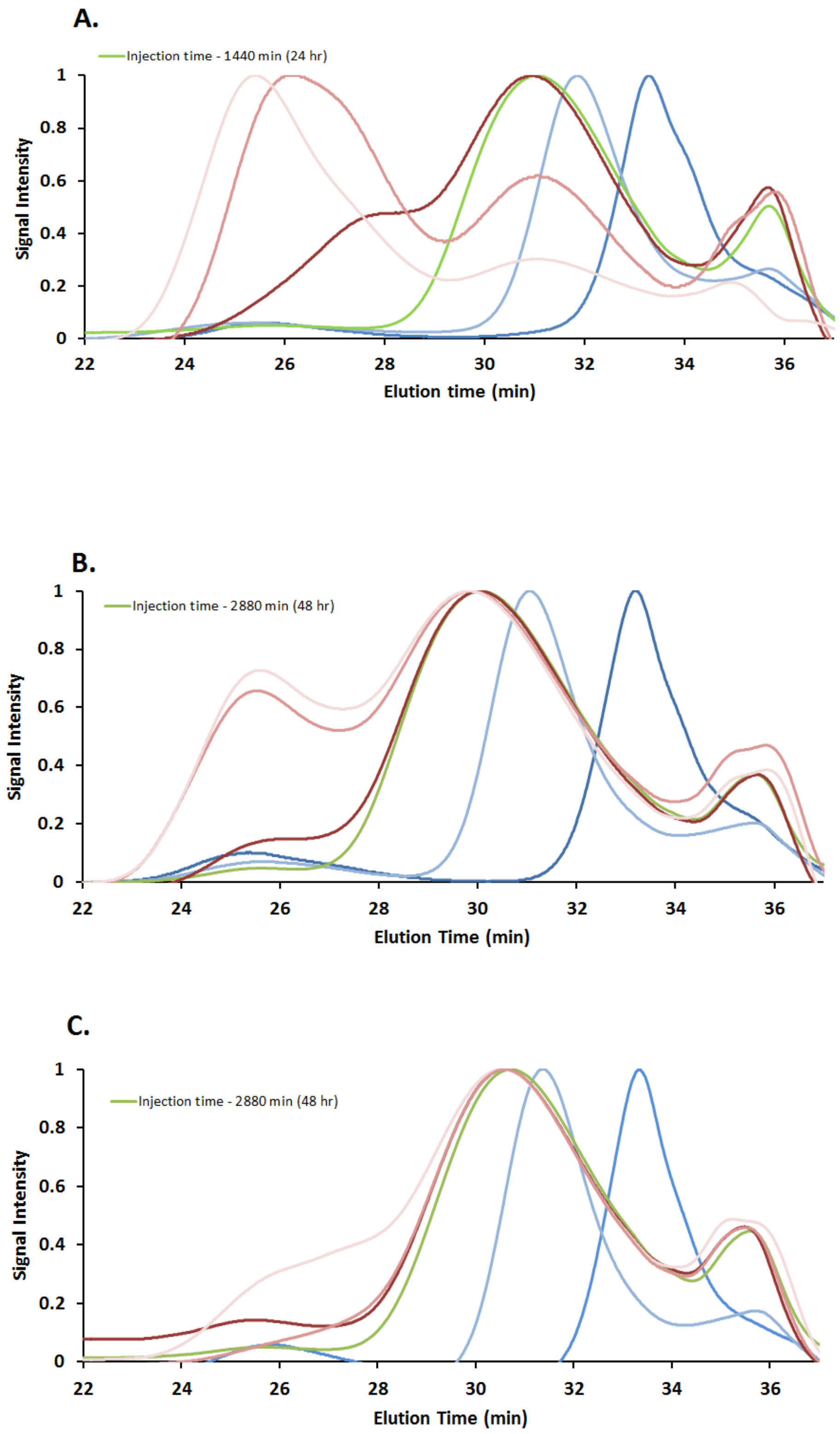

Figure 5.3: GPC traces for the semi-batch reactions A. PFS/MAA SB I, B. PFS/MAA SB II and C. PFS/MAA SB III. The samples before MAA solution injection are represented by decreasing order of shades of blue, the green line represents the sample at injection,

and lines of decreasing shades of red represent the samples after injection. The legend entry shows the time of injection in each reaction.

It is also important to note the apparition of a new peak at 36 min, suggesting the growths of oligomers. We surmise that these oligomers are a result of chain transfer to MAA monomer followed by fast termination. This hypothesis is consistent with the literature for chain transfer to monomer under high monomer to initiator ratio and almost instantaneous termination of methacrylic homopolymerization.[80]

In the semi-batch reaction PFS/MAA SB II (Figure 5.3.B), the major peak at the point of injection occurred at 30 min (green line) and the shift in peaks after injection was not as pronounced as in the first reaction. It can be seen that the amount of polymers eluting at 31 mins in the final sample is even higher than the previous reaction suggesting that the irreversible termination in this case was even higher. This is expected since the conversion of the poly (PFS) block increased as the reaction time was higher (48 hrs). The apparition of a new peak at 36 mins suggests the growths of oligomers resulting of chain transfer to MAA monomer followed by fast termination.

The MAA and solvent added were halved for PFS/MAA SB III and the effect it had on the traces was negligible. Results from PFS/MAA SB III (Figure 5.3.C) were similar to the results from PFS/MAA SB II as the initial concentration of PFS used and the time of injection of the MAA solution were identical (48 hrs). Significant amount of polymers were eluting at 32 mins suggesting irreversible termination. Again, similar to PFS/MAA SB I and PFS/MAA SB II, the apparition of a new peak at 36 min, suggesting the growths of oligomers resulting of chain transfer to MAA monomer followed by fast termination. Regardless, these results suggest that the semi-batch approach is possible; however, the problem of irreversible termination needs to be addressed.

The final composition of the block copolymers were measured by using FT-IR and T_g values were obtained by DSC, similar to the random copolymers. Since the samples contained irreversibly terminated PFS and presumed poly (MAA) oligomers as evident from the GPC data, it affected the data from both FT-IR and DSC. The results from these characterizations have been included as supporting information at the end of the thesis (Appendix I).

5.4. CONCLUSION

The semi-batch reactions conducted were successful in synthesizing poly(PFS)-*b*-poly(PFS-*ran*-MAA) block copolymers as evident from the GPC results. The problem of irreversible termination existed in all three semi-batch reactions and the termination rate increased with increase in conversion of the PFS homopolymer block. The time of injection of the MAA solution must therefore be precise to allow minimum chances of irreversible termination.

Chapter 6

CONCLUSION AND SUGGESTIONS FOR FUTURE WORK

This thesis work was aimed at synthesizing fluorinated amphiphilic block copolymers of 2, 3, 4, 5, 6 - pentafluorostyrene (PFS) and methacrylic acid (MAA) by NMP. Prior to synthesizing block copolymers, poly (PFS-*ran*-MAA) random copolymers were made and the kinetics of the reaction was studied.

The random copolymerizations were characterized as being controlled (defined as a linear increase in M_n versus X) under specific conditions. Unlike other styrenics, it was experimentally determined that a high ratio of PFS (roughly 70%) was needed in the feed to result in a controlled polymerization. The reason for this apparent inefficiency of PFS as the controlling comonomer was identified to be resulting from the unfavourable reactivity ratios of PFS and MAA (r_{PFS} = 0.012 and r_{MAA} = 8.12), which favours the MAA addition over the PFS addition, resulting in irreversible termination. In addition, DSC was used to measure the glass transition temperatures of poly(PFS-*ran*-MAA) copolymers and the general trend was that the T_g values decreased with the addition of PFS in the final polymer.

Owing to the highly difference in reactivity of PFS and MAA, block copolymers were synthesized using one pot semi-batch reactions. Three semi batch reactions were conducted with initial PFS addition and injection of MAA solution at different times at a later stage.

GPC analysis suggests that the semi-batch approach was successful in synthesizing on-pot block copolymers. However, further analysis revealed that irreversible termination of the PFS chain was significant resulting in only a portion of poly(PFS) polymers successfully initiating the MAA monomers. The GPC traces also suggest an increase in oligomer formation upon MAA injection. This increase in oligomer formation is likely due to chain transfer to monomer reactions which result in the uncontrolled formation of poly(MAA) chains that irreversibly terminate. This result presented the importance of the time of MAA injection as it can influence the formation of clear blocks in the final copolymer mixture. The same conclusion can also be inferred from the difference in the final polymer compositions predicted by FT-IR and GPC (Appendix I). The T_g curves obtained from DSC analysis of the final polymers showed two distinct drops for PFS and MAA further suggesting the presence of PFS and MAA containing block copolymers (Appendix I).

The results from the semi-batch reactions have provided enough reasons to believe that they might be the right way to proceed further. But they need further exploration in terms of reducing the problem of irreversible termination. This might involve trying out higher initial concentration of PFS and reacting to a lower conversion or precise optimisation of the time of MAA injection. The addition of MAA solution in small quantities using a syringe pump over the course of the entire reaction can also produce interesting results.

. The ability to make amphiphilic block copolymers with fluorine based monomer provides a stronger and resistive hydrophobic end. This combined with the possibility of obtaining relatively pure and well-defined polymers via NMP is especially attractive to drug delivery and other related applications as it means fewer processing steps and predictable macromolecular architectures. Some other fields of application may include membrane studies and selective ion transfer.

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APPENDICES

APPENDIX I: Definitions and Supporting Information

1. **Random copolymers** are polymers containing more than one monomer repeat unit chemically bonded in a random sequence.
2. **Block copolymers** are polymers containing more than one monomer repeat unit in which each monomer unit is found as a homopolymerized “block” within a polymer chain.
3. **Oligomers** are smaller polymer chains containing between 10 to 100 monomer repeat units.
4. **Living Polymerization** is a polymerization in which the termination of the reaction is controlled by chemically stabilizing the polymer growth chain thus providing control over the polymer architecture and molecular weight distribution. Livingness can be achieved in various ways. Nitroxide mediated polymerization uses stable free nitroxide radicals (SG1 in this case) to achieve it by reversibly terminating the polymer chain.
5. **Reactivity Ratios** are defined as the ratio of reaction of species to its own monomer. Consider two monomers M_1 and M_2 and their corresponding reactive species M_1^* and M_2^*. The reactivity ratios of monomer 1 (**r_1**) and monomer 2 (**r_2**) can be expressed as

$$M_1 + M_1^* \xrightarrow{k_{11}} M_1M_1^* \qquad M_2 + M_2^* \xrightarrow{k_{22}} M_2M_2^*$$

$$M_1^* + M_2 \xrightarrow{k_{12}} M_1M_2^* \qquad M_2^* + M_1 \xrightarrow{k_{21}} M_2M_1^*$$

$$\mathbf{r_1} = k_{11}/k_{12} \qquad \mathbf{r_2} = k_{22}/k_{21}$$

where, k_{11}, k_{12}, k_{22}, k_{21} are the rate constants.

6. **Number average molecular weight (M_n)** is the statistical average molecular weight of all the polymer chains in the sample. It can be expressed as

$$M_n = \frac{\Sigma\, \mathrm{N_i} M_i}{\Sigma\, \mathrm{N_i}}$$

where, M_i is the molecular weight of the single polymer chain and N_i is the number of chains of that particular molecular weight.

7. **Weight average molecular weight (M_w)** is given by,

$$M_w = \frac{\Sigma\, \mathrm{N_i} M_i^2}{\Sigma\, \mathrm{N_i} M_i}$$

In addition to M_n, M_w also considers the effect of molecular weight of the polymer chain. Larger the polymer chain higher the M_w value.

8. **Polydispersity Index / Dispersities (PDI)** is the ratio of weight average molecular weight and the number average molecular weight.

$$PDI = \frac{M_w}{M_n}$$

It is a measure of broadness of molecular weight distribution of a polymer. Higher the PDI value broader the distribution will be. Best controlled polymerizations will have a PDI value closer to 1.0.

9. **The target number average molecular weight** is the theoretical number average molecular weight at 100% conversion. It is calculated based on the monomer to initiator ratio used during the polymerization reactions.

The formula used for the calculation of target M_n values for the PFS/MAA is as follows:

$$Target\ M_n = \frac{W_{PFS} + W_{MAA}}{\frac{W_{NHS-BB}}{MW_{NHS-BB}}}$$

where, W_{PFS} is the weight of PFS used in grams, W_{MAA} is the weight of MAA used in grams, W_{NHS-BB} is the weight initiator used in grams and MW_{NHS-BB} is the molecular weight of the initiator.

10. **The theoretical number average molecular weight** is the product of the conversion obtained (*X*) and the target molecular weight.

11. **Mayo lewis equation** describes how a monomer distributes itself in a polymer. For two monomers M_1 and M_2,

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2]([M_1] + r_2[M_2])}$$

where, the concentrations are marked with the square brackets and r_1, r_2 are the reactivity ratios of monomer 1 and 2 respectively. It can be represented in an instantaneous form in terms of mole fractions f_1 and f_2 as follows:

$$F_1 = 1 - F_2 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2}$$

where, f_1 and f_2 are the initial molar fractions of monomer 1 and 2 in the feed and F_1 and F_2 are the final molar fractions of monomer 1 and 2 in the polymer.

APPENDIX II: Supporting Information

Final composition of poly(PFS)-*b*-poly(PFS-*ran*-MAA) block copolymers:

The final copolymer composition was determined using Fourier transform infrared spectroscopy (FT-IR). Similar to the poly (PFS-*ran*-MAA) copolymers, distinct FTIR traces namely, the carbonyl peak (C=O) at ~1680 cm^{-1} and (C=C) aromatic carbon bond stretch at ~1502 cm^{-1} were used to identify MAA and PFS, respectively. Based on the kinetics and the GPC traces, it would appear that the growth of block copolymers containing a pure PFS block and a mostly MAA second block were synthesized.

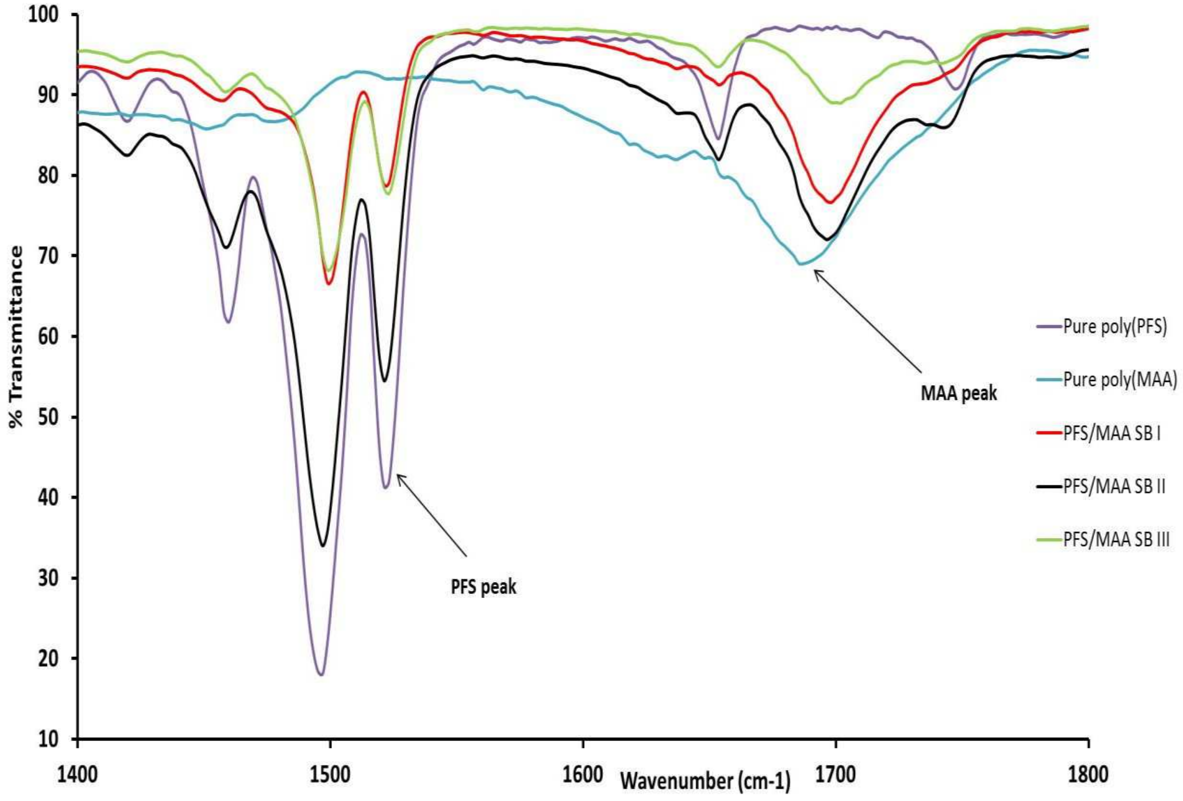

Figure S1: FT-IR spectra for various semi-batch reactions conducted for the synthesis poly(PFS)-*b*-poly(PFS-*ran*-MAA) block copolymers.

Figure S1 illustrates the FT-IR spectra of the final products of PFS/MAA SB I, PFS/MAA SB II and PFS/MAA SB III. The relative intensity of the peaks varied and the difference in the peak heights were compared to a calibration curve built (Figure 4.4.B) in a similar manner to that was explained previously in Chapter 4. The final copolymer composition values (F_{PFS}) obtained using this method is found in Table 5.2.

As a comparison, the copolymer composition was estimated from GPC analysis. By knowing the M_n of the poly(PFS) at the point of semi-batch injection and assuming the second block is purely poly(MAA) we could estimate $F_{PFS,GPC}$ (Table 5.2). It would appear that $F_{PFS,FTIR}$ values increase for the semi-batch addition where the final PFS composition was greater than the final PFS composition of the random copolymers. This observation is consistent with the fact that the poly(PFS) chains have a chance to grow prior to the MAA addition which is highly favoured. For similar initial molar feed composition of $f_{PFS,\ 0} = 0.5$; $F_{PFS,\ block} = 0.20$ for the semi batch addition while $F_{PFS,} = 0.12$ was obtained for the simple batch copolymerization. It is important to note however that, as mentioned in the previous section, the sample includes not only the irreversibly terminated poly(PFS) chains but also the presumed poly(MAA) oligomers effecting the $F_{PFS,GPC}$ and $F_{PFS,FTIR}$ values (Figure 5.3). Regardless, the results suggest that the semi-batch reactions can therefore serve as an effective way to increase the fluorine content in the final copolymer which can be useful for certain applications.

Differential scanning calorimetry (DSC) characterizations of poly(PFS)-*b*-poly(PFS-*ran*-MAA) block copolymers:

The block copolymer glass transition temperatures (T_g) were determined using differential scanning calorimetry (DSC). The values of T_g (°C) obtained are tabulated in Table S1. Figure S2 represents a typical T_g curve obtained for the block copolymers synthesised by semi batch reactions. From the GPC traces, it became apparent that the final block copolymer constituted of two distinct homopolymer blocks of PFS and MAA. Since their homopolymer glass transition temperatures are far apart from each other there were two characteristic drops clearly visible on the T_g curve. The MAA drop is much more significant on the curve which is expected as its concentration in the final copolymer is higher than the PFS concentration (Table 5.2).

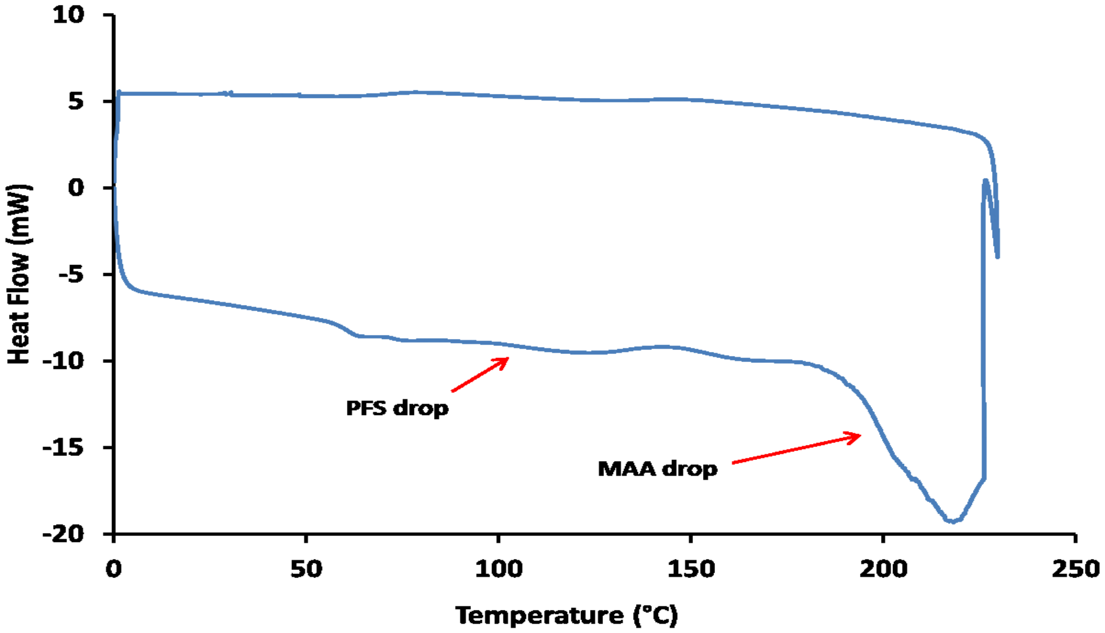

Figure S2: A typical T_g curve for poly(PFS)-*b*-poly(PFS-*ran*-MAA) block copolymers showing two distinct drops representing PFS and MAA blocks. The curve represented here is the T_g plot obtained for the reaction PFS/MAA SB II. The feed contained 50% molar ratio of PFS and MAA and final polymer contained 20% PFS and 80% MAA (Table 5.2) which justifies the significantly larger drop corresponding to MAA.

Table S1: Glass transition temperatures for the poly(PFS)-*b*-poly(PFS-*ran*-MAA) block copolymers obtained from differential scanning calorimetry (DSC).

Experiment ID [a]	$T_{g,PFS}{}^{b}$	$T_{g,MAA}{}^{b}$
PFS/MAA SB I	100	211
PFS/MAA SB II	109	201
PFS/MAA SB III	98	195

a) Experiment Id = is the experimental identification where PFS = 2,3,4,5,6-pentafluorostyrene, MAA = methacrylic acid, NHS-BB = NHS-BlocBuilder, SB # = semi-batch and the experimental number.

b) $T_{g,PFS}$ = Glass transition temperature for the 2,3,4,5,6-pentafluorostyrene homopolymer block.

c) $T_{g,MAA}$ = Glass transition temperature for the methacrylic acid homopolymer block.