CHARACTERIZATION OF COMPLEX POLYMERS OF POLY(STYRENE) AND POLY(ACRylATE) BY THERMAL FIELD-FLOW FRACTIONATION WITH LIGHT SCATTERING AND OTHER DETECTION

by

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ABSTRACT

Polymers are an important class of materials, with applications in medicine, construction, personal care, textiles, safety, packaging, and still other fields. Their properties are derived from their chemical compositions and architectures. Advances in their synthesis have led to chemical compositions of more than one component in various arrangements and architectures that yield configurations that go beyond linear polymers to form stars, bottlebrushes, rings, dendrimers, pom-poms and others.

The large sizes of polymers pose special challenges for characterization which are further complicated by the variations in sizes of polymers. Issues with the workhorse approach in polymer characterization, size-exclusion chromatography (SEC), such as its effective range, propensity to reduce sample recovery, the risk of shearing polymers apart, and its significant cost are addressed by thermal field-flow fractionation (ThFFF). In this work, other limitations such as its non-selectivity for polymer composition and the need for linear standards are more deeply investigated and addressed by ThFFF.
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CHAPTER 1

INTRODUCTION

Polymers are an important class of materials selected for applications because of their properties for engineering applications\(^1\)–\(^\text{4}\) and their chemical features.\(^5\)–\(^\text{9}\) The far-reaching applications of such polymers cannot be understated and include packaging materials,\(^\text{10},\text{11}\) adhesives,\(^\text{9},\text{12}\) optics,\(^\text{11,13,14}\) architectural coatings,\(^\text{15–17}\) therapeutic drugs,\(^\text{8}\) medical imaging adjuncts\(^\text{8}\) and textiles.\(^\text{18–20}\) These materials are often synthesized as linear chains of the same small chemical unit but, it is possible to introduce architectural traits like branching\(^\text{21–26}\) and chemical units of different chemistry.\(^\text{5,27–30}\) Polymer size, chemical composition, and architectural traits increase the complexity of the system and allow for tuning of the overall function of the polymer. The performance of a given material depends on the level of control applied in its synthesis, the size, the number and kind of architectural traits present, the ratio of chemical monomers used in synthesis, and the presence of dispersity in any of these traits. Additionally, when more than one chemistry is used, the arrangements of the monomer units will affect polymer performance. For example, a diblock copolymer (two domains comprised each of a unique repeating unit) comprised of half styrene, half ethylene repeat units will behave differently than an alternating copolymer of the same composition. Accurate characterization methods are needed to identify the nature of these traits in a given polymer sample and to understand their effects on material performance.

Many methods of characterizing polymers exist, and one of the primary focuses of chapter two is to give an overview of the polymer characterization approaches available. These approaches include nuclear magnetic resonance, mass spectrometry, several chromatographic approaches, and multiple detector options to go with these chromatographic approaches. These
methods and detection are potentially selective for or sensitive to differences in the polymer composition, architecture, and size, and make them excellent options when trying to address samples that are more complicated than linear polymers of known, uniform composition with linear standards available for reference.

Chemical separations are an especially useful approach to determining polymer traits, as they can yield a sense of the distribution of properties within a sample. Gel permeation chromatography (GPC) is the workhorse separations method for polymer characterization. It yields size-based separation based on the interactions of dissolved polymers with a porous stationary phase. Larger analytes cannot sample the pore volumes as easily as smaller analytes, and a separation order is obtained going from largest to smallest. GPC is not sensitive to differences in the chemical composition of polymers, but the introduction of architectural traits will reduce the overall size of the polymer and increase its retention in the column. Additionally, SEC introduces shear stress, and its size range is limited by the selected column or columns for the separation. For these reasons, GPC is not ideally suited to the determination of changes in the polymer composition, the presence of architectural traits in polymers, or the determination of mass for polymers that lack linear standards of the same composition.

The aforementioned limitations are particularly problematic when dealing with characterization needs centering around polymers of unique composition, of large size, or of such high branching that concerns of shearing the polymer apart arise. This thesis particularly highlights thermal field-flow fractionation (ThFFF) as a means of characterizing polymers for their compositional polydispersity and architectural traits. ThFFF separations occur in an open channel. This physical difference from packed chromatography columns makes it much easier to analyze samples of very high molecular weight (> 10^6 Da) as there is a lower risk of sample
adsorption to the separation media and lower shear. A detailed explanation of the Soret coefficient and thermal diffusion is provided in chapter three and emphasizes the advantages of ThFFF over other polymer characterization techniques.9,27,37–40

It is particularly difficult to characterize composition distribution in polymers of three or more chemical components. Chapter four presents the first work ever completed to characterize composition distribution in a triblock terpolymer.37 ThFFF introduces the ability to separate based on a combination of the polymer size and its chemical composition because separation occurs on the basis of the Soret coefficient ($S_T$), the ratio of the thermal diffusion coefficient (which is dependent on the polymer and the solvent composition) to the translational diffusion coefficient (which is dependent on the polymer size). Elution occurs with polymers of lower $S_T$ eluting earlier and polymers of greater $S_T$ eluting later. Since retention is dependent on polymer composition, UV absorbance (UV) and differential refractive index (dRI) detector signals could provide the composition of the polymer components eluting at a given time. Fractions were collected, and trends in polymer compositional changes were confirmed by nuclear magnetic resonance (NMR). ThFFF was able to detect an impurity in the triblock terpolymer, specifically, a minor diblock component. The ability to detect this impurity highlights the advantages of a separation technique and the selectivity of ThFFF.

An ongoing difficulty in polymer characterization is the ability to detect the architecture of a polymer sample, and to be able to determine the number and kind of architectural traits present. One class of polymers of interest is bottlebrush polymers, which feature a linear backbone from which several side chains are grown.5,8,41–45 Traits of interest in these polymers include the mass of the polymer, the length of its backbone, the length of the side chains, and the number of branches present on the backbone. All these characteristics are illustrated in Figure
1.1. Chapter 4 expands on prior work done by the Williams research group to characterize the number of chain ends on star-like polymers\textsuperscript{46} to study the dimensions and traits of bottlebrushes comprised of poly(2-bromoisobutyryloxyethyl methacrylate) (PBiBEM) backbones and poly($n$-butyl acrylate). This work takes advantages of the separation mechanism of ThFFF to be able to quantify the length of the polymer’s side chain or backbone when one of these dimensions is known. This is a new development in the characterization of polymers, and can be expanded to polymers of other chemistries, even when linear standards are unavailable for the characterization.

Chapter six concludes this thesis by identifying and explaining the paths forward with this work. It looks at the capabilities of ThFFF developed in this work as a springboard for future characterization abilities.
CHAPTER 2
APPROACHES IN POLYMER CHARACTERIZATION

The complexity of polymers poses unique challenges with respect to their characterization. Numerous methods of polymer characterization have been developed due to the potential for varied masses (polydispersity) in a sample, variations in chemical composition (composition distribution) and differences in architectural traits (architectural distribution). These techniques can be broken down into categories of non-chromatographic (bulk) methods, chromatographic methods and detector technologies for chromatographic methods.

2.1 Non-Chromatographic Methods

Common approaches in polymer characterization involve methods that directly analyze a bulk trait of the polymer. These techniques provide determinations of a polymer’s average properties. Examples of these approaches include nuclear magnetic resonance (NMR), temperature rising elution fractionation (TREF), crystallization analysis fractionation (CRYSTAF) and mass spectrometry (MS).

2.1.1 Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) is one of the most powerful techniques available for determining the chemical compositions and structures of polymers. The methodology has found use for the determination of polymer diffusion coefficient,\textsuperscript{47} composition,\textsuperscript{38,48–52} and architecture.\textsuperscript{23,25,53,54}

The measurement of polymer diffusion is most readily determined by the use of a specially designed probe in an NMR system. The magnetic field used to align the spins of the atomic nuclei is focused on a specific region of the sample tube. The species in the tube are then allowed to move freely within the sample tube. As species migrate and relax, the areas of the probe distal from the
focus of the magnetic field see an increase in relaxation signal. The rate at which this signal changes is monitored and fit to determine the diffusion coefficient of the polymer in solution. The fit is then used to back-calculate the diffusion coefficient of the polymer.\textsuperscript{55}

The diffusion coefficient is useful because it can be converted into a hydrodynamic radius measurement through the Stokes-Einstein equation.\textsuperscript{56} One advantage to measuring diffusion coefficient by NMR is that it is quantitative, direct and has better reproducibility than dynamic light scattering (DLS), another quantitative and direct method.\textsuperscript{57}

NMR has also found extensive use for the determination of copolymer composition.\textsuperscript{48–51} Since the electromagnetic emission of relaxing nuclei in NMR depends on the chemical environment experienced by a given atom, NMR is especially sensitive to the chemical makeup of copolymers. When given sufficient time, it is possible to examine the relaxation of specific signals from monomers to determine the relative quantities of each monomer present in a given polymer system.

Since this sensitivity to chemical environment exists, it is also possible to apply NMR to the determination of branching points in polymers. If a specific initiator for a polymer is detectable, it can be compared to the number of branch points indicated by relaxation signal to obtain a quantity of branches per polymer. This enables determination of the average number of chain ends and polymer architectures.

\textbf{2.1.2 Temperature Rising Elution Fractionation}

Temperature Rising Elution Fractionation (TREF) separates polymers at an analytical or preparative scale by their solubility temperature in a given solvent system.\textsuperscript{58} First, polymers are dissolved in hot solvent. The solution is then loaded onto a column packed with an inert stationary phase, and cooled slowly to room temperature, typically over the course of a few days.
The column is then connected to a system through which the native solvent can flow, and is slowly heated again. This heating causes polymers to become soluble in the solvent, and elute from the column. Outlet detection can be used to monitor the elution of polymers, and fractions can be collected for additional studies.

TREF is particularly useful because it can separate polymers of different physical and chemical structures. Such insights are helpful when trying to understand how physical and chemical structure affect material properties. It has found applications in the studies of polypropylene copolymers,\textsuperscript{58,59} low-density polyethylene,\textsuperscript{60,61} and linear polyolefin copolymers.\textsuperscript{62,63}

2.1.3 Crystallization Analysis Fractionation

Crystallization Analysis Fractionation (CRYSTAF) works in the reverse of TREF, where samples are cooled, and changes in the infrared absorbance of the solution are observed.\textsuperscript{64} It is often used as a step following TREF to find subpopulations within fractions. Changes in the absorbance with respect to temperature show a hysteresis effect within the fraction and indicate the temperature at which the polymers crystallize. CRYSTAF combined with TREF yields a 2D characterization of the overall polymer sample, and has found use in studying short-chain branching,\textsuperscript{65} molecular weight\textsuperscript{66,67} and monomer content in copolymers.\textsuperscript{66–70}

2.1.3 Mass Spectrometry

Mass spectrometry (MS) is frequently used in the characterization of polymers because of its ability to detect polymers across a broad range of masses exceeding 1,000 kDa.\textsuperscript{71} The sensitivity of the technique enables identification of the repeat unit in polymers and can be used to gather information about polymer composition, composition distributions, and polydispersity.
The leading approaches for polymer ionization in MS are electrospray ionization (ESI)-MS and matrix-assisted laser desorption ionization (MALDI)-MS. ESI has a high propensity to produce multiply charged polymers, which allows characterization of high molecular weight polymers through significantly reduced mass-to-charge (m/z) ratio. MALDI typically forms singly charged polymer ions resulting in a simpler mass spectrum than ESI. The challenge with MS is that many common polymers, e.g., polyolefins, are difficult to ionize, and selective ionization can occur when analyzing polydisperse polymers or polymer mixtures. MALDI has been shown to detect up to 1,500 kDa polystyrene, but polymers larger than this are difficult to ionize.

2.2 Chromatographic Approaches

Chromatography separations are the result of a molecule’s interactions with a flowing mobile phase and a stationary phase in a packed column. Analytes that interact more strongly with the mobile phase (or less strongly with the stationary phase) will elute from the chromatography column first. The retention of a polymer can be affected by changing the flow rate of the mobile phase, the chemistries of the mobile and stationary phases, the pore size of the packing material, and the temperature at which the separation takes place.

2.2.1 Size Exclusion Chromatography

Size exclusion chromatography (SEC) is the workhorse method separations of polymers, and is broken down into two sub-categories, gel permeation chromatography (GPC, for organic-soluble systems) and gel filtration chromatography (GFC, for aqueous-soluble systems). In both cases, a column is packed with a porous material. A mobile phase solvent is pumped through the column carrying with it dissolved polymer sample species that selectively permeate into and out of the pores of the packing material. Different size polymers
spend different amounts of time inside the pores leading to size-based separations. Large polymers spend less time in the pores and have shorter retention times than their smaller counterparts. Each SEC column contains packing material with a specific pore size which in turn dictates the column’s applicable size or MW range.\textsuperscript{80}

SEC is most frequently used to obtain molecular masses of polymers, although this is done through the use of linear standards. The actual separation in SEC occurs on the basis of a polymer’s hydrodynamic size. Overall, masses may range from 100 Da to over 10,000 kDa, but selectivity is limited to less than 0.2 for masses over 50 kDa.\textsuperscript{81} This selectivity is low compared to ThFFF, which has selectivities that increase with mass from 0.4 to near 0.6.\textsuperscript{81} Often, mixtures of polymer masses will require the use of a series of columns with different pore size packing materials to obtain adequate separation resolution. These column sets are expensive, have a limited lifespan, and the packing material can introduce shear forces, breaking polymers into smaller portions and confounding accurate characterizations.

2.2.2 Temperature Gradient Interaction Chromatography

Temperature gradient interaction chromatography (TGIC), also known as thermal gradient interaction chromatography, is a mode of interaction chromatography where the column temperature is controlled to adjust the strength of interactions between the analyte and the stationary phase.\textsuperscript{82} Typically, the temperature starts at a low value and then is increased with time to decrease polymer-stationary phase interactions. This has the effect of sufficiently retaining samples that weakly interact with the stationary phase while speeding up elution of strongly interacting components. TGIC enables effective retention and separation of samples of polydisperse mass,\textsuperscript{82–86} composition distributions,\textsuperscript{87} and varying architectures.\textsuperscript{29,88–92} Architectures include stars and randomly branched polymers, though ultimately the separation
occurs on the basis of polymer mass, making branching most easily characterized with the presence of well-defined branching units. The main drawback with TGIC is the potentially lengthy wait period in between analyses as the column temperatures are returned to the appropriate initial value.

2.2.3 Gradient Polymer Elution Chromatography

In gradient polymer elution chromatography (GPEC) the magnitude of analyte-stationary phase interactions is varied by changing the chemical composition of the carrier liquid.\textsuperscript{93} This technique is most frequently used for separations by chemical composition, although separations based on mass or architecture are possible in theory. As the composition of the mobile phase is changed, the strength of analyte interactions with the column also changes. Most frequently, GPEC has been used for the characterization of composition distributions in copolymers.\textsuperscript{94} The challenge associated with GPEC is the tedious optimization of separation temperature, the chemistry of both the stationary and mobile phases, and the selection of detectors that can adequately handle gradients in the carrier liquid composition.

2.2.4 Liquid Chromatography at Critical Conditions

Liquid chromatography at critical conditions (LCCC) is typically used to characterize block co-polymers\textsuperscript{87} and functionalized branched polymers.\textsuperscript{95–97} Separations in LCCC are optimized to retain a given polymer chemistry while rendering the other blocks of the polymer entropically and enthalpically invisible. For example, a series of polystyrene (PS) – poly(butadiene) (PB) block copolymers could be considered for characterization.\textsuperscript{87} The chemistry of the mobile phase, stationary phase, and the column temperature would be selected to eliminate the effects of the PS block on retention thereby yielding a separation based solely on the size of the PMMA block. This offers insight into the size distribution of the PMMA block.
without regard to the effects of the PS block. Alternately, branched polymers with end groups of a unique chemistry could be retained solely by the number of said end groups, yielding a separation based solely on polymer branching.\textsuperscript{91,95,97}

Similar to the other chromatography techniques, it is difficult to identify the optimized conditions for a given polymer chemistry, frequently requiring adjustments to the stationary phase, mobile phase, and column temperature. Like the other techniques, this approach is frequently trial-based and iterative.

2.3 On-line Detectors for Separations Methods

Detection methods are required to obtain information about polymer components as they elute from the separation column. Additionally, on-line detectors can provide information about a polymer’s properties. Most frequently, these detectors include UV-visible light absorbance (UV-Vis), differential refractive index (dRI), viscometry and light scattering.

2.3.1 UV-Visible Light Absorbance

UV-Visible light absorbance (UV-Vis) is a concentration sensitive detector option for separations based methods. The detector shines light of a known wavelength through a flow cell. The selected wavelength is typically one that is not absorbed by the solvent but is absorbed by the polymer chemistry of interest. For instance, the UV cutoff of tetrahydrofuran (THF) is 230 nm. Wavelengths greater than 230 nm will not be absorbed by the carrier liquid. Styrene absorbs light most effectively at 254 nm. Absorbance of light $A$ can be related to the concentration of a chemical component $c$ and the path length $b$ through which light must travel by the Beer-Lambert law:

$$A = \varepsilon bc$$

where $\varepsilon$ is the extinction coefficient.
2.3.2 Differential Refractive Index

The refractive index of a material describes the ratio of the speed of light in a vacuum to the speed of light in that material. It is possible to measure changes in an eluent’s refractive index through the use of a differential refractometer (dRI). As long as the carrier liquid and analyte have different refractive indices, the dRI will detect eluent. As the detector is sensitive only to changes in refractive index, it is considered a “universal” detector. The change in refractive index with respect to an analyte’s concentration is described by:

\[ dRI = (\frac{dn}{dc})c \]  

where \((dn/dc)\) is the analyte’s increment of refraction and \(c\) is its concentration. Additional terms can be added as other components are added to the polymer, described in more detail in chapter four of this dissertation.

2.3.3 Viscometry

Differential viscometry evaluates changes in the viscosity of a solution by use of a four-capillary bridge viscometer.\(^{33}\) This is represented in Figure 2.1. Eluent enters the viscometer and

![Figure 1.1. Technical schematic of differential viscometer.](image-url)
is split evenly at point C to travel evenly down both paths CA and CB. Along path BD, the
eluent encounters a column that results in a change in the pressure across that path. The
difference is pressures at points A and B gives a difference in pressure while the overall pressure
between points C and D gives an overall internal pressure. These differences enable the
determination of a change in pressure as eluent elutes through the detector. Accurate mass
determination can be obtained through universal calibration, which relates intrinsic viscosity to
polymer mass. This relationship is described by:

$$[\eta] = KM^a$$  \hspace{1cm} (2.2)

in which $[\eta]$ is the intrinsic viscosity, $M$ is the polymer mass, and $K$ and $a$ are both constants.\textsuperscript{98}
The constants are dependent on polymer and solvent chemistry, and may be looked up in
literature sources.

2.3.4 Multi-Angle Light Scattering

Multi-angle light scattering (MALS) is carried out by shining a laser light source on
analytes and detecting the light scattered by the analytes in all directions. The intensity of light
scattering increases with analyte size and concentration.\textsuperscript{99} The effect of concentration is most
readily accounted for by use of an online concentration detector such as UV-Vis or dRI. The
most common way of determining polymer traits through light scattering is by the use of a Zimm
plot,\textsuperscript{100} using the equation:

$$\frac{Kc}{R(c,q)} = \frac{1}{M_w} \left( 1 + \frac{q^2<S^2>_z}{3} \right) + 2A_2c$$  \hspace{1cm} (2.3)

in which $K$ is an optical constant describing the behavior of the light in the system, $c$ is the
analyte concentration, $q$ is the light scattering vector amplitude, $M_w$ is the molar mass of the
dpolymer, $<S^2>_z$ is the root mean square radius, $A_2$ is the second virial coefficient, which
describes the change in scatter intensity with respect to concentration and $R(c,q)$ is the excess
Rayleigh scattering ratio, or the ratio of the intensity of the light scattered to that when only solvent is present in the path of the laser. From this, it is possible to obtain the root mean square radius of the polymer (also called the radius of gyration $r_g$) and its molecular mass. When used in an on-line capacity with a separation technique, MALS provides an orthogonal method for determining the size and mass distributions present in a sample.

2.3.5 Dynamic Light Scattering

Dynamic light scattering (DLS) works similarly to MALS with respect to the concept of examining the intensity of laser light scattered by a species but is different in that it evaluates small changes in the intensity of the light scattered, associated with the movement of the analyte. Smaller analytes have greater translational diffusion, resulting in faster fluctuations in light intensity while larger analytes have smaller translational diffusion and slower fluctuations in light intensity. By looking at the magnitude of these changes through the use of an autocorrelation function, it is possible to determine quantitatively the translational diffusion coefficient of an analyte.$^{55,27,37}$ This can be converted to a hydrodynamic size by the Stokes-Einstein equation. Batch-mode DLS is limited by the need for at least a 2-3 fold difference in hydrodynamic size for different size subpopulations to be discernible and reported. In the on-line mode, the concentrations of the eluting species are often too low to provide sufficiently strong light scattering intensities for accurate size measurements.
CHAPTER 3

THERMAL FIELD-FLOW FRACTIONATION FOR POLYMERS

The separations in this work are completed by thermal field-flow fractionation (ThFFF). Three primary methods of ThFFF exist. The most common are flow field-flow fractionation and sedimentation field-flow fractionation, with ThFFF being less popular as it is less well understood and more difficult than the other two forms.

3.1 General Principles of Normal Mode Separations

Separations by field-flow fractionation take place in an open, ribbon-like channel. A carrier liquid is pumped down the length of the channel at flow rates sufficiently low to generate a parabolic flow profile. An analyte is introduced into the carrier liquid through the use of an injector assembly and is pushed down the length of the channel by the carrier liquid. The position of the analyte across the channel thickness is determined by its interactions with a field as well as its translational diffusion coefficient, $D$. The field applied is up to the instrument designer, and work has been done exploring the benefits of flow, sedimentation, thermal, dielectric, acoustic, magnetic and other fields to obtain a separation. The field applied has implications on the overall retention parameter for the separation. For instance, flow fields yield a separation based wholly on analyte size, whereas a sedimentation field separates based on reduced mass and a thermal field yields a separation based on both chemical composition and size. ThFFF is particularly useful in the characterization of polymers because the movement of a polymer in a temperature field is dependent on the chemical composition of the polymer, the solvent and the magnitude of the field. This movement is called thermal diffusion and is described the thermal diffusion coefficient, $D_T$. Although
theories exist that accurately determine $D_T$ within an order of magnitude of observed values, the overall phenomenon is not well understood and has been the subject of ongoing research.

The applied field drives analytes towards the accumulation wall of a channel, a motion which is countered by the analyte’s translational diffusion. Thus, analytes experiencing weaker thermal diffusion or stronger translational diffusion will sample domains of the channel that are further away from the accumulation wall compared to analytes experiencing stronger thermal diffusion or weaker translational diffusion. This sampling determines which velocities of the parabolic flow profile of the channel are experienced by the analyte, and results in selectivity based on the analyte’s translational and thermal diffusion coefficients. Mathematically, retention is described by:

$$R = \frac{t^0}{t_r} = 6\lambda \coth \left( \frac{1}{2\lambda} \right) - 12\lambda^2$$ (3.1)

$$\lambda = \frac{D}{D_T\Delta T} = \frac{1}{S_T\Delta T}$$ (3.2)

where $R$ is the analyte retention ratio, $t^0$ is the void time or time it takes to elute a complete channel volume, $t_r$ is the retention time of the analyte, and $\lambda$ is the retention parameter, a function of the analyte’s $D$, $D_T$, and the difference in temperature across the channel thickness given by $\Delta T$. The ratio of $D_T$ to $D$ is also described as the Soret coefficient, $S_T$.

It is feasible to obtain $D$ values for analytes by online determinations with dynamic light scattering or calculations using literature sources and measurements of polymer molecular mass. With a determined $D$ and controlled $\Delta T$, it is possible to measure a polymer’s $D_T$.

**3.2 Considerations in Thermal Field-Flow Fractionation Experimental Design**

Several parameters must be considered in the design of a ThFFF experiment. These factors include the design of the channel, the carrier liquid, the magnitude of the field and detectors at the channel outlet.
3.2.1 Channel Design

Many parameters around channel design need to be considered. Although FFF can be performed at the analytic and semi-preparative scales,\textsuperscript{105,106} ThFFF has only been performed on the analytic scale. The long, ribbon-like channel optimally features inlets and outlets that come to a point at a 60° angle just beyond the inlet and outlet holes to minimize sample broadening in the channel. The spacer itself should have a breadth-to-thickness ratio of 30:1 or greater to minimize interactions between the sample and the channel walls. The channel thickness may be reduced to enhance the overall selectivity of the system, although smaller thicknesses require more work on the part of the channel and the recirculating water chiller to obtain comparable $\Delta T$s across the channel thickness. Channel selectivity ($S$) scales with channel length ($L$) as $S \propto L^{0.5}$, so while it is helpful to maximize length, it is a best practice to consider other opportunities to improve channel performance.

3.2.2 Carrier Liquid

When characterizing polymers by ThFFF, the separation is dependent on the interaction of a polymer with a given thermal field. This can be maximized by careful selection of a carrier liquid. Typical solvents for work include methyl ethyl ketone (MEK) and tetrahydrofuran (THF) for this reason. When separations that are sensitive to the polymer composition, it is most helpful to select solvents where the components of the polymer have different $D_T$ values, with greater differences in $D_T$ leading to greater selectivity for a given component. Lastly, it may be worth considering the overall toxicity and cost of the solvents.

Although some ThFFF has been completed in water, it remains a difficult solvent for fractionations. Besides yielding low $D_T$ values, there are also risks of corrosion of the metal walls.
of the channel. Water-soluble polymers are presently regarded as an exceptional case in ThFFF, and other methods of separation such as AF$^4$ or SdFFF should be considered first.

3.2.3 Field Strength

The field strength is what primarily determines the overall selectivity and resolution of a separation by ThFFF. Typical separations should be carried out at $\Delta T = 65 – 85\text{K}$. Separations at lower temperatures may be helpful when seeking to decrease the amount of time a separation takes, especially when working with polymers of high molecular mass.

3.2.4 Detectors

ThFFF is generally compatible with any of the detectors typically used with GPC systems, including MALS, DLS, RI, Viscometer, and UV. DLS is of particular interest because of the separation mechanism in ThFFF. When working with polymers of an unknown or mixed chemistry, DLS enables the online determination of $D$. This can be substituted into ThFFF equations and used to obtain $D_T$ values to determine the composition of a copolymer. Since dRI is regarded as a “universal” detector, it too can be used to obtain information about the overall composition of a polymer. These two measurements combined can be used to determine a polymer’s composition distribution.

3.3 Thermal Diffusion

Separations in ThFFF occur because of the movement of the analytes in a temperature field. This phenomenon is called thermal diffusion. Thermal diffusion is different from convection in that convection is movement due to heat rising and thermal diffusion is movement through a gradient of temperatures, often towards colder regions. One way that convection is avoided in ThFFF channels is by heating from above and cooling from below.$^{107}$ Although thermal diffusion has been observed for quite some time,$^{108}$ a quantitative explanation of the
phenomenon remains elusive. This section explains the various methods of measuring thermal diffusion as well as the theories which explain thermal diffusion.

3.3.1 Determination of Thermal Diffusion Coefficients

Besides ThFFF, there are four major methods of measuring thermal diffusion: Soret cell, beam deflection, and thermal diffusion forced Rayleigh scattering. Each method operates on the principle of generating a temperature gradient and then studying the movement of species in the field.

3.3.1.1 Soret Cell

The simplest and classical approach to measuring the Soret coefficient is by use of the Soret cell. The Soret cell consists of a chamber where one wall is held at a constant temperature, and its opposite wall is held at a different constant temperature, generating a temperature gradient. The greatest challenge associated with the Soret cell is the inability to observe what is actually happening within it. Some approaches have included windows which can be opened to access analytes in the cell, but this is difficult to achieve with accuracy.

3.3.1.2 Beam Deflection

One way of avoiding the need to open the Soret cell is by use of the beam deflection technique. The approach is same as that of the Soret cell, with the exception that transparent walls are placed perpendicular to the temperature-controlled surfaces. This enables a laser beam to be shined through the cell. When no temperature gradient is applied, the laser will travel horizontally. With the application of a temperature field, the analytes will migrate, creating a field of refractive indices, bending the laser. The degree of change in the direction of the laser beam can be associated with the movement of the analyte and be used to calculate the thermal diffusion coefficient.
3.3.1.3 Thermal Diffusion Forced Rayleigh Scattering

Thermal diffusion forced Rayleigh scattering (TDFRS) uses light to generate the temperature gradient instead of heated surfaces. A laser beam is split and then focused to create a grating. A dye capable of absorbing the light is added and heats in areas of high light intensity. An additional laser is then shined through the system, which measures the change in refractive index of the system. One advantage of TDFRS is that measurements occur very quickly, on the order of milliseconds, although they must be repeated many times and then averaged.

3.3.2 Thermal Diffusion Theories

Thermal diffusion theories are typically rooted in evaluating how a given molecule interacts with its surroundings. For polymers, this may be evaluated by looking at solubility parameters, which describe compatibility between the polymer and the solvent, or its Hamaker constants, which describe Van der Waals interactions. These are used as the basis of the thermal diffusion theories described by Schimpf and Semenov, Würger and Mes.

3.3.2.1 Schimpf and Semenov

Schimpf and Semenov approach thermal diffusion as a result of the generation of an osmotic pressure gradient by the temperature field in the channel.\textsuperscript{110,111} Their work led to the generation of Equation 3.3:

\[ D_T = \frac{-8\alpha_T r_m^2 A}{27\eta v_0} \]  

(3.3)

In Equation 3.3, \( \alpha_T \) is the solvent thermal expansion coefficient (change in molar volume with respect to temperature), \( \eta \) is the solvent viscosity, \( r_m \) is the monomer radius, \( v_0 \) is the solvent specific volume, and \( A \) is the Hamaker constant. From this work, it can be seen that thermal diffusion will increase with stronger Van der Waals interactions. One important assumption in
this work is that the magnitude of thermal diffusion is independent of polymer mass and allows 
the polymer in solution to be treated like a whole particle.\textsuperscript{111}

3.3.2.2 Würger

By comparison to Schimpf and Semenov, Würger considers that at lower molecular 
weights thermal diffusion is observed to depend on mass.\textsuperscript{112} This yields the treatment:

\[ D_T = \frac{\beta \varepsilon_p}{6 \pi \eta a} - \frac{\beta \varepsilon_s + (\varepsilon_s - \varepsilon_p)/T}{\kappa \eta R} \] (3.4)

where $\beta$ is the thermal expansivity of the solvent, $\varepsilon_p$ describes the energy of a bead of polymer, $\varepsilon_s$ describes the energy of solvent, $\kappa$ is a constant, $R$ is the ideal gas constant and $a$ is the radius of a 
solvent molecule. As the number of beads in the polymer chain is increased, the magnitude of the 
second term continuously decreases until it becomes zero for an infinitely long chain. In this 
case, the remaining $\varepsilon_p$ is the same as the Hamaker constant $A$ from Equation 3.3, and the 
equations are quite similar to each other.

3.3.2.3 Mes

By contrast to the previously described approaches, Mes\textsuperscript{113} considered thermal diffusion 
as resulting from changes in the chemical potential with respect to temperature and further 
predicted that the overall thermal diffusion coefficient could be predicted from changes in the 
enthalpic portion of the Flory-Huggins polymer interaction parameter ($\chi$). This resulted in 
Equation 3.4:

\[ D_T = \phi^2 D_{\text{seg}} \frac{T}{T} \frac{\partial^2 T^2 (\frac{\partial \chi}{\partial T})}{\partial T} \] (3.4)

In the above equation, $\phi$ is the solvent volume fraction, and $D_{\text{seg}}$ is the diffusion 
coefficient of a single monomer in the polymer chain. This theory tends to produce the most 
accurate predictions of thermal diffusion coefficient.\textsuperscript{39}
CHAPTER 4

SEPARATION AND COMPOSITION DISTRIBUTION DETERMINATION OF TRIBLOCK COPOLYMERS BY THERMAL FIELD-FLOW FRACTIONATION

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Abstract

Thermal field-flow fractionation (ThFFF) is used to separate a linear triblock copolymer of polystyrene, poly(\textit{tert}-butyl acrylate), and poly(methyl methacrylate) by composition. Fractions were collected and subjected to off-line NMR analysis. The resultant mole fraction versus retention time plots for each of the three polymer components confirmed the success of the separation and yielded the composition distribution of the copolymer. The composition distribution was also obtained using a second approach that involved solving a series of equations comprised of polymer thermal diffusion coefficients and quasi-elastic light scattering (QELS), differential refractive index (dRI), and UV detector responses. Both sets of data showed similar trends of composition variations in each polymer component as a function of retention time. However, discrepancies were observed in the mole fraction values. The ability to compositionally separate and to determine composition distribution of copolymers is important as demonstrated by the presence of diblock impurities in the ThFFF with off-line NMR results.

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4.1 Introduction

Terpolymers are comprised of three different monomers with each imparting its unique properties to the resulting copolymer. An example is acrylonitrile-butadiene-styrene (ABS) which is commonly used for manufacturing products that can be extruded or injection molded, e.g., medical devices and automotive components. This versatile thermoplastic polymer’s heat resistance arises from the acrylonitrile component, impact resistance from the butadiene, and glossy surface from the styrene\textsuperscript{114}. Slight variations in relative proportion of monomers in the synthesis step can significantly change mechanical and physical properties of the resultant ABS terpolymer. Chemical composition, molar mass, and microstructure averages and distributions are some of the important parameters that need to be determined.

Analytical methods that are used to characterize polymers can be differentiated into two categories depending on whether they measure average values only or also provide information about distributions. The former includes ensemble methods such as NMR\textsuperscript{48} and light scattering\textsuperscript{34} while the latter is dominated by separations-based methods. Size exclusion chromatography (SEC) is the workhorse technique for polymer analysis\textsuperscript{38,34}. The separation is based on the hydrodynamic size of the polymer and the pore size of the SEC column and is hence solvent and column dependent\textsuperscript{31}. Calibration curves relating molar mass (MM) to retention time are established using polymer standards. This is a problem if standards are not available for the polymer of interest, a situation often encountered for complex polymers. The requirement for existing polymer standards also applies to other techniques such as flow field-flow fractionation (flow FFF)\textsuperscript{115}. This problem is readily resolved for linear homopolymers by using on-line detectors that measure the absolute molecular mass of polymers as they elute from the column. Multiangle light scattering (MALSS)-differential refractive index (dRI) detectors are now
frequently coupled to separation devices that measure the MM of eluting polymers and to
determine the average MM and MM distributions\textsuperscript{27,34,116}.

The analysis of copolymers has the additional dimension of composition determination.
Separation methods that have been shown to be useful for polymer composition analyses include
liquid chromatography at critical conditions (LCCC)\textsuperscript{50}, gradient polymer elution chromatography
(GPEC)\textsuperscript{117}, and temperature gradient interaction chromatography (TGIC)\textsuperscript{118}. These methods
require the use of polymer standards or size or composition sensitive detection. All three
methods control retention levels through the balance between enthalpic and entropic interactions
between the polymer and the stationary and mobile phases. This balance can be shifted by
varying the mobile phase composition and temperature. In LCCC, the mobile phase composition
and column temperature are selected to render one component of the copolymer essentially
“invisible” to the system causing retention to be based on the other component. LCCC with on-
line NMR has been used to separate polystyrene-block-polyisoprene copolymers according to
block length and to determine block length distributions\textsuperscript{50}. GPEC is performed by shifting the
mobile phase composition from a relatively poor solvent (which causes polymer retention) to a
relatively good solvent (which eventually causes a critical-condition state for the polymer and
hence elution)\textsuperscript{119}. GPEC was recently expanded to work under size exclusion conditions for the
measurement of the chemical composition distribution of poly(methyl methacrylate-stat-
methacrylic acid)\textsuperscript{117}. The main drawback to LCCC and GPEC is the lack of theory for solvent
selection. While one solvent should be “good” and the other “poor” for one component of the
copolymer, the optimization of mobile phase composition and column temperature is tedious and
requires an experimentally iterative process\textsuperscript{120}. Furthermore, an assortment of copolymers with
different MM “invisible” blocks can co-elute and complicate the determination of polymer
composition by LCCC. Like LCCC and GPEC, TGIC separates polymers by controlling the relative contributions of enthalpic and entropic interactions. In this case, the temperature of the column is increased over the duration of the run\textsuperscript{86}. This allows different composition copolymers to experience critical conditions and elute at different times. TGIC has been used to quantify the impurities present in H-shaped polybutadienes and explain variations in sample viscosities\textsuperscript{118}. The analysis time is usually greater than GPEC because the column needs to be re-equilibrated to the lower initial temperature before starting the next analysis.

Field-flow fractionation (FFF) is a family of separation techniques with capabilities that complement those of chromatography\textsuperscript{121–123}. FFF’s open channel design and subsequently low shear rates make it ideally suited for analyzing high and ultrahigh molar mass polymers\textsuperscript{124}. Microgel-containing samples can also be characterized and information simultaneously obtained about the size of the microgels and the MM of the soluble polymer\textsuperscript{9,40,104}. The two FFF techniques that have been used for polymer analyses are flow FFF and thermal FFF. The former has been used predominantly in applications with aqueous carrier liquids and the latter with organic solvents. Flow FFF separates polymers according to their diffusion coefficients or hydrodynamic size. Thermal FFF possesses additional capabilities such as sensitivity\textsuperscript{27,51,74} to polymer composition and is discussed in further detail below.

The thermal FFF channel in Figure 4.1 shows a hot wall and a cold wall that sets up the temperature gradient which supplies the driving force to move analytes towards a sample accumulation wall. The motion of materials in the presence of a temperature gradient is termed thermophoresis and its magnitude is represented as a thermal diffusion coefficient $D_T$. A concentration gradient perpendicular to the flow stream is thereby created, where the thermophoresis is balanced by normal diffusion acting to drive analytes away from the high
concentration region at the accumulation wall to less concentrated regions at rates dependent on their normal diffusion coefficients $D$. Depending on the $D_T/D$ ratio, different polymers will occupy different velocity streamlines and will elute at different times. The equation for retention time, $t_r$, for thermal FFF is

$$t_r = \frac{D_T \Delta T \rho^0}{6D}$$

(4.1)

where $\Delta T$ is the temperature difference between the hot and cold walls, and $\rho^0$ is the void time. To reduce retention times, $\Delta T$ can be decreased across the duration of a run – high initially to obtain a separation, then low to allow faster elution. Such operations do not allow the analytic use of the above equation. The distorted parabolic flow profile shown in Figure 4.1 takes into account the variation in viscosity caused by the temperature gradient.

Thermal FFF can be used to separate polymers of the same composition by their molar mass (Figure 4.2a). Since $t_r$ is inversely proportional to $D$, low MM polymers elute first. A number of ThFFF studies have established that $D_T$ is usually independent of MM and so $D_T$ does not affect the separation of a series of polymers having the same composition. However, $D_T$
is dependent on the polymer-solvent combination. This means that the choice of solvents is important and composition-based separations are possible. Figure 2b shows the baseline separation of two different composition homopolymers with similar $D$ but different $D_T$. This separation demonstrates that composition and $D_T$ are correlated. Extending beyond homopolymers to copolymers, the measurement of $D_T$ can give information about relative polymer composition. In this case, the measured $D_T$ is expected to be an average of individual $D_T$ contributions from each monomer of the copolymer. For random copolymers

$$
(D_T)_{A-B-C} = a(D_T)_A + b(D_T)_B + c(D_T)_C \tag{4.2}
$$

where A, B, and C represent three different polymers and a, b, and c are their respective mole fractions. Equation 4.2 applies to both selective and nonselective solvents provided the solvent is thermodynamically favorable for all polymer components. Molar mass distributions (MMD) and chemical composition distributions (CCD) of \textit{polystyrene-co-poly(n-butyl acrylate)} and \textit{polystyrene-co-poly(methyl acrylate)} diblock copolymers have been determined using ThFFF

Figure 4.2 a. ThFFF fractograms of PS standards of different molar masses. b. Separation of 123 kDa PS and 32.7 kDa PMMA with comparable diffusion coefficient ($D_{PS} = 1.04 \times 10^{-6}$ cm$^2$s$^{-1}$, $D_{PMMA} = 9.02 \times 10^{-7}$ cm$^2$s$^{-1}$). Both separations were done in THF with $\Delta T = 80.0$ K and flow rate = 0.1 mL/min.
coupled with multiangle light scattering, differential refractive index and quasi-elastic light scattering (MALS-dRI-QELS) detection\textsuperscript{27}. This combination of detectors allowed on-line determination of $D$, $D_T$, and concentration of copolymers eluting from the ThFFF channel.

The CCD determination of terpolymers or triblock copolymers is a challenging analysis\textsuperscript{125}. Traditional NMR provides an average composition, but not the distribution, unless coupled with a separations technique such as ThFFF\textsuperscript{51}. SEC requires terpolymer standards of known MM, but yields no chemical information. The application of LCCC, GPEC, and TGIC will be complex and perhaps not practically feasible. The thermal FFF work reported here builds on our prior work with diblock copolymers. The objective of this present work is to demonstrate that ThFFF with multiple detectors (QELS-dRI-UV) can be used to obtain the average composition of a terpolymer. Results are confirmed by collecting fractions as they elute from the ThFFF channel with NMR analysis of each fraction.

4.2 Experimental

This section describes the materials, instrumentation and data analysis performed in the completion of this work.

4.2.1 Materials

A linear poly(styrene) standard of 123 kDa weight average molecular weight ($M_w$) and polydispersity index (PDI) = 1.08 was obtained from Pressure Chemical Company (Pittsburgh, PA, USA). A linear atactic poly(methyl methacrylate) standard with $M_w$=151 kDa, PDI=1.09, a linear poly(tert-butyl acrylate) standard with $M_w$=282 kDa, PDI=1.2; and a linear triblock copolymer of poly(styrene)-poly(tert-butyl acrylate)-poly(methyl methacrylate) (PS-PtBA-PMMA) with number average molecular weights ($M_n$) of 18.6, 64.3, and 22.1 kDa respectively (mole fractions are 0.177, 0.612, and 0.210 respectively), were obtained from Polymer Sources,
Inc. (Dorval, Quebec, Canada). This terpolymer was selected for this work because it is a readily available and well characterized commercial standard. HPLC-grade tetrahydrofuran (THF) and methyl ethyl ketone (MEK) were obtained from Avantor Performance Materials, Inc. (Phillipsburg, NJ, USA). HPLC-grade acetonitrile (ACN) was obtained from Sigma-Aldrich (St. Louis, MO, USA).

4.2.2 Instrumentation

A model TF2000 ThFFF channel (Postnova Analytics, Salt Lake City, UT, USA) was connected to a Dawn EOS multiangle light scattering (MALS)-quasi-elastic light scattering (QELS) detector, an Optilab DSP differential refractive index (dRI) detector (all from Wyatt Technologies, Santa Barbara, CA, USA) and a Model 757 UV-Vis detector (Applied Biosystems, Carlsbad, CA, USA). The QELS fiber optic cable was positioned at an angle of 38° from the incident light from the laser source in the MALS instrument. Light collection at a low detector angle has been shown to reduce the contribution of angular-dependent scattering from higher MM sample components and minimize error in $D$ values$^{115}$. Multi-angle light scattering (MALS) data was collected simultaneously with QELS data due to the design of the instrument. Although MALS is frequently used to measure the molar mass of analytes, this is dependent on the assumption that the analyte is homogeneous and interacts only with itself and the solvent. In the case of a block terpolymer, interactions between the separate blocks and selective solvent enrichment at the draining outer shell of the polymer add complicating factors to the interpretation of the light scattering signal$^{126}$. (A polymer with an outer shell that is enriched with one solvent will have a different $dn/dc$ than a polymer surrounded equally by both solvents of the binary mixture. This phenomenon can be avoided if isorefractive solvents were used.) Hence, the MALS detector response was not used and MM information is not reported.
The ThFFF channel consisted of a 127 µm polyimide spacer that was 2.0 cm in breadth and 45.6 cm tip-to-tip length. Carrier liquids were MEK, THF, or 50/50 v/v THF-ACN pumped through the channel at a flow rate of 0.4 mL/min. The \( \Delta T \) used to retain polymer samples for characterization of \( D_T \) and fractionation of the triblock sample ranged from 50–100 K. A JEOL 500 MHz liquid state NMR (JEOL USA Inc., Peabody, MA, USA) was used to determine the triblock composition in deuterated chloroform. Detectors were connected to the channel in series with interdetector delay times determined by injection of low-polydispersity polystyrene.

### 4.2.3 Data Analysis

Three equations are needed to solve for the three unknown compositions of the triblock polymer. The first equation involving mole fractions is

\[
a + b + c = 1
\]  
(4.3)

The second equation takes the form of

\[
\left( \frac{dn}{dc} \right)_{A-B-C} = a \left( \frac{dn}{dc} \right)_A + b \left( \frac{dn}{dc} \right)_B + c \left( \frac{dn}{dc} \right)_C
\]  
(4.4)

In Eq. 4.4, the \( (dn/dc) \) is used in units of \( (\text{cm}^3 \text{ mol}^{-1}) \) rather than \( (\text{cm}^3 \text{ g}^{-1}) \), allowing the use of mole fraction coefficients for a, b, and c. The third equation is Eq. 4.2 relating the copolymer \( D_T \) to the mole fractions. The thermal diffusion coefficient \( D_T \) is calculated from Eq. 4.1. The average terpolymer composition is determined from the value of \( D_T \) of the polymer at peak maximum and the average \( D \) measured by batch mode QELS. Determination of terpolymer composition distribution on the other hand requires the measurement of \( D \) and concentration as a function of \( t_r \). The former is accomplished by on-line QELS and the latter by dRI and UV detectors. The relationship between the measured detector response and the concentrations of each polymer component in the eluting terpolymer are:

\[
(dRI)_{A-B-C} = a' \left( \frac{dn}{dc} \right)_A + b' \left( \frac{dn}{dc} \right)_B + c' \left( \frac{dn}{dc} \right)_C
\]  
(4.5)
and

\[(UV)_{A-B-C} = a'\epsilon_A\]  \hspace{1cm} (4.6)

In equations 4.5 and 4.6, \(a', b', \text{ and } c'\) represent the molar concentrations of PS, PtBA, and PMMA, respectively and \(\epsilon\) is molar absorptivity. As only PS absorbs UV light at 254 nm, only one term is necessary for equation 4.6. The third equation used to obtain concentration is equation 2, modified here to use molar concentration instead of mole fraction

\[(D_T)_{A-B-C} = \frac{a'(D_T)_A + b'(D_T)_B + c'(D_T)_C}{a' + b' + c'}\]  \hspace{1cm} (4.7)

To obtain composition distribution, \((D_T)_{A-B-C}\) is calculated for different retention times using Eq 4.1. Solving equations 4.5-4.7 for different \(t_r\)s, yields molar concentration distributions of PS, PtBA, and PMMA. Mole fraction distribution is then calculated by taking the individual concentration of a given component and dividing it by the sum of the concentrations of all three components.

4.3 Results and Discussion

The following section is a description of the results and discussion. Topics include carrier liquid selection, the determination of mean terpolymer composition, the ThFFF separation and the determination of terpolymer composition distribution. The choice of solvent to be used as the carrier liquid is critical to the success of the ThFFF analysis. Previous publications have shown that the magnitude of \(D_T\) for a particular polymer can vary significantly depending on the solvent\(^{115,120}\). In the extreme case where \(D_T\) is zero, the polymer will not be retained. THF, MEK, and ACN are commonly used solvents in ThFFF analyses. All three solvents could solubilize and retain the terpolymer sample as shown in Figure 4.3. The different retention times are due to
variations in $D_T/D$. THF was the carrier liquid used for ThFFF with off-line NMR (although MEK and ACN would have also been suitable). Of note is the better quality signal obtained from using ACN, which can be attributed to the higher $D_T$ giving better fractionation. In working with multi-detector systems, sample and solvent compatibility with each detector must also be considered. MEK has a UV absorbance cutoff at 329 nm and is thus unsuitable for use with a UV detector. THF is a good solvent for PS, PtBA, and PMMA but the low $dn/dc$ values for PMMA and PtBA in THF cause low QELS intensities and subsequently unreliable $D$ values (unpublished results). ACN yielded excellent retention of the PS-PMMA-PtBA terpolymer and enhanced QELS signal as PMMA and PtBA have higher $dn/dc$ values in this solvent. However, polystyrene homopolymer is insoluble in pure acetonitrile and the measurement of $dn/dc$ and $D_T$ is thus not possible. Taking into consideration the detectability and compatibility of the polymers in each solvent, a 50/50 (v/v) binary solvent consisting of THF and ACN was selected as the carrier liquid for ThFFF with QELS/dRI/UV detection. This represented a good

Figure 4.3 Fractionation of triblock terpolymer: in THF (red) $\Delta T = 109.0$ K, temperature at cold wall $T_{cw} = 309.6$ K; in MEK (blue), $\Delta T = 100.5$ K, $T_{cw} = 309.2$ K; in ACN (black), $\Delta T = 24.9$ K, $T_{cw} = 292.1$ K. In all cases channel flow rate = 0.4 mL/min.
compromise between enhanced scattering for QELS and adequate solubility of all three polymer components.

It should be noted that the use of binary solvents is not without its complexities. Prior works have shown that solvent partitioning occurs in the presence of temperature gradients and can result in enrichment of a solvent by up to 20% at a given ThFFF channel wall\textsuperscript{101}. If this enriched solvent is also the preferred solvent for the polymer, there will be an additional contribution to $D_T$ from thermophoresis of solvent molecules\textsuperscript{104,127}. In other words, the apparent $D_T$ determined for each pure polymer component in the ACN/THF binary solvent incorporates both polymer and solvent thermal diffusion. If the terpolymer is affected in the same manner as the individual polymer components, the contribution of solvent thermophoresis to the apparent $(D_T)_{A-B-C}$ and the apparent $D_T$s of the individual polymers will be similar. In which case, solvent thermophoresis would not have a large impact on the characterization of polymer composition by ThFFF. The use of binary solvents to enhance polymer retention remains an interesting and rich area for future experimental and theoretical studies.

4.3.2 Determination of Mean Terpolymer Composition

The average composition of the PS-PtBA-PMMA terpolymer was determined in the following manner. First, $D_T$ was determined for the terpolymer and each constituent homopolymer standard. This was accomplished by substituting values for $t_r$ at peak maximum and QELS batch mode $D$ for each polymer into Eq 4.1. For example, a measured $t_r$ of 13.0 min (in MEK, $\Delta T$ of 100K), $D$ of $6.29 \times 10^{-7}$ cm$^2$s$^{-1}$, and $t_0$ of 3.47 min, yielded a $D_T$ of $1.42 \times 10^{-7}$ cm$^2$s$^{-1}$K$^{-1}$ for the terpolymer. In the second step, the $dn/dc$ of the terpolymer and each homopolymer were measured by direct injection of different concentrations into the dRI. By solving equations 4.2-4.4, the average mole fractions for PS, PtBA, and PMMA were found to be
These ThFFF results are not in agreement with the nominal composition reported by the polymer manufacturer of 0.20, 0.56, and 0.24, respectively. The discrepancy is likely due to the manufacturer’s use of an SEC calibration curve established with polystyrene standards. Polymers of the same molecular weight but different compositions will likely have different hydrodynamic sizes. NMR analysis of the unfractionated terpolymer yielded average mole fractions of 0.29 PS, 0.38 PtBA, and 0.34 PMMA which are in good agreement with ThFFF.

4.3.3 Thermal FFF Separation and Determination of Terpolymer Composition Distribution

The ThFFF dRI fractogram of the PS-PtBA-PMMA terpolymer exhibits a single broad peak (Figure 4.4). Retention in Figure 4.4 should not be compared to retention in Figure 4.3 due to different operational conditions. The overlaid $D$ values were measured on-line and the decreasing trend with increasing $t_r$ confirms that a successful size separation was achieved. $D_T$ was calculated as a function of time and showed a slight increase with increasing $t_r$. Although the change in $D_T$ appears to be small, this does not suggest the composition of the polymer is unchanging. From Equation 4.2, it is apparent that different mole fraction combinations can yield the same $D_T$. The noisy $D_T$ data observed on the two ends of the fractogram are likely a result of low concentrations of polymers giving inadequate light scattering intensities to obtain reliable $D$ and $D_T$ values. The composition distribution of the terpolymer was determined from $D_T$ values as outlined in the Data Analysis section. This distribution can be represented as the concentration or mole fraction of each polymer component eluting as a function of retention time. Concentration plots for the three polymer components are overlaid as shown in Figure 4.5a. Three distinct curves are observed, each of which generally follows the elution profile of the terpolymer. PtBA is present in the highest concentration and PS having the lowest
concentration. PS has a much cleaner signal because its mole fraction is determined directly from the UV response at 254 nm whereas PtBA and PMMA mole fractions are determined from $D_T$ values which are calculated from noisy QELS measurements of $D$. Mole fractions versus $t_r$ plots are shown in Figure 4.5b. Lines are drawn through the PtBA and PMMA data to help guide the eye. These results are qualitatively consistent with the average mole fractions reported in Section 4.3.2 in that PtBA is the primary component and PS is the minor component. The PS curve exhibits a steep decrease at the early retention time (4.5 to 5 min) where lower MM polymers elute. Since PS is the starting block from which PtBA and then PMMA is grown, the drop in PS mole fraction may signify the presence of polymer that is mainly PS. When PtBA is first added on, the PS mole fraction will experience a large decrease. As more PtBA is attached, the change in PS mole fraction will flatten out. While the mole fraction trends qualitatively agree with our measured averages, there is poor quantitative agreement. This is attributed to noise in the measured on-line $D$ values (see Figure 4.4) which subsequently affects $D_T$. A 5% error in $D$ translates to 5% error in molar concentration. Depending on the magnitudes of the molar
concentrations, this can translate into as high as a 14% error in the calculated mole fraction. The $D_T$ measurements are expected to be significantly improved if an on-line QELS instrument with a more intense light source was used.

By combining data from Figures 4.5a and 4.5b, it is possible to gather another view of the composition distribution of the terpolymer sample, shown in Figure 4.6. Such a plot gives hysteresis-like loops, showing asymmetry in the mole fraction versus the concentration. The horizontal breadth of a loop indicates the overall uniformity of a given component relative to concentration, with PS being the most constant and PtBA and PMMA being very similar. This makes sense given that PS was the first block grown in the synthesis, that it would have the least polydispersity. The vertical breadth of the loop gives the overall uniformity of a component making up a given polymer sample, relative to the other components. PtBA has the smallest vertical breadth by far, and given that it is the main block in the synthesis, it follows that it would stay most consistently the main component in the polymer.
The $D_T$-derived results plotted in Figure 4.5 show variations in composition with retention time. These findings were confirmed by collecting fractions and analyzing them by NMR. Ten terpolymer separations were performed and the collected fractions (15 s intervals) were pooled to obtain sufficiently high concentrations for $^1$H-NMR analysis. Mole fractions for each polymer component were calculated by integrating peaks representative of each polymer type, using signal at 7.0 ppm for PS, signal at 3.6 ppm for PMMA, and signal at 1.4 ppm for PtBA. The results plotted in Figure 4.7 confirm that a composition-sensitive separation has indeed taken place by ThFFF. The trends of decreasing PtBA, increasing PMMA, and approximately constant PS mole fraction with increasing $t_r$ mirror those determined from $D_T$ values. The initial sharp drop for PS in Figure 5b is again observed in these NMR results.

Figure 4.6 Plot of mole fractions versus sum of concentrations for PS, PtBA, and PMMA. The color of each point on the plot represents the sum of the concentrations of PS, PtBA, and PMMA.
Furthermore, the first two fractions appear to be a PS-PtBA copolymer impurity rather than the desired PS-PtBA-PMMA terpolymer.

4.4 Conclusions

Thermal FFF has been demonstrated to successfully separate a PS-PtBA-PMMA triblock copolymer sample according to composition. This challenging separation was verified by NMR analysis of collected fractions. The terpolymer composition distribution determined using the two approaches of $D_T$ with QELS, UV, dRI and of ThFFF with off-line NMR yielded trends that agreed well with each other. While there was good qualitative agreement, discrepancies were observed in the mole fractions determined for each polymer component. These discrepancies may be resolved by the use of a more powerful laser source in the MALS/QELS combination detectors that would produce greater photon counts and subsequently enable a better on-line measure of $D$ and thus $D_T$. The results presented in this study show thermal FFF’s promising
abilities to separate by polymer composition, determine trends in composition distributions, and yield information about impurities.
CHAPTER 5
CHARACTERIZATION OF ARCHITECTURAL TRAITS OF BOTTLEBRUSH POLYMERS
BY SORET COEFFICIENT FROM THERMAL FIELD-FLOW FRACTIONATION
EXPERIMENTATION

A paper to be submitted to *Macromolecules*

Charles A. Ponyik,¹ James Oliver, Joanna Burdyńska,² David T. Wu, Krzysztof Matyjaszewski,³
S. Kim Ratanathanawongs Williams⁴

Abstract

The leading techniques for characterizing branching (size exclusion chromatography, viscometry, and light scattering) depend on the availability of linear standards, well-characterized subunits (temperature gradient interaction chromatography) or require long experimental times (nuclear magnetic resonance). Thermal field-flow fractionation (ThFFF) has established retention theories that enable reasonable predictions of a linear polymer’s retention time in a system. Poly(2-(2-bromoisobutyryloxy)ethyl methacrylate)-*graft*-poly(n-butyl acrylate) bottlebrushes with backbone lengths ranging from 20 – 400 monomer units and side chain lengths ranging from 20 - 100 monomer units are characterized by ThFFF for their retention times and masses. The individual effects of side chain and backbone length are clearly determined and the method is shown to accurately determine side chain or backbone length when one of the dimensions is known. The method is also shown to be more broadly sensitive to the

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overall architecture of a polymer, which is particularly useful for dealing with characterizations of natural polymers or in reverse engineering applications.

5.1 Introduction

Recent advancements in the use of polymers result from the introduction of branching and novel architectures to achieve desired performance characteristics. Architectures include stars,**97,128–131** pom-poms,**32** combs,**90,132** bottle-brushes,**133** dendrimers,**22,90,134,135** and rings.**136–138** Such traits are often found in natural rubbers and have also been applied in synthetic polymers to modify the performance of polyethylene,**10,124** to reduce viscosity during processing,**10,132,139** to self-assemble as lithography templates, or as drug delivery and tumor imaging hybrid systems.**22,90,134** The material properties of these assemblies are typically characterized by small angle neutron scattering (SANS)**133,140** to gain insight into the physical behavior of the backbones and side chains, scanning electron microscopy (SEM)**45** to observe the self-assemblies and small angle x-ray scattering (SAXS)**7** to detect lamellar phase formations.

Further analysis of these polymers by methods capable of observing the polymer architecture, degree of branching, or number of branches enables correlation between structure and function. Nuclear magnetic resonance (NMR)**23,49,52,53** is a powerful technique for determining the structure because it is sensitive to both the number and types of bonds present on a given atom. It has been successfully used to determine branching information for synthetic polymers such as polyacrylates**23,25** polyethylene,**52,141** polystyrene**142** and copolymers**143** as well as natural macromolecules such as starch.**49,53** NMR on its own cannot provide detail about the distribution of the individual branches present, nor how their sizes vary. The desired information may only be attained by first performing a separation of the sample, further diluting the sample and increasing the difficulty and length of the NMR study. Studies by **13**C NMR of non **13**C
labeled monomers require long run times to provide detailed branching, and are further confounded when samples are in low concentration. Effective methods of determining architectural traits at lower concentrations include multi-angle light scattering (MALS), dynamic light scattering (DLS), and viscometry. Since these methods work comparatively well at low concentrations, they are often implemented as detection systems for chromatographic methods of polymer separations including gel permeation chromatography (GPC), temperature gradient interaction chromatography (TGIC), and liquid chromatography at critical conditions (LCCC). The determination of branching by these methods remains difficult, however, with GPC requiring a linear standard for comparison, TGIC performing its separation wholly on mass, and LCCC requiring unique functionality changes with the addition of branches. GPC is further complicated in that its packed column introduces band broadening, may shear degrade analytes, and has low selectivity. These issues are comparatively resolved in thermal field-flow fractionation (ThFFF), a complementary separation technique in which the separation occurs in an open, ribbon-like channel. The top side of the channel is heated, and the bottom side cooled, generating a temperature gradient across the channel. Simultaneously, a carrier liquid is pumped down the length of the channel. Due to the laminar flow in a thin channel (typically ~100 μm), a parabolic flow profile is formed. Analytes are driven towards the cold wall depending on their chemistry, the chemistry of the solvent, and the magnitude of the temperature gradient in a phenomenon called thermal diffusion, described by the thermal diffusion coefficient ($D_T$). This movement is countered by the analyte’s translational diffusion, described by the translational coefficient ($D$). When $D_T$ is constant, such as the case for homopolymers, separation is on $D$ with smaller polymers showing greater $D$ and sampling faster flow regimes of the parabolic flow profile and eluting earlier. The ratio of $D_T$ to $D$ is called
the Soret coefficient \((S_T)\), and when combined with the magnitude of the temperature gradient \((\Delta T)\) determines the retention parameter \((\lambda)\) as shown in Equation 5.1:

\[
\lambda = \frac{D}{D_T \Delta T} = \frac{1}{S_T \Delta T} \quad (5.1)
\]

The retention time of an analyte \((t_r)\) is dependent on the time it takes to empty channel of one volume of carrier liquid \((t^0)\), the retention parameter, and a correction factor \((\nu)\) that accounts for perturbations to the parabolic flow profile that result from the temperature gradient, as shown in Equation 5.2:

\[
\frac{t^0}{t_r} = 6\lambda [\nu + (1 - 6\lambda \nu) (\coth 1/2\lambda) - 2\lambda] \quad (5.2)
\]

By the combinations of Equations 5.1 and 5.2, it is shown that the retention time of a polymer is directly related to its \(S_T\). By the application of theories, it is possible to calculate the value of \(S_T\) for a linear polymer of the same mass as the one being analyzed and assess the degree of branching present in a polymer without the need for a linear standard. A theoretical \(S_T\) can be obtained by calculation of theoretical \(D_T\) and theoretical \(D\). The leading quantitative theory for \(D_T\) of polymers evaluates changes to the Flory-Huggins \(\chi\) parameter with respect to temperature.\textsuperscript{113}

This is shown in Equation 5.3.

\[
D_T = \phi_1^2 \frac{D_{seg} \theta [\tau^2 (\partial \chi / \partial T)]}{\tau} \quad (5.3)
\]

In Equation 5.3, \(D_{seg}\) is the translational diffusion coefficient of a monomer in the overall polymer and \(\phi_1\) is the solvent volume fraction, taken to be unity for dilute systems. The change in \(\chi\) with respect to temperature can be obtained from experimentation, reported elsewhere.\textsuperscript{113} The theoretical value for \(D\) is also obtained by theory using a modification of the Stokes-Einstein equation:\textsuperscript{102}

\[
D = \frac{k_B T}{6\pi \eta_r m^{0.5}} \quad (5.4)
\]
In Equation 5.4, $k_B$ is the Boltzmann constant, $\eta$ is the solvent viscosity, $r_m$ is the radius of the monomer in the polymer, and $n$ is the number of monomers in the polymer. The power of 0.5 on $n$ assumes theta-solvent conditions for the polymer, a compromise as it may not be known at the time of the experiment whether the system is a good solvent or poor solvent. In practical use, this value varies from 0.4-0.8 depending on the solvent and polymer chemistries.

This work uses theoretical $S_T$ values calculated from theoretical $D$ and $D_T$ to study how backbone and side chain lengths of bottlebrush polymers affect observed $S_T$ relative to a linear polymer of the same mass, how the differences in polymer sizes and configurations influence polymer rigidity and ultimately how ThFFF can elucidate effects of polymer rigidity on a given system.

5.2 Experimental

This section details the materials and instrumentation used to complete this work. In specific, it describes the polymer library used and how it was dissolved, and the ThFFF apparatus and associated detectors.

5.2.1 Materials

The materials studied in this work are part of a library of RAFT and ATRP polymerized bottlebrushes with poly(2-(2-bromoisobutyloxy)ethyl methacrylate) (PBiBEM) backbones ranging from 20 to 400 monomer units and poly($n$-butyl acrylate) (PBA) side chains ranging from 20 to 100 monomer units with a 100% nominal graft density. Polymer dimensions were determined by SEC. The library is illustrated in Figure 1.1.

Bottlebrush polymer solutions were prepared by dissolving the neat polymer in chloroform. Low heat (30 °C) was applied as needed for up to three days. The solution was added to a sample vial where the solvent was allowed to evaporate. The polymer was then
dissolved into HPLC grade tetrahydrofuran (Avantor Performance Chemicals, Center Valley, Pennsylvania) to yield concentrations ranging from 0.2 – 2 mg mL\(^{-1}\).

5.2.2 Instrumentation

Fractionation was carried out in a TF2000 Polymer Fractionator (Postnova Analytics, Salt Lake City, Utah) outfitted with a 20 µL sample loop. The spacer was cut from 127 µm thick Kapton tape (Fralock, Valencia, California). HPLC grade tetrahydrofuran was pumped through the channel at flow rates ranging 0.1-0.4 mL min\(^{-1}\). The applied temperature field ranged 60 – 80 °C, with the cold wall temperature held at 30 °C. The detector array comprised a Dawn Heleos II (Wyatt Technology, Santa Barabara, CA) multi-angle light scattering instrument with external WyattQELS attachment (Wyatt Technology) and an Optilab T-rEX (Wyatt Technology) differential refractometer. Data was collected and analyzed with ASTRA 6 software (Wyatt Technology).

5.3 Results and Discussion

This section covers the determination of the polymer mass by SEC as well as ThFFF. It goes on to explain the determination of the Soret coefficient, the effect of polymer size on the Soret coefficient, how theoretical Soret coefficients were calculated and how predicted and observed Soret coefficients are related.

5.3.1 Determination of Polymer Mass by SEC and ThFFF/dRI/MALS

The molar mass of a polymer is linked to its properties and hence impacts its end use. The bottle-brush polymers’ molar masses were determined by SEC and ThFFF-MALS-dRI and compared to calculated (Nominal \(M_n\)) values from NMR studies. The Nominal \(M_n\) calculated for polymers assumed a 100% graft density (every backbone monomer yields a side chain, and every side chain has an equal number of monomers). This data is reported in Table 5.1.
For all systems, the mass of the polymer increases with side chain length, as expected. ThFFF-MALS consistently shows an increase in the polydispersity of the polymer samples as the side chain lengths increase, an expected result with ATRP,\textsuperscript{151} which was used for the polymerization of the side chains. ThFFF-MALS also shows smaller PDI values than SEC as it is subject to less band broadening. This is due to ThFFF’s open channel design, which effectively eliminates eddy diffusion.\textsuperscript{81,152} The values reported by ThFFF were closer to the expected nominal $M_n$ values than those determined by SEC. The nominal polymer $M_n$ is always greater than the value reported by SEC. As SEC separates based on the volume of a polymer and is calibrated with linear standards, it will generally underestimate the masses of branched polymers as monomers are more densely packed into the same volume of space.\textsuperscript{12} More accurate molar mass values may be determined by SEC-MALS however SEC is also subject to secondary interactions as well as size limitations\textsuperscript{76} due to the presence of a stationary phase.

The nominal $M_n$ is generally smaller than the measured values by ThFFF-MALS except for the 20x22, 100x20 and 400x40 polymer. This could be due to underestimation of the side chain and backbone length which the calculation of Nominal $M_n$ is based off and hence it is difficult to compare the nominal $M_n$ values to ThFFF values as the theoretical mass is based on NMR results and ThFFF-MALS is a direct measurement of mass online. An added advantage of ThFFF-MALS is the ability to characterize branching from measured $S_T$. Retention time in ThFFF is directly correlated to $S_T$, making determination both accurate and convenient.

**5.3.2 Initial Determination of $S_T$**

The retention time from ThFFF is directly related to $S_T$, shown in Equations 5.1 and 5.2. $S_T$ provides information about the polymers hydrodynamic properties (through $D$) as well as its composition (through $D_T$), (Equation 5.1). Differences in $D_T$ resulting from the different molar
Table 5.1 Summary of Bottlebrush Characterization Data by NMR, SEC, and ThFFF-MALS.

<table>
<thead>
<tr>
<th>Backbone length (n)</th>
<th>Side chain length (n)</th>
<th>Nominal M&lt;sub&gt;n&lt;/sub&gt;&lt;sup&gt;2&lt;/sup&gt;</th>
<th>PnBA content (%)</th>
<th>SEC</th>
<th>ThFFF-MALS&lt;sup&gt;1&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>M&lt;sub&gt;n&lt;/sub&gt;</td>
<td>M&lt;sub&gt;w&lt;/sub&gt;</td>
<td>M&lt;sub&gt;n&lt;/sub&gt;/M&lt;sub&gt;w&lt;/sub&gt;</td>
</tr>
<tr>
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<td>95</td>
<td>-</td>
<td>-</td>
</tr>
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<td>60</td>
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<td>98</td>
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<td>99</td>
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<td>1,986,500</td>
</tr>
</tbody>
</table>

1. Determined by NMR
2. Based on the assumption that every backbone monomer has a side chain of equal length
3. Based on a dn/dc of 0.0783 ml/g
5.3.2 Initial Determination of $S_T$

The retention time from ThFFF is directly related to $S_T$, shown in Equations 5.1 and 5.2. $S_T$ provides information about the polymers hydrodynamic properties (through $D$) as well as its composition (through $D_T$), (Equation 5.1). Differences in $D_T$ resulting from the different molar ratios of poly(2-(2-bromoisobutyryloxy)ethyl methacrylate backbone) and poly(n-butyl acrylate side chain) would theoretically influence retention. However, in this study, the effect should be negligible as the bottlebrushes are all $>95\%$ poly(n-butyl acrylate) (Table 5.2). Furthermore, although the backbone is comprised of poly(2-(2-bromoisobutyryloxy)ethyl methacrylate), it will be well shielded from the surrounding solution by the side chains, which greatly restrict its movement in solution. For polymers of the same composition, the separation in ThFFF is based on differences in their hydrodynamic properties observed via $D$. Better known polymer separation methods such as GPC and AF4 separate solely on hydrodynamic properties (hydrodynamic volume in GPC and Stokes radius or $D$ in AF4). ThFFF is unique in that $S_T$ can be determined from retention time without need for calibration as GPC requires, and is well established for separations in an organic solvent without concern for interactions with the retention wall, unlike AF4. Based on previous studies, retention should decrease with an increase in branching (as the contraction from branching leads to a decrease in $R_b$ and thus an

<table>
<thead>
<tr>
<th>Backbone Length ($L$) (monomer units)</th>
<th>Side chain Length ($M$) (monomer units)</th>
<th>$S_{\text{meas}}$ ($\pm 0.5%$) (K$^{-1}$)</th>
<th>$D$ ($\pm 5%$) ($10^{-7}$ cm$^2$s$^{-1}$)</th>
<th>$D_T$ ($\pm 5%$) ($10^{-7}$ cm$^2$s$^{-1}$K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.11</td>
<td>9.23</td>
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</tr>
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</tr>
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</tr>
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<td>1.1</td>
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<td>2.80</td>
<td>1.1</td>
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<tr>
<td>400</td>
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<td>0.61</td>
<td>1.57</td>
<td>0.95</td>
</tr>
<tr>
<td>400</td>
<td>100</td>
<td>0.85</td>
<td>1.24</td>
<td>1.1</td>
</tr>
</tbody>
</table>

1. Determined from NMR.
increase in $D$). Since $D$ can also be directly related to the number of monomers in a polymer (Equation 5.4), or molecular mass, the relationship with retention can be associated with changes in molecular mass. In this study, it is expected that $D$, and thus retention time, will change with respect to the lengths of the bottlebrushes’ side chains and backbones. The current drawback is that $D$ will change with molecular mass as well as branching, and the effect that side chain and backbone lengths have on the change in hydrodynamic properties is not well known. To investigate this, fractograms of the 20x112 and 100x20 bottle-brush polymers (both have $M_n$ nominal near 425 kDa) as well as the 100x120 and 400x20 bottle-brush polymers (both $M_n$ determined by ThFFF-MALS near 2,600 kDa) were overlaid. These polymers were directly compared to identify how retention changes with respect to molar mass and architecture (Figure 5.1).

In figure 5.1a, the 100x20 bottlebrush polymer shows a shorter retention compared to 20x100. This may be the result of the differing architectures altering the hydrodynamic properties of the polymer or the difference in $M_n$ as measured by ThFFF-MALS. If the separation
is one of molecular mass then changes in side chain and backbone length between polymers has little effect on the hydrodynamic properties (see 5.3.5 Relationship between Predicted and Observed $S_T$). This is supported by the very similar elution times of the 100x120 and 400x20 polymers in figure 5.1b. The two polymers have similar masses (as determined by ThFFF-MALS), but both being bottlebrushes, co-elute. The broadness of the 100x120 peak is a result of the greater PDI from the side chains of the polymer. Polymers synthesized by ATRP have increases in PDI with increases in size.\textsuperscript{151}

### 5.3.3 Effect of Polymer Size on $S_T$

To quantify the change in bottlebrush architecture by a change in retention, the $S_T$ can be examined. The $S_T$ for each polymer was determined from its retention time by Equations 5.1 and 5.2. The measured $S_T$ values for the polymer library are listed in Table 5.2 and were obtained from retention time. $D$ values were obtained by DLS, and $D_T$ values were calculated from $S_T\text{ meas}$ and $D$ by Equation 5.1. The $D$ values consistently decrease with respect to increases in side chain length in each backbone family. This is expected as the molar mass increases as both the backbone and side chain length are increased. $D_T$ values all fall near $1.01 \times 10^{-7}$ cm$^2$s$^{-1}$K$^{-1}$, the literature value for PBA in MEK, and show that architecture does not affect the magnitude of the thermal diffusion coefficient.

Increases in $S_T$ with both side chain and backbone length are expected as larger polymers have a larger mass, lower $D$ and are retained longer(Equation 5.4). This proves the earlier assumption that the poly(2-(2-bromoisobutyloxy)ethyl methacrylate) does not significantly influence $D_T$ was correct. To identify how changes in backbone length may affect polymer retention, the measured $S_T$ values of polymers are plotted versus their backbone lengths (Figure 5.2a) with side chain lengths indicated by the numbers by each data point. To identify how
changes in side length affect polymer retention, the measured $S_T$ values of polymers are plotted versus their side lengths (Figure 5.2b), with backbone length indicated by the numbers by each data point.

For polymers with a constant side chain length, $S_T$ increased linearly with backbone length. For polymers with a constant backbone length, $S_T$ was observed to increase linearly with side chain length. As the backbones were polymerized by a controlled synthesis, there is a linear correlation between the side chain length and the measured $S_T$. By contrast, a less well-controlled synthesis would increase the polydispersity of the sample and increase the backbone lengths present in the sample. The slope of the line in Figure 5.2b increases with respect to backbone length. This is expected as larger backbones will have smaller $D$ and thus a larger $S_T$. This also suggests that the approach has better selectivity for side chain length with larger polymer backbones.

Correlation between backbone length, side chain length, and $S_T$ allows the backbone or side chain length to be quantified from $S_T$ if the other is known. To the authors’ knowledge, no
prior work offering this level of detailed information has been previously available from a single experiment except by small-angle neutron scattering, a bulk method requiring specialized, limited-availability instrumentation.\textsuperscript{44}

In the case of this library, the lines in Figure 5.2b can be predicted from the equations $m = 2.9 \times 10^{-4} L^{0.5} + 8 \times 10^{-5}$ and $b = 5.2 \times 10^{-4} L + 5.7 \times 10^{-2}$ where $L$ is the backbone length, $m$ is the slope, and $b$ is the intercept. Thus, for a polymer of a known backbone length, a simple, linear equation is readily realized to determine the lengths of side chains. In a situation where well-characterized macromonomers are used to make a graft-through bottlebrush, the equations can be combined and then the value of the side chain length $M$ added in to solve for the length of the bottlebrush backbone. The net equation, derived from substitution using the just mentioned equations for $m$ and $b$ is

$$S_T = (2.9 \times 10^{-4} L^{0.5} + 8 \times 10^{-5})M + 5.2 \times 10^{-4} L + 5.7 \times 10^{-2} \quad (5.5)$$

Using equation 5.5, the value of a polymer’s backbone length $L$ could be substituted in, leaving a direct relationship between $S_T$ and side chain length $M$ and the reverse also holds true.

5.3.4 Calculation of Theoretical $S_T$

Theoretical $D_T$ and $D$ values were calculated for each polymer in the library. As each polymer is comprised mostly of $n$-butyl acrylate, and the poly(2-(2-bromoisobutyryloxy)ethyl methacrylate) backbone is shielded by the side chains, the composition was treated as 100% $n$-butyl acrylate monomer to simplify these calculations. This assumption is validated by the measured $D_T$s reported in Table 1 since the results are all very close to the measured value of $1.01 \times 10^{-7}$ cm$^2$ s$^{-1}$ K$^{-1}$ for linear PBA. A nominal $D_T$ was calculated from the theory developed by Mes et al. (Equation 5.3). As data is unavailable for the change in the solubility parameter of $n$-
butyl acrylate with respect to temperature, the monomer is assumed to behave the same as styrene, as described by Runyon.\textsuperscript{39} This gives a theoretical $D_T$ of $1.86 \times 10^{-7}$ cm$^2$ s$^{-1}$ K$^{-1}$.

The theoretical $D$ value was calculated from the measured $MW$ of the polymer using a modification of the Stokes-Einstein equation, shown in Equation 5.4 where $T$ is taken to be the absolute temperature (293.15 K), the solvent viscosity of MEK is 0.430 cP, and the radius of the monomer is 6.11 Å. $S_{T\text{Theor}}$ is then calculated from the ratio of the theoretical $D_T$ to the theoretical $D$ and is tabulated in Table 5.2. The predicted $S_T$ may then be used to compare observed $S_T$ for the bottlebrush polymers to that of a linear analogue of the same mass, yielding a contraction factor.

### 5.3.5 Relationship Between Predicted and Observed $S_T$

When dealing with a sample of unknown architecture, for instance, a natural polymer, it would be helpful to be able to determine the presence of and kinds of architectures present. The simplest comparison to this end is looking at the effect of polymer architecture on $S_T$, shown in Figure 5.3. As expected, $S_T$ increases with mass. However, linear polymers have much lower $D$ values because they occupy more space for the same mass relative to a branched polymer. This is why ThFFF separations are sensitive to polymer architecture.

![Figure 5.3 Plot of experimentally determined $S_T$ values for branched polymers (■) and theoretical $S_T$ values for linear (●) PBA in MEK, vs $M_W$.](image)

Figure 5.3 Plot of experimentally determined $S_T$ values for branched polymers (■) and theoretical $S_T$ values for linear (●) PBA in MEK, vs $M_W$. 

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The level of contraction for a polymer may indicate the actual architecture of the polymer. As shown in Figure 5.4, the predicted and observed \( S_T \) collapse to a single line. The linear relationship is predicted by Equation 5.4 which shows an inverse square relationship between \( D \) and number of monomers, and the comparable relationship between \( S_T \) and \( M_W \) (and thus number of monomers) in Figure 5.3. Since the theoretical \( S_T \) will always be greater than the experimental \( S_T \), all branched polymers will fall below the \( y=x \) line in Figure 5.4. In these cases, the contraction factor appears to be roughly constant. While this is expected and reasonable for the star polymers, it is not quite accurate for the bottlebrushes, where slight changes should be expected based on the polymer dimensions. This is best indicated by Equation 5.5 where \( S_T \) changes uniquely by backbone length and side chain length, and both must be considered to obtain an accurate \( S_T \) prediction based solely on the polymer dimensions. Literature has also shown that contraction factor is identical only for polymers of identical architecture.\(^\text{132}\) Such low contraction factors have been reported\(^\text{132}\) for the most highly branched polymers.

As seen by the slope of the line in Figure 5.4, the theoretical \( S_T \) of a linear polymer of same \( M_W \) is shown to be ten times greater than the observed \( S_T \) for each bottlebrush. The
approach for predicting $S_T$ described here has been used previously to predict accurately retention of linear polymers,$^{39}$ indicating that individual architectural types show different degrees of deviation from the theoretical value. This is illustrated by the data points for linear, 4-arm, 6-arm, 12-arm and 18-arm PBA polymers as plotted in figure 5.4. The experimental values for the linear and stars were calculated using literature models for the contraction of a polymer’s diffusion coefficient with the addition of branching.$^{21}$ Although these contraction factors change slightly across polymer chemistries, the point that polymers of different architectures fall in different regions on Figure 5.4 illustrates the ability of this approach to discern the presence of and type of branching in a given polymer of known chemistry, making the $S_T$ plot in Figure 5.4 especially useful. In specific, this work introduces the ability to identify the type of branching on a polymer without the need for linear standards of the same chemistry.

5.4 Conclusions

This study conveys usefulness of the Soret coefficient and ThFFF in the determination of architectural traits in polymers. The simplicity of measuring $S_T$ and $MM$ of a well-characterized polymer to obtain dimensional traits combined with advancements in accuracy over both NMR and SEC must not be understated. Furthermore, other methods which evaluate contraction of size or diffusion coefficient require linear standards of the same chemistry to assess accurately polymer architecture. These are not always available and makes ThFFF particularly desirable to this end.

In the future, it may be possible to develop calibration lines which predict polymer architecture by comparing a measured $S_T$ to a predicted $S_T$ for polymers of a known mass and chemistry. It follows that polymers with high degrees of branching will show greater contraction relative to linear polymers or less branched polymers. One challenge facing this approach to
characterizing polymer architecture is the relative absence of ThFFF equipment in polymer research laboratories despite its merits over other chromatographic techniques. This deficiency may not entirely inhibit the effective use of $S_T$ values to obtain architectural information about polymers. The ability to obtain or estimate $D$ values from DLS, MALS, asymmetric flow field-flow fractionation, or GPC is well documented, as are literature values for $D_T$ of many common polymer-solvent systems. From this data, a measured $S_T$ value may be computed, and compared to a theoretical $S_T$ value as described here.

This work clearly illustrates that the Soret coefficient is sensitive to the architecture present in polymers, and is correlated with the magnitudes of polymer dimensions in a solution, regardless of its nominal architecture. This is particularly useful for the development of synthetic materials, as polymers of similar theoretical and measured $S_T$ values may provide comparable performance in the development of artificial materials.
CHAPTER 6
CONCLUDING REMARKS

This work is an advancement in the characterization of composition distributions in triblock terpolymers and the dimensions of bottlebrush polymers by thermal field-flow fractionation. The advancements, in particular, address issues not previously addressed with success by separations methods, particularly size-exclusion chromatography. Many opportunities for future developments are realized by these works.

Other architectures of polymers should be considered and studied, similar to the work done with the bottlebrush polymers. The differences in the contraction factor with respect to polymer architecture indicate promise that the method may enable a determination of polymer architecture simply by measurement of mass and retention time for polymers of known composition. This may have applications in reverse engineering and the development of materials that mimic those found in nature.

One particularly complex sample to study is hyperbranched polystyrene as developed by the research group of Dr. Lian Hutchings of Durham University. These materials are comprised of highly monodisperse polystyrene segments. The segments are monofunctionalized at one end, difunctionalized with a complementary group on the other end, and allowed to undergo condensation polymerization with each other. This yields a highly polydisperse sample of polymers with dendrimeric architectures. The difficulties associated with this sample are twofold. Firstly, the resulting sample has a broad range of mass samples present within. Secondly, there is a need to understand the degree of branching present in the sample. ThFFF is established as capable of characterizing ultrahigh molecular weight materials\textsuperscript{9,154} and this work
furthers work done previously in the group\textsuperscript{46} to identify architectural traits in polymers, giving promise to the idea of using it to characterize such complex materials.

Further work may also address the composition and architecture of branched materials of more than one chemical component, such as that of miktoarm stars. In particular, the effect of solvents which are good for one component of the star while poor for another component may hold promise for composition-selective separations. Additionally, the question of whether thermal diffusion is driven by the exposed surface of the molecule or other interactions remains unanswered. This work, in addition to the characterization of a polystyrene coated nanoparticle, would help to answer that question.
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