SYNTHESIS AND SURFACE DYNAMICS OF COMB POLYSTYRENES AND
THEIR INTERFACIAL SEGREGATION AND BULK THERMODYNAMICS IN
BLENDs WITH LINEAR POLYSTYRENES

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SYNTHESIS AND SURFACE DYNAMICS OF COMB POLYSTYRENES AND
THEIR INTERFACIAL SEGREGATION AND BULK THERMODYNAMICS IN
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ABSTRACT

A series of densely branched comb polystyrenes with well-defined architectural details were prepared by living anionic polymerization via the “grafting-through” approach. A new, general method was developed for the synthesis of well-defined, comb polystyrenes with controlled, variable amounts and types of branch end functionalities (C₈F₁₇, OH or COOH), by combining living anionic polymerization and thiol-end “click” chemistry. Characterization by NMR, SEC, and MALDI-TOF mass spectrometry established their chemical structures and chain-end functionalities, which indicated precisely defined comb polystyrenes with controlled degrees of functionalization.

Surface segregation in blends of well-defined comb and linear polystyrenes was investigated by neutron reflectivity (NR) and Static Time-of-Flight Secondary Ion Mass Spectrometry (STOF-SIMS) measurements. The results indicate strong enrichment of combs at the blend surface. In contrast to previously reported examples of blends of long-branched and linear chains, a thermal annealing process is not necessary for achieving significant surface segregation in these comb/linear blends. It is found that architecture details of the comb component have a strong impact on the bulk miscibility with the linear component in a blend and therefore also on its surface segregation. A self-consistent field theory by Wu and Fredrickson is able to describe the surface
segregation behavior in the comb/linear blends reasonably well after accounting for a surface attraction for the ends higher than anticipated by the theory. Measurements of the surface segregation, as well as macroscopic hydrophobicity in blends containing branch end-functionalized comb polystyrenes, show that comb molecules with 25% branch chain ends functionalized with hydrophobic or hydrophilic groups still enrich the surface, though the contact angle of a blend depends on whether the functionalities themselves reside right at the surface, or are buried beneath the outermost layer of chain segments.

The surface height fluctuation dynamics of melt films of densely branched unfunctionalized comb polystyrenes of thickness greater than 55nm and at temperatures 23 to 58 °C above the bulk $T_g$ can be rationalized using the same hydrodynamic continuum theory (HCT) useful for describing the behavior of melt films of linear and cyclic chains. The film viscosities inferred from fits of the HCT to intensity-intensity time correlation functions measured by X-ray Photon Correlation Spectroscopy (XPCS) are the same as those measured in bulk with conventional rheometry for three combs, though for two of the comb architectures the films viscosities are distinctly higher than the bulk viscosities. These combs are the one most like a star polymer and the one closest to showing bulk entanglement behavior. These discrepancies between film and bulk viscosities are much smaller than those seen for less densely branched polystyrenes. The fact that surface dynamics data for various combs do not collapse onto a single curve in a plot that accounts for differences in $T_{g,\text{bulk}}$ among the various chains indicates that besides
the important value of $T_{g,bulk}$, the chain architecture also plays a key role in determining surface fluctuations.
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CHAPTER I

INTRODUCTION

Blending polymers with different chain architectures (i.e. branched vs. linear) has been proved useful in controlling interfacial properties by controlling interfacial segregation. Application of this surface modification strategy has been found in several examples including creating protein-resistant surfaces for biomaterials,\textsuperscript{1} tuning cell responses to tissue engineering scaffolds,\textsuperscript{2} and designing anti-fouling ultrafiltration membranes for water purification.\textsuperscript{3-6} It is of great practical significance for understanding the effect of chain architectures on surface or interface segregation. Various theoretical works have been reported to explain the phenomenon of surface or interfacial segregation of polymers by driving forces originating from the architectural asymmetry in blends. In this work we focus on surface segregation driven by long-chain branching. We note that many branched/linear blends in previous experimental reports were far more complicated than those studied using current theoretical models, causing difficulties in making direct comparisons between the experimental results and theoretical predictions. For example, the degree to which a branched component is preferred at the surface may be altered due to some chemical mismatch between the branched and linear components;\textsuperscript{1} chemical
differences between the linear and branched chain may have been present at branch ends or junctions. Control over architectural details of the branched polymers has not always been so well-defined, due to the polymerization method used to create the branched chains. Experimental studies of the composition depth profile of surface segregation in blends of components that differ essentially only in larger scale molecular architecture (i.e. not "short chain branching") have been extremely limited. Therefore, to provide the most incisive test of the existing theories for surface segregation of long-chain branched polymers, an athermal branch/linear blend for which entropic contributions dominate is needed.

Among the properties of a polymer blend surface that can be altered by surface segregation, or surface enrichment, of a blend component are the surface dynamics. The bulk dynamics of melts of polymers with branched architectures have attracted considerable attention, both because such branched chains can be used to facilitate processing and improve properties, and because a number of unsolved problems remain in the area. Bulk melts of unentangled branched polymers can have remarkably low viscosities and high compliances as compared to melts of linear chains with the same average overall molecular weight. Recent investigations of the bulk rheology of comb polymer melts highlight their unusual bulk behaviors. Even at high molecular weights they do not show classic entanglement behavior. Not much is known about the dynamics of thermally induced surface height fluctuations on branched chain melts, however, even though these affect the wetting, adhesion, and friction of such surfaces.
Opportunities now exist, though, to change this situation with the introduction of X-ray Photon Correlation Spectroscopy (XPCS), which has been used to experimentally verify the validity of the hydrodynamic continuum theory (HCT) for describing surface dynamics of films of linear polystyrenes.\textsuperscript{18} It is of great interest to see if the HCT, which does not consider chain architectures, is still valid for non-linear polymers.

Synthesis, blend thermodynamics and surface fluctuation dynamics of a series of well-defined densely branched comb polystyrenes (PS) are discussed in this dissertation. In the first part of the dissertation, the preparation of comb PSs with extremely high branch density by living anionic polymerization via the “grafting-through” approach is described. A schematic description of these combs is shown in Figure 1.1. The distance between adjacent branches in terms of number of styrene repeat units (L) is fixed at one for all the combs, while the number of branches (P) and length of each branch (M) are precisely controlled. One unique feature of these combs is that the backbone, branches and branch points all consist of styrene repeat units. The sec-butyl group at each branch end differs only slightly from a styrene repeat unit in terms of surface energy. Also discussed is the development of a new, general method for the preparation of well-defined, comb polystyrenes with controlled, variable amounts and types of branch end functionalities (C\textsubscript{8}F\textsubscript{17}, OH and COOH), by combining living anionic polymerization and thiol-ene “click” chemistry.
Figure 1.1 Highly idealized scheme of a densely branched comb.

In the second part thermodynamics of blends of comb and linear polystyrenes, including bulk miscibility and surface segregation, are discussed. Chain architectures have been shown to readily influence thermodynamic interactions in blends.\textsuperscript{19-21} When highly branched chains (i. e. combs) are blended with linear chains, bulk phase separation is predicted to readily take place.\textsuperscript{22} In this work we study bulk thermodynamics of blends consisting of comb and linear polystyrenes using differential scanning calorimetry (DSC) and small angle neutron scattering (SANS). DSC provides a qualitative measurement of blend miscibility, while SANS provides a quantitative measurement of the exchange interaction parameter, $\chi_{\text{eff}}$.

Long-chain branching promotes surface segregation of branched polymers in blends with linear polymers. Previous work\textsuperscript{23} has shown that the magnitude of surface segregation increases with increasing number of chain ends as well as branch points in the branched polymer. Therefore comb polymers synthesized in this work are expected to
strongly segregate to the surface. We investigated the surface segregation in blends of comb and linear polystyrenes with neutron reflectivity (NR) and Static Time-of-Flight Secondary Ion Mass Spectrometry (STOF-SIMS). Concentration depth profiles of films of comb/linear blends were obtained by fitting the NR data. STOF-SIMS, as a complementary tool to NR, directly measures surface chemical composition of these blend films. It is noteworthy that the backbone, branches, branch points and ends of each comb consist of the same chemical structures (styrene repeat units and sec-butyl groups) as those in a linear chain, except that the styrene repeat units in the linear PS are deuterated in order to provide contrast for NR and STOF-SIMS measurements. Therefore it is reasonable to consider the interaction between the linear and comb polystyrenes in this study to be mostly entropic. Moreover, driven by the ultimate goal of modifying surface properties of commercial polymer materials by blending comb polymers as additives, we characterized the surface segregation as well as macroscopic hydrophobicity in blends containing branch end-functionalized comb polystyrenes and linear polystyrenes. In this case both the branching effect and chain end chemistry effect on surface segregation are simultaneously present.

Since long-chain branching of a polymer is known to remarkably affect chain dynamics in the bulk, we probe the melt film surface fluctuations for these comb polystyrenes with extremely branched structures in the third part of this work. In particular, we consider whether the HCT (which neglects molecular architecture) can be applied as successfully with these chains as with linear\textsuperscript{18} and macrocyclic\textsuperscript{24} chains. It has recently been found
that for chain architectures with less dense branching, film viscosities inferred from XPCS data from 100 nm thick films using the HCT can be much higher than the bulk viscosities.\textsuperscript{25} Also, the size of this discrepancy is strongly dependent on how far above $T_{g,\text{bulk}}$ the temperature is and on details of the branching.\textsuperscript{25} These results suggest that long-chain branching can have a profound effect on surface fluctuations in thin films. Therefore, here we consider densely branched combs as a limiting case of long-chain branching and study the surface dynamics of thin films using XPCS with comparison to the HCT.
CHAPTER II

BACKGROUND

In this chapter the synthesis of comb polymers via the “grafting through” approach is reviewed in Section 2.1. Then the previous research relevant to the study of bulk thermodynamics (Section 2.2) and surface segregation (Section 2.3) in comb/linear blends is discussed. Next the bulk dynamics of comb polymers and surface dynamics of linear, macrocyclic and long-chain branched polystyrene films are reviewed (Section 2.4). Finally in Section 2.5 the characterization techniques used in this work are introduced: Small Angle Neutron Scattering, Neutron Reflectivity, Static Time of Flight Secondary Ion Mass Spectrometry, and X-ray Photon Correlation Spectroscopy.

2.1 Synthesis of comb polymers

The comb polymer is a special type of branched polymer with a high density of side branches along the backbone, which has attracted considerable research interest due to its unusual architecture. The synthetic methodologies for comb polymers have been extensively investigated and covered in several review articles. In general, methods for synthesizing comb polymers are divided into three major categories: “grafting onto”,

16, 17, 26-31
32-36
“grafting from” and “grafting through”, as represented in Figure 2.1. In the “grafting onto” strategy, polymeric branches are attached to a pre-existing backbone via a coupling reaction between the pendant functional groups on the backbone and functional groups at the chain ends of grafts. In a “grafting from” process, initiating sites are attached to a polymeric backbone at first and then branches grow by polymerization of monomers initiated from these sites. The “grafting through” method involves homo- or copolymerization of macromonomers, which are functional polymers with a polymerizable group at one chain end. The particular type of well-defined comb polymer of interest here is that in which every backbone repeat unit has one side branch. The grafting density of comb polymers synthesized with the “grafting onto” method is often limited by the increasing steric hindrance during the grafting process. In the “grafting from” method, information about the length and number of side branches can not be easily obtained. When combined with living anionic polymerization techniques, the “grafting through” method provides a solution for overcoming these problems and achieving the targeted comb structure. There are comprehensive reviews describing this "grafting through" or macromonomer technique. In this section the focus is on reviewing both synthesis and polymerization of macromonomers by living anionic polymerization by the “grafting through” method. At the end a survey of a few examples in the literature of combs with functionalized branch ends will be also provided.
2.1.1 Synthesis of macromonomers

Well-defined macromonomers with a polymerizable functional group at one end can be synthesized by living polymerization methods.\textsuperscript{39,40} Alkyllithium-initiated living anionic polymerization is one of the most reliable methods for the synthesis of well-defined, chain-end functionalized polymers with controlled molecular weights, narrow molecular weight distributions, and high end-group functionality.\textsuperscript{41-43} In general two approaches have been taken to prepare macromonomers by living anionic polymerization: the use of either an initiator or a terminating agent containing the polymerizable moiety (Figure 2.2). Examples adopting both approaches are discussed below.
2.1.1.1 Macromonomer synthesis using an anionic initiator with a polymerizable group

This approach requires that the initiators contain a polymerizable group that will not be affected by the polymerization reaction, besides the general requirement of fast and quantitative initiation by living anionic polymerization. Takano et al. demonstrated that 4-pentenyllithium could be used as an efficient anionic initiator to obtain well-defined PS macromonomers with one olefinic vinyl group per chain end. While these PS macromonomers remained stable during anionic polymerization, they were subjected to polymerization techniques for polyolefins.

Gnanou et al. developed an anionic initiator with a norbornenyl group starting from 5-hydroxymethylbicyclo [2.2.1] hept-2-ene and applied it in the synthesis of a series of...
α-norbornenyl macromonomers, including PS\textsuperscript{45}, polybutadiene\textsuperscript{46} and PEO\textsuperscript{47}. These macromonomers were homopolymerized by ring opening metathesis polymerization using a Schrock catalyst.

Well-defined PEO macromonomers were also obtained by anionic ring opening polymerization of ethylene oxide initiated by potassium $p$-vinyl- or $p$-isopropenyl-benzylates.\textsuperscript{48, 49} It is noteworthy that the relatively low nucleophilicity of these anionic initiators prevented polymerization of the double bond under the conditions used.

Polyester macromonomers from $\varepsilon$-caprolactones and lactides were prepared by the coordinated anionic ring-opening polymerization with initiators based on an aluminum alkoxide.\textsuperscript{50-52} This aluminum alkoxide contains a methacrylic or styryl double bond, resulting from the reaction of triethylaluminum with 2-hydroxyethyl methacrylate or $p$-hydroxymethylstyrene, respectively. The resulting polycaprolactone or polylactide macromonomers had either methacryloyl or styryl as the polymerizable end groups.

2.1.1.2 Macromonomer synthesis using a terminating agent with a polymerizable group

Most of the macromonomers based on living anionic polymerization were prepared by end-capping of the living anionic chain-end with an electrophilic terminating agent containing a polymerizable group.\textsuperscript{40} Polystyrene macromonomers functionalized with styryl end groups have been prepared by termination of living poly(styryl)lithium with 4-vinylbenzyl chloride in the presence of THF.\textsuperscript{53, 54} Side reactions in the termination step may be avoided by adopting strict reaction conditions, such as low reaction temperature
(-78 °C) and a large excess of 4-vinylbenzyl chloride. Another approach to prevent side reactions is to lower the reactivity of the living chain end by addition of 1,1-diphenylethylene.\textsuperscript{55} The resulting diphenylmethyl anion is sterically hindered and stabilized by delocalization, and is thus less nucleophilic. Living poly(styryl)lithium was also end-capped with ethylene oxide to decrease the nucleophilicity of chain end, followed by reaction with methacryloyl chloride to afford macromonomer with a methacrylate end group.\textsuperscript{27, 56, 57} Lutz et al.\textsuperscript{55, 58, 59} synthesized well-defined polystyrene, polyisoprene and poly(styrene-\textit{b}-isoprene) macromonomers with \(\omega\)-allyl and \(\omega\)-undecenyl end groups by terminating living anionic chain ends with allyl bromide and undecenyl bromide, respectively. Homopolymerization and copolymerization with ethylene of \(\omega\)-allyl and \(\omega\)-undecenyl PS macromonomers were achieved in the presence of transition metal catalysts for coordination polymerization. \(\omega\)-Norbornenyl PS macromonomers were synthesized by Gnanou et al.\textsuperscript{60} using 5-norbornene-2 carbonyl chloride as the terminating agent for anionic polymerization. They further extended this technique to prepare \(\omega\)-norbornenyl polybutadiene\textsuperscript{46} and poly(styrene-\textit{b}-butadiene)\textsuperscript{61} macromonomers.

Hogen-Esch et al.\textsuperscript{62} synthesized poly(2-vinylpyridine) macromonomers by terminating living anionic polymerization of 2-vinylpyridine with 4-vinylbenzyl chloride in THF at -78 °C. Hadjichristidis et al.\textsuperscript{63, 64} prepared styryl-functionalized polyisoprene and polybutadiene by reacting living polyisoprene or polybutadiene chains with 4-(chlorodimethylsilyl)styrene. End-capping of living PEO chains with either
methacryloyl chloride or 4-vinylbenzyl bromide yields PEO macromonomers.\textsuperscript{65} Oligodimethylsiloxanes with a polymerizable 3-methacryloxypropyl group at the chain end were prepared by anionic ring-opening polymerization of hexamethyldicyclosiloxane (D\textsubscript{3}) followed by reaction with 3-methacryloxypropyl dimethylchlorosilane.\textsuperscript{66}

2.1.2 Polymerization of macromonomers

In most examples of comb polymers in the literature, the combs are prepared by conventional radical polymerization of macromonomers.\textsuperscript{26, 27, 32, 53, 67} However, conventional radical polymerization has the limitations of poor molecular weight control, high polydispersity, and incomplete conversion. All of these limitations can be overcome with living or controlled polymerization methods, such as anionic polymerization,\textsuperscript{63, 64, 68-71} cationic polymerization,\textsuperscript{72, 73} group transfer polymerization (GTP),\textsuperscript{74} atom transfer radical polymerization (ATRP),\textsuperscript{75-80} reversible addition-fragmentation chain transfer polymerization (RAFT),\textsuperscript{78, 81} nitroxide mediated radical polymerization (NMP),\textsuperscript{82} and ring-opening metathesis polymerization (ROMP).\textsuperscript{60, 83-85}

Living anionic homopolymerization of macromonomers is very suitable for preparing well-defined comb polymers with extremely high branching density. Since macromonomers are often solids, their purification in order to meet the demanding standards of living anionic polymerization is challenging. Impurities can also originate from glassware used as the reactor and from the solvent used for polymerization. These trace impurities significantly undermine or even completely disable the living anionic
polymerization by quenching initiators and terminating growing macro anions, which is especially problematic when a high degree of polymerization is desired. For their kinetic studies Gnanou and Lutz\textsuperscript{68} titrated impurities in the solvent with a small amount of sec-BuLi/styrene and then the copolymerization of macromonomer and styrene was initiated with poly(styryl)lithium. In the work of Tsukahara et al.\textsuperscript{70} macromonomers were dried with CaH\textsubscript{2} in benzene solution and freeze-dried several times under high vacuum. However, they reported that it was rather difficult to efficiently prepare poly(macromonomer)s with a high degree of polymerization (DP > 34) because their procedure was unable to remove impurities in the macromonomers to the level required by living anionic polymerization. Later Yamashita and coworkers\textsuperscript{71} reported the use of crosslinked polystyrene particles with pendant benzophenone sodium complexes as purging reagent (Figure 2.3) for the purification of macromonomers. Living anionic polymerization of the purified macromonomers was able to produce combs with moderate degrees of polymerization (DP \leq 10). Hadjichristidis and coworkers\textsuperscript{63, 64} bypassed the step of purifying macromonomers by performing the synthesis of macromonomers and the subsequent polymerization in the same reactor under high vacuum. Their strategy was successful for preparing combs with PS backbones and PI, PB, or PS-\textit{b}-PI branches. However their strategy required a complicated reactor design and forfeited the convenience provided by synthesizing, characterizing and polymerizing macromonomers in two separate processes.
Another interesting topic about living anionic polymerization of macromonomers is the copolymerization with small molecular comonomers or another type of macromonomer. Gnanou and Lutz\textsuperscript{68} carefully investigated the kinetics in anionic copolymerization of \(\omega\)-styryl PS macromonomers with styrene or \(p\)-methylstyrene. With a selected system excluding all the complicating factors due to the incompatibility between polymers, they concluded that the substituent group (H- or CH\(_3\)-) associated with the styrene monomers determined the reactivity of the macromonomer and the reactivity ratios appeared to be independent of the macromonomer chain length. Ishizu and Kuwahara\textsuperscript{86} studied the anionic copolymerization of \(\omega\)-styryl PS and PI macromonomers and found that the reactivity ratios were affected by their respective molecular weights. When both
macromonomers had similar molecular weights, the reactivity ratios corresponded to an azeotropic copolymerization. PI macromonomers of higher molecular weight than PS ones seemed to be more reactive. It should be noted that PS and PI macromonomers were immiscible with each other.

2.1.3 Synthesis of comb polymers with end-functionalized branches

Most of the comb polymers with end-functionalized branches reported in the literature have been prepared by ring-opening polymerization or conventional radical polymerization.\textsuperscript{50-52, 66, 87-92} There are a few examples applying controlled radical polymerization to synthesize such combs.\textsuperscript{93-96} A survey of examples reported in the literature is listed in Table 2.1, in which the chemical composition of backbones and branches, the branch end functional groups, and polymerization methods are summarized for each example. The polymerization methods mentioned here include techniques for both the synthesis of macromonomers and polymerization of macromonomers.
Table 2.1 Examples of comb polymers with end-functionalized branches in the literature.

<table>
<thead>
<tr>
<th>Example</th>
<th>Backbone monomer</th>
<th>Branch</th>
<th>Polymerization technique&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Branch end group</th>
</tr>
</thead>
<tbody>
<tr>
<td>1&lt;sup&gt;52&lt;/sup&gt;</td>
<td>styrene, methacrylate</td>
<td>PCL</td>
<td>AROP&lt;sup&gt;b&lt;/sup&gt;+RP&lt;sup&gt;c&lt;/sup&gt;</td>
<td>-OH</td>
</tr>
<tr>
<td>2&lt;sup&gt;87&lt;/sup&gt;</td>
<td>2-phenyl-2-oxazoline</td>
<td>PEO</td>
<td>AROP+CROP&lt;sup&gt;d&lt;/sup&gt;</td>
<td>-OH</td>
</tr>
<tr>
<td>3&lt;sup&gt;88&lt;/sup&gt;</td>
<td>styrene</td>
<td>PEO</td>
<td>AROP+RP</td>
<td>Perfluoroalkyl-</td>
</tr>
<tr>
<td>4&lt;sup&gt;89&lt;/sup&gt;</td>
<td>styrene</td>
<td>PEO</td>
<td>L&lt;sup&gt;e&lt;/sup&gt;AP&lt;sup&gt;f&lt;/sup&gt;(backbone first)+AROP</td>
<td>-OH</td>
</tr>
<tr>
<td>5&lt;sup&gt;93&lt;/sup&gt;</td>
<td>acrylate</td>
<td>PEO</td>
<td>AROP+ATRP&lt;sup&gt;g&lt;/sup&gt;</td>
<td>-N&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>6&lt;sup&gt;90&lt;/sup&gt;</td>
<td>vinyl acetate</td>
<td>PS</td>
<td>RP+RP</td>
<td>-N&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>7&lt;sup&gt;94&lt;/sup&gt;</td>
<td>styrene</td>
<td>Poly(styrenesulfonate)</td>
<td>NMP&lt;sup&gt;h&lt;/sup&gt;+NMP</td>
<td>-OSO&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>8&lt;sup&gt;91&lt;/sup&gt;</td>
<td>1,3-diisopropenylbenzene</td>
<td>PEO</td>
<td>LAP+AROP</td>
<td>-OH</td>
</tr>
<tr>
<td>9&lt;sup&gt;92&lt;/sup&gt;</td>
<td>divinylbenzene</td>
<td>PEO</td>
<td>AROP+RP</td>
<td>-NH&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>10&lt;sup&gt;95&lt;/sup&gt;</td>
<td>acrylamide+allyl acetamide</td>
<td>2-(dimethylaminoethyl) methacrylate</td>
<td>ATRP+RP</td>
<td>-N(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt;</td>
</tr>
<tr>
<td>11&lt;sup&gt;96&lt;/sup&gt;</td>
<td>methacrylate</td>
<td>PEO</td>
<td>Commercial macromonomer</td>
<td>-OH</td>
</tr>
<tr>
<td>12&lt;sup&gt;51&lt;/sup&gt;</td>
<td>HEMA+methacrylate</td>
<td>Polylactide</td>
<td>ROP+RP</td>
<td>-OH</td>
</tr>
<tr>
<td>13&lt;sup&gt;50&lt;/sup&gt;</td>
<td>HEMA+methacrylate</td>
<td>Polycaprolactone</td>
<td>ROP+RP</td>
<td>-OH</td>
</tr>
<tr>
<td>14&lt;sup&gt;66&lt;/sup&gt;</td>
<td>methacrylate</td>
<td>PDMS</td>
<td>AROP+RP</td>
<td>Pyridyl-</td>
</tr>
</tbody>
</table>

<sup>a</sup> Polymerization technique is introduced in the following format: (synthesis of macromonomer) + (polymerization of macromonomers).

<sup>b</sup> AROP: Anionic Ring-Opening Polymerization

<sup>c</sup> RP: free Radical Polymerization

<sup>d</sup> CROP: Cationic Ring-Opening Polymerization

<sup>e</sup> LAP: Living Anionic Polymerization

<sup>f</sup> ATRP: Atom Transfer Radical Polymerization

<sup>g</sup> NMP: Nitroxide Mediated Radical Polymerization
However, no one has yet taken advantage of the precise control and high efficiency provided by living anionic polymerization to prepare vinyl-based combs with functionalized branch ends. Macromonomers with functionalizable groups at one end and polymerizable groups at the other end are suitable building blocks to prepare comb polymers with end-functionalized branches by living anionic polymerization. One of the best ways to synthesize such well-defined, $\alpha,\omega$-difunctional macromonomers is to initiate a living anionic polymerization with a functional initiator and then terminate it with a functional terminating agent.\textsuperscript{97} The functionalizable end group from the initiator should remain stable during anionic polymerization and should be amenable to various transformation chemistries in the subsequent functionalization step.

The rapidly developing area of thiol-ene “click” chemistry\textsuperscript{98} provides an ideal option for further functionalization of vinyl-functionalized comb polymers. Thiol-ene “click” reactions, which involve the photo- or thermally-initiated radical addition of thiols to vinyl groups, are highly efficient, rapid, regio-selective (anti-Markovnikov addition), and insensitive to moisture and oxygen.\textsuperscript{99-114} Moreover, isolated vinyl groups reactive to thiol-ene reactions are inert during anionic polymerization. Recently Quirk et al.\textsuperscript{115} have demonstrated successful incorporation of thiol-ene “click” chemistry reactions into the general functionalization methodologies (GFM) of anionic polymerization. In their work $\alpha$-vinylpolystyrenes, which were prepared by living anionic polymerization with 4-pentenyllithium as the initiator, were efficiently functionalized with various groups,
such as quaternary ammonium groups, carboxylic acid groups and perfluoroalkyl groups, using photoinitiated thiol-ene “click” chemistry.

2.2 Bulk thermodynamics in polymer blends

In the framework of the Flory-Huggins mean field theory, the bulk thermodynamic interactions in a binary polymer blend can be described on a local level using the exchange interaction parameter, $\chi_{\text{eff}}$. $\chi_{\text{eff}}$ considers the nearest neighbor interactions between a single segment of polymer 1 and a single segment of polymer 2. $\chi_{\text{eff}}$ is given as:

$$
\chi_{\text{eff}} = \frac{z \Delta \varepsilon_{12}}{kT},
$$

(2.1)

where $k$ is the Boltzmann constant, $T$ is temperature, and $z$ is the coordination number of a lattice. In the simplest manifestation of the Flory-Huggins theory, $\Delta \varepsilon_{12}$ is the change in interaction energy per segment due to the mixing and is defined as:

$$
\Delta \varepsilon_{12} = \varepsilon_{12} - \frac{1}{2} (\varepsilon_{11} + \varepsilon_{22}),
$$

(2.2)

where $\varepsilon_{11}$ or $\varepsilon_{22}$ is the interaction energy between two segments of the same polymer 1 or 2, and $\varepsilon_{12}$ is the interaction energy between one segment of polymer 1 and one segment of polymer 2. In general, it is found that in order to better describe the behavior of real blends $\Delta \varepsilon_{12}$ must be understood as a difference in free energy, that is, as having both an enthalpic and entropic part:

$$
\Delta \varepsilon_{12} \equiv \Delta \varepsilon_h - T \Delta \varepsilon_s,
$$

(2.3)

where $\Delta \varepsilon_h$ is the enthalpic contribution and $\Delta \varepsilon_s$ is the entropic contribution. As a result,
\( \chi_{\text{eff}} \) contains both enthalpic and entropic contributions as well and is given as:

\[
\chi_{\text{eff}} = \frac{z\Delta \varepsilon_h}{kT} - T \left( \frac{z\Delta \varepsilon_s}{kT} \right).
\]

(2.4)

Note that the entropic part of \( \chi_{\text{eff}} \) is temperature-independent.

A single \( \chi_{\text{eff}} \) can be determined experimentally for a binary blend of homopolymers using the assumptions of ignoring the chemical difference between end and interior segments and taking the system to be incompressible. In the following sections, we will discuss factors affecting bulk thermodynamics in polymer blends, which include isotopic labeling, chain end chemistry, molecular weight, composition, and branching.

2.2.1 Isotopic labeling effect

It is important to know the isotopic labeling effect on bulk thermodynamics because deuterium labeling is a common technique for providing contrast in studies of polymer blends. Bates et al.\textsuperscript{116-118} found evidence supporting the existence of an isotopic effect in polystyrene and polybutadiene isotopic binary blends. This isotopic effect originated from the small difference in the C-D and C-H bond lengths and their corresponding polarizabilities, according to work by Bates and Wignall.\textsuperscript{119} They reported the temperature dependence of \( \chi_{\text{eff}} \) for a 50/50 blend of deuterated linear PS (1290 kg/mol) and hydrogenous linear PS (90 kg/mol) to be:

\[
\chi_{\text{eff}} = \frac{(0.2 \pm 0.01)}{T} - (2.9 \pm 0.4) \times 10^{-4},
\]

(2.5)

for a segment volume of 100 cm\(^3\)/mol.
2.2.2 Molecular weight effect

According to the Flory-Huggins theory, the number of segments (N) in a polymer chain is assumed not to affect the thermodynamic interaction parameter, $\chi$. The interaction between chains is defined purely in a local manner on the segment level. However, a dependence of $\chi_{\text{eff}}$ on chain length in isotopic blends has been reported in various works\cite{120, 121}. Melenkevitz\cite{122} proposed the chain length dependence of $\chi_{\text{eff}}$ to be:

$$
\chi_{\text{eff}} = \chi_{\text{eff}}(\infty) + D / N ,
$$

(2.6)

where $D$ is a constant. This relationship was found to describe well the experimental results by Londono et al.\cite{120} and Greenberg et al.\cite{123}

2.2.3 Composition effect

Composition ($\Phi$) independence of $\chi_{\text{eff}}$ is assumed by the Flory-Huggins Theory. However, mixed experimental results have been reported regarding the composition effect on $\chi_{\text{eff}}$. SANS measurements have shown that the minimum of $\chi_{\text{eff}}$ is located at $\Phi = 0.5$ for isotopic linear blends of PVE\cite{121}, PEE\cite{124}, and PE\cite{120}. For isotopic PS blends\cite{118}, the maximum of $\chi_{\text{eff}}$ is located at $\Phi = 0.5$. Balsara et al.\cite{125} reported that no compositional dependence of $\chi_{\text{eff}}$ was found in isotopic blends of PEE within experimental uncertainty.

The origin of the composition dependence of $\chi_{\text{eff}}$ remains an unsolved problem. Several theoretical studies\cite{126-128} demonstrated that the effects of compressibility and density fluctuations were not the reasons for the composition dependence of $\chi_{\text{eff}}$ observed by SANS experiments. Instead the observed divergences at compositions far from $\Phi = 0.5$
should be attributed to experimental errors. Painter and Berg\textsuperscript{129} considered extremely small changes in the fraction of same-chain contacts in polymer blends as the reason for divergences at the composition extremes. Gujrati and Rane\textsuperscript{130} argued that effective $\chi_s$, which always contained contributions from compressibility effects, were expected to show weak composition dependence without divergences at the composition extremes.

2.2.4 Chain end chemistry effect

Chain end chemistry plays a critical role in determining the compatibility of polymer blends. Lee et al.\textsuperscript{131} studied the phase behavior by measuring the UCST cloud point curves for binary blends of polyisoprene (PIP, 1250 g/mol) and polydimethylsiloxanes (PDMS) with various chain end chemistries. They found that the apparent critical points, $T_c$, of these blends decreased inversely as the polarity of the PDMS end groups, or $T_{c,CH_3} > T_{c,COOH} > T_{c,NH_2}$. They argued that the better compatibility of the PIP/PDMS-NH$_2$ blend is due to the fact that the repulsive interaction between the PDMS backbone and the NH$_2$ end group was stronger than the repulsive interaction between the PIP backbone and the PDMS chain end. Hwang\textsuperscript{132} used SANS to study the effect of chain end chemistry on bulk thermodynamics of blends of star and linear polybutadiene (PB). Three chain end functionalities for the star PS were studied, varying from 3-(tert-butyldimethylsiloxy)-1-propyl (SO) to hydroxypropyl (OH) to 2,2,2-trifluoroethanesulfonxypropyl (CF). They found that $\chi_{\text{eff}}$ values of these blends
measured from SANS increased significantly as the chain ends of star PB varied from SO to OH to CF at constant temperature.

2.2.5 Branching effect

In order to precisely understand its effect on bulk thermodynamics, branching is divided into two categories: short-chain and long-chain branching. Branches of a polymer in the short-chain branching case contain a few chemical groups, e.g. ethyl or propyl, while in the long-chain branching case branches contain many repeat units.

The effect of short-chain branching on bulk thermodynamics, especially compatibility in binary blends has been extensively studied\textsuperscript{22, 133-136}, driven by the strong desire to improve miscibility in polyolefin blends. Alamo et al.\textsuperscript{134, 135} studied the phase behavior in blends of deuterated high-density polyethylene (HDPE) and hydrogenous low-density polyethylene (LDPE) with short branches. They found that phase separation occurred when the degree of branching was above 8 branches per 100 backbone carbons. Graessley et al.\textsuperscript{136} studied blends of poly(ethylene-\textit{r}-ethylethylene) (PEE) copolymers with known short branch contents and their results revealed that $\chi_{eff}/\Delta y^2$ increased with the higher average content of the short branches in the blend, where $\Delta y$ is the difference in short branch contents between the two copolymers. Krishnamoorti et al.\textsuperscript{137} studied the effect of the short branch length on $\chi_{eff}$ using SANS and found that $\chi_{eff}$ of the blend containing short-chain branching components with slightly longer branches was larger than that of the blend with shorter branching. Theoretical studies of the short-chain
branching effect by Schweizer\textsuperscript{138,139} using the polymer reference interaction site model (PRISM) indicated that the predominant contribution to $\chi_{\text{eff}}$ was from enthalpy due to compressibility. On the other hand, Fredrickson et al.\textsuperscript{22,133} argued that the short-chain branching effect on $\chi_{\text{eff}}$ was mainly due to an entropic origin based on their results using Gaussian field theory.

Several experimental studies\textsuperscript{19-21,23,123,132,140-145} have been reported on the effect of long-chain branching on bulk thermodynamics in polymer blends. Faust et al.\textsuperscript{142} investigated the miscibility of blends containing poly(vinyl methyl ether) (PVME) and PS with cloud-point experiments. They found that changing the PS architecture from linear to a 22-arm star in the blend did not change the shape of the LCST curve significantly. This finding is contradictory to the findings of Russell et al.,\textsuperscript{143} which were that the cloud-point curve of a 4-arm star PS/PVME blend was shifted up 10 °C higher than that of a linear PS/PVME blend. Chen et al.\textsuperscript{144} found that the miscibility in PEE blends decreased when one PEE component in the blend had a long-chain branching structure. Although qualitative results from these compatibility studies provide evidence of a long-chain branching effect on the bulk thermodynamics, quantitative measurements of the strength of this architecture effect are needed.

Our group has been systematically studying the effect of long-chain branching on bulk thermodynamics with SANS and has compared the experimental results with the theory by Fredrickson et al.\textsuperscript{22} In this theory athermal binary blends in which the components have identical chemistries but various architectures are considered. The interaction
parameter, $\chi$, is expressed as:

$$\chi = \alpha \left( v_1 v_2 \right)^{1/2},$$  \hspace{1cm} (2.7)

where $v_1$ and $v_2$ are the segmental volumes of the two components. $\alpha$ is an invariant interaction parameter that is independent of how the segments of the blend components are defined.$^{146, 147}$ $\alpha$ contains both an enthalpic contribution, $A(\Phi)$, and an entropic contribution, $B(\Phi)$, with

$$\alpha = A(\phi) / T + B(\phi).$$  \hspace{1cm} (2.8)

The entropic contribution to $\alpha$, $\alpha_\epsilon$, may be given in terms of the number of arms, $p$, and the arm radius of gyration, $R_2$, for blends of star/linear homopolymers. When the condition $(p-3)(R_1/R_2)^2 >> 1$ is met, where $R_1$ is the radius of gyration of the linear polymer, the universal form of $\alpha_\epsilon$ is given as:

$$\alpha_\epsilon \approx \frac{1}{64\pi \sqrt{2}} \frac{(p-3)^{3/2}}{(1-\phi)^{1/2} R_2^3},$$  \hspace{1cm} (2.9)

where $\Phi_1$ is the volume fraction of the linear component in the blend. Fredrickson et al.$^{22}$ predicted that $\chi$ is small in the star/linear blend and the magnitude of $\chi$ increases with an increasing number of arms. The size of $\chi$ in comb/linear blends is predicted to be much larger because there are more branch points per molecule than for the star polymer.

Greenberg et al.$^{19, 123, 148}$ used SANS to obtain values of $\chi_\epsilon$ in binary blends containing linear PS and 4-, 5-, or 6-arm star PS and they found that the magnitude of $\chi_\epsilon$ increased monotonically with the number of arms of the star PS. The magnitude of $\chi_\epsilon$ in a 6-arm comb/linear PS blend was about 20 times larger than that in a 6-arm star/linear PS blend.
These results were in agreement with the predictions of Fredrickson et al.’s theory. Martter et al.\textsuperscript{140} measured values of $\chi_{\text{eff}}$ for blends of linear and well-defined star PBs with SANS. In their results, $\chi_\varepsilon$ varied in a nonmonotonic fashion with number of arms: $\chi_{\varepsilon,12\text{-arm}} > \chi_{\varepsilon,4\text{-arm}} > \chi_{\varepsilon,6\text{-arm}} > \chi_{\varepsilon,8\text{-arm}}$. Another measurement of $\chi_{\text{eff}}$ by Martter et al.\textsuperscript{141} in star/linear PMMA blends indicated that the value of $\chi_\varepsilon$ increased monotonically with the number of arms up to 14. Hwang\textsuperscript{132} measured $\chi_{\text{eff}}$ values in blends of linear PB and star PB with functionalized end groups and their results showed that $\chi_{\text{eff}}$ increased monotonically with number of arms when the end group chemistry was fixed. Lee et al.\textsuperscript{21} studied the effects of the number of branch points and chain ends on bulk thermodynamics by measuring $\chi_{\text{eff}}$ values in blends of branched and linear polystyrenes using SANS. The values of $\chi_{\text{eff}}$ increased as the number of branch points in the branched PS increased from 1 to 2 to 4 for a fixed number of chain ends, and $\chi_{\text{eff}}$ values increased as the number of chain ends increased from 6 to 9 to 13 for a fixed number of branch points. Comparison with the prediction of Fredrickson’s Gaussian field theory, which only considered entropic contributions indicated the existence of an enthalpic contribution to $\chi_{\text{eff}}$. They argued that the incorporation of branch points with chemistries different from the chemistry of the repeat units was responsible for the enthalpic contribution. Yang\textsuperscript{149} investigated a series of “pom-pom” polystyrenes with various backbone lengths between the two branch points. Except for the “star” molecule, for which the backbone length between the two branch points was zero, the values of $\chi_\varepsilon$
increased as the two branch points moved closer to each other, as predicted by the Gaussian field theory.

2.3 Surface segregation in polymer blends

In a binary polymer blend, the compositions at the interfaces may be different from the composition in the bulk. The component with lower surface energy will segregate to the surface due to the tendency to minimize the overall free energy of the system. This phenomenon in a binary blend film is illustrated with a schematic composition depth profile in Figure 2.4. The degree of surface segregation for the low surface energy component is often quantified by the surface excess, $Z^*$, which is defined by

$$Z^* = \int_0^Z [\phi(z) - \Phi_{\text{bulk}}(z)] dz,$$  \hfill (2.10)

where $\Phi_{\text{bulk}}$ is the bulk volume fraction of the segregating component and $\Phi(z)$ is the volume fraction of the segregating component at depth $z$. Since $\Phi(z)$ is unitless, the surface excess, $Z^*$, has units of length. Several important factors in determining the surface and interfacial segregation will be discussed in the following sections.
2.3.1 Isotopic labeling effect

Because isotopic labeling is widely used as a technique to boost contrast in NR measurements of polymer materials, it is important to discuss its effect on surface segregation. The C-D bond is 1.6 % shorter than the C-H bond. Therefore, the polarizability and cohesive energy of the deuterated component are slightly lower than those of the hydrogenous component, which results in a slightly lower surface energy for the deuterated component. Jones et al. first reported the small surface segregation driven by deuteration in isotopic blends of linear PS using Forward-Recoil Spectrometry (FRES). They found enrichment of deuterated PS at the blend surface after annealing at 184 °C under vacuum for up to a week. Quantitative measurements of surface segregation in symmetric isotopic PS blends using NR by Hariharan et al. indicated that deuterated PS segregated to the surface and the degree of surface segregation increased as the molecular weight increased. The surface segregation in isotopic PMMA blends was insignificant according to the NR and static secondary ion mass spectrometry (SSIMS) measurements by Hopkinson et al. They argued that this was due to the smaller
difference in surface energy between dPMMA and hPMMA (0.00-0.04 mJ/m$^2$) than between dPS and hPS (0.08 mJ/m$^2$).\textsuperscript{153}

2.3.2 Molecular weight effect

The number of configurations that one polymer chain can take is less when it is located at the surface than in the bulk, as a result of the chain’s connectivity. This effect becomes stronger as the chain length increases. Therefore, short polymer chains are enriched at the surface in a blend of short and long polymers of equivalent chemistry in order to minimize the loss in configurational entropy. Surface segregation of the low molecular weight component in an asymmetric blend was predicted by Hariharan et al.\textsuperscript{154} using a mean-field lattice model. Their prediction was confirmed by NR experimental results\textsuperscript{151} showing that the surface was enriched by a low molecular weight hydrogenous PS (12 or 30 kg/mol) when blended with a high molecular weight deuterated PS (571 kg/mol). The investigation of molecular weight effect in isotopic polymer blends is often complicated by the opposite effect of isotopic labeling. For example, no surface segregation of hydrogenous or deuterated PS was found when the molecular weight of hydrogenous PS was increased to 52 or 96 kg/mol in a blend with 571 kg/mol deuterated PS.

2.3.3 Composition effect

Jones et al.\textsuperscript{150} and Sokolov et al.\textsuperscript{155} studied the effect of bulk composition on surface segregation in isotopic linear PS blends using FRES. Their results indicated the surface
excess of deuterated PS increased as the bulk concentration of deuterated PS increased within the range of $\Phi_{\text{bulk}} = 0.025-0.2$. Theoretical studies by Hariharan et al.\textsuperscript{156} predicted that when normalized by its bulk volume fraction the surface excess of the segregating component was larger when the species enriching the surface was present in a dilute condition ($<0.05$).

2.3.4 Chain end effect

Chain end effects on surface segregation include both enthalpic and entropic contributions. The enthalpic contribution comes from the chemical difference between chain ends and repeat units and could favor or disfavor surface enrichment by a species with many chain ends. Entropically chain ends are always preferred at the surface as compared to interior segments of a polymer chain. This preference is driven by the tendency to minimize the loss of conformational entropy. Dorego et al.\textsuperscript{157} reported evidence of surface segregation of deuterated chain ends of hydrogenous PS using high resolution electron energy loss spectrum (HREELS) experiments. They found that the deuterium concentration in a 1 or 2 monomer thick layer near the surface was more than 2 times the bulk concentration. Calculation of the chain end distribution near the surface of an incompressible polymer melt by Wu et al.\textsuperscript{158} found an entropic attraction of chain ends to the surface due solely to chain connectivity.

It is expected that modifying chain end chemistry would affect the surface segregation in blends. Schaub et al.\textsuperscript{159} studied the effect of low surface energy fluorinated chain ends
on surface segregation in binary PS blends. They found surface segregation of hydrogenous PS with oligotetrafluoroethylene chain ends (hPS-TFE) in all the studied blends and the degree of surface segregation of hPS-TFE increased as the bulk concentration increased from 2 to 20%. Tanaka et al.\textsuperscript{160} also reported surface segregation of fluoro-functionalized PS when blending with unfunctionalized PS using NR and XPS. They further found that the annealing condition, in vacuum or in boiling water, was critical for determining whether surface segregation would occur. Kajiyama et al.\textsuperscript{161} studied the effect of chain end chemistry on surface segregation in PS/PMMA blends. PS was found to cover the surface of PS/PMMA and PS/α,ω-PMMA(COOH)\textsubscript{2} blend films as expected, due to the higher surface energy of the PMMA main chain. On the other hand, PMMA was enriched at the film surface of an α,ω-PS(COOH)\textsubscript{2}/PMMA blend, due to the hydrogen bonding via carboxyl end groups of PS chains and the high surface energy of carboxyl groups. Tanaka et al.\textsuperscript{162} combined NR, XPS and secondary ion mass spectrometry (SIMS) to study the effect of chain end chemistry on surface and interfacial segregation in symmetric isotopic blends of PS. Both chain ends of hydrogenous PS (hPS) in the blend were functionalized with fluoroalkyl- (Rf) or carboxyl (COOH) groups. The hPS component was found enriched at the surface of α,ω-hPS(Rf)\textsubscript{2}/dPS blend films, but depleted from the surface of α,ω-hPS(COOH)\textsubscript{2}/dPS blend films. Both Rf and COOH end groups were attracted to the substrate interface, resulting in the segregation of hPS component to the substrate interface for both blends.
2.3.5 Branching effect

The effect of branching on surface segregation depends on the types of branching, which can be divided into two categories, short-chain branching or long-chain branching, in a manner similar to the division done with the discussion of bulk thermodynamics.

2.3.5.1 Short-chain branching effect

Short-chain branching (e.g. ethyl, propyl) is usually found in polyolefins and therefore its impact on surface segregation in blends has great practical importance. Steiner et al.\textsuperscript{163} used nuclear reaction analysis (NRA) to study the surface segregation in a bilayer film of two olefinic copolymers. They found that after the two layers were allowed to interdiffuse and create a blend layer at equilibrium the film surface was completely wet with the component that had the higher content of short chain branches and that the thickness of this wetting layer increased with the annealing time. Scheffold et al.\textsuperscript{164} reported that in binary poly(ethylene-\textit{r}-ethylethylene) (PEE) blends the component with higher level of ethyl branching was preferred at the air surface, but no enrichment at the substrate interface was found. Budkowski et al.\textsuperscript{165} summarized that the degree of surface segregation in binary PEE blends was determined by the degree of chemical mismatch, i.e., the difference in the amount of ethyl branches between the two components. Somorjai et al.\textsuperscript{166} used X-ray photoelectron spectroscopy (XPS) and sum frequency generation spectroscopy (SFG) to study surface segregation in blends of atactic polypropylene (aPP) and random poly(ethylene-co-propylene) rubber (aEPR). The aPP
component segregated to the surface in both miscible and immiscible blends, and the thickness of the surface enrichment layer was related to the bulk miscibility in the blends. They argued that the higher surface activity of αPP was due to the fact that methyl side branches adopted a preferred configuration at the surface according to SPG measurements. Later Somorjai et al.\textsuperscript{167} studied αEPR blends with crystalizable isotactic polypropylene (iPP) and found that the surface segregation of iPP depended on the processing conditions. iPP enriched the surface of blends melted in open air, which was consistent with their previous results,\textsuperscript{166} while surface segregation of iPP was suppressed in blends melt-pressed between substrates.

Fredrickson et al.\textsuperscript{168-170} theoretically predicted the surface segregation of the more flexible component in polyolefin blends due to entropic driving forces, which was in contrast with the Monte Carlo simulation results by Yethiraj et al.\textsuperscript{171-173} Yethiraj et al. argued that the stiffer chain should be favored at the surface due to the better local packing for stiffer chains. They concluded that linear chains were preferred at the surface in a system without fluid-fluid attraction forces and branched chains segregated to the surface when there were strong fluid-fluid attraction forces.

2.3.5.2 Long-chain branching effect

Several theoretical works have been reported to explain the effect of long-chain branching on surface segregation by purely entropic driving forces originating from the architectural asymmetry in binary blends of components with two different architectures.
The first theoretical study was carried out by Balazs and Siemasko\textsuperscript{174} using Monte Carlo simulation in blends of comb and linear polymers containing identical repeat units. They found comb polymers had a slight preference for the surface due to the localization of branches near the surface and predicted stronger surface segregation for the comb polymers with shorter branches. Wu and Fredrickson\textsuperscript{175} studied the effect of different types of branching on surface segregation in athermal blends using a self-consistent field theory and found that the chain ends were attracted while the junctions were repelled from the surface by entropic forces. For star/linear blends symmetric in molecular weight, the degree of segregation of the star was predicted to increase with an increase in its number of arms. For comb/linear blends, the magnitude of segregation increased as the distance between branch points decreased. Walton and Mayes\textsuperscript{176} employed a self-consistent mean-field to examine the surface segregation of a comb-shape polymeric additive in a linear polymer matrix with and without the existence of enthalpic interactions. Yethiraj\textsuperscript{177} studied blends of star and linear polymers using an integral equation theory which considered both the packing and conformational entropic effects and this theory predicted that linear polymer enriched the surface while star polymer had a maximum concentration at a small depth from the surface comparable to its $R_g$. Recently Archer et al. investigated several topics regarding surface segregation of star polymers in linear hosts, including enthalpic contributions\textsuperscript{178} and compressibility near the surface\textsuperscript{179}; and they extended their theory to highly branched architectures\textsuperscript{180}, such as multi-arm stars, dendrimers and combs. In the studies of highly branched polymers, they
proposed to use the primary segment fraction, which was defined as the ratio of the total number of polymer segments between chain ends and their nearest branch points to the total number of segments in the molecule, as a parameter to qualitatively compare the tendency of polymer architectures to segregate to interfaces in branched/linear blends. The surface tensions of stars were calculated by Archer et al.\textsuperscript{181, 182} to be lower than those of linear analogs, a prediction which was confirmed by microfiber Wilhelmy measurements of star and linear PS melts. Their analysis revealed that both entropic and enthalpic contributions were responsible for the reduced surface tension of star melts. Surface tension measurements of linear/linear and star/linear PS blends showed a convex surface tension-composition profile for both blend systems, with higher curvature for the star/linear blends than for the linear/linear blends, indicating stronger surface segregation of the star component relative to the linear chains.\textsuperscript{183} In order to simulate the highly convex surface tension-component profiles of the 11-arm star/linear blends with the self-consistent field lattice models, an architecture-dependent Flory interaction parameter ($\chi = 0.004$) had to be assumed. However, Cahn-Hilliard theory was able to predict a large surface segregation of star molecules in blends seen by surface tension measurements with a nearly neutral interaction parameter, indicating that these blends were still in one phase.

Blending polymers of different chain architectures has been proven to be useful in controlling interfacial properties by controlling interfacial segregation. Mayes et al.\textsuperscript{1} created a PEO-like surface on PMMA by segregation of a comb polymer with a PMMA
backbone and PEO branches when blending with linear PMMA. This strategy has been investigated for a series of biomedical applications, such as providing biomaterials with resistance to both protein adsorption and cell adhesion\(^1\), and tuning cell responses to tissue engineering scaffolds.\(^2\) Amphiphilic comb copolymers were added as macromolecular surfactants migrating to the surface to provide strong anti-fouling and improve flux of current filtration membranes for water purification.\(^3-6, 184-186\)

Our group has been systematically performing experimental studies on the effect of long-chain branching on interface segregation with well-defined polymers. Greenberg et al.\(^7, 148\) investigated the surface segregation behavior in blends of star and linear PS using NR and NRA. They found the surface segregation of star PS increased as the number of arms increased, which was consistent with the theory by Fredrickson et al.\(^175\) For blends containing deuterated star PS and hydrogenous linear PS, the star PS segregated to the surface as well, but the magnitude of the surface excess was smaller than that of hydrogenous star PS in blends with deuterated linear PS. In star and linear PB blends, the deuterated linear PB segregated to the surface according to Matter.\(^187\) In this case the long-chain branching effect was overwhelmed by the isotopic labeling effect. Lee et al.\(^23, 188\) used NR and surface enhanced Raman spectroscopy (SERS) to study the contributions of chain ends and branch points to surface segregation in blends of end-branched and linear PS. They found for a series of branched PS with a fixed number of chain ends that the surface excess increased as the number of branch points increased; for another series of branched PS with fixed number of branch points, the surface excess increased as the
number of chain ends increased as well. Yang\textsuperscript{149} studied surface segregation of “pom-pom” PS molecules with varying distance between branch points in blends with linear PS. Results from NR and SERS measurements indicated that the magnitude of surface segregation varied with the compactness of the “pom-pom” molecules, although these “pom-pom” molecules had the same number of branch points and chain ends.

2.4 Dynamics of comb polymers

Both bulk dynamics (Section 2.4.1) and surface dynamics (Section 2.4.2) of comb polymers are discussed with examples reported in literature in this section.

2.4.1 Bulk rheology

The bulk rheology of polymers with various long-chain branched architectures, such as star,\textsuperscript{189-191} comb,\textsuperscript{192} H-shape,\textsuperscript{193} and dendrimer,\textsuperscript{194} has been examined by various groups. The introduction of long-chain branching significantly alters the chain dynamics. The melt viscosity of an unentangled branched polymer is less than that of a linear polymer with similar molecular weight. However, the viscosity of the branched polymers can be several orders of magnitude larger than that of linear ones once their molecular weights surpass a critical molecular weight, $M_c$. In the entanglement regime (above $M_c$), the scaling relationship $\eta \sim M^{3.4}$ is valid for linear chains. In contrast, the scaling exponent with molecular weight for long-chain branched polymers is much higher than 3.4 when the branched chains are entangled. The rheological behaviors of long-chain branched
polymers have been evaluated with several models based on the reptation and fluctuation theory.\textsuperscript{12,191,195-198} In general, these polymers experience hierarchical relaxation, in which the branches relax first, followed by the junction points, and at last the backbone reptates in a dilated tube.\textsuperscript{195,196} The relaxed branches act as a solvent. Therefore, they facilitate the reptation of the backbone and decrease the rubbery modulus.\textsuperscript{195,199}

Two rubbery plateaus are observed in the master curves of comb polymers with extremely high branching density, which are usually explained by the hierarchical relaxation mechanism as well.\textsuperscript{16,30,200-204} The higher plateau corresponds to the relaxation of branches, while the lower one is considered as the rubbery plateau of the whole chain. Tsukahara et al.\textsuperscript{16,30,200} studied bulk properties of a series of comb polymers prepared by homopolymerization of polystyrene macromonomers. They found that it was difficult to form entanglements in these densely branched comb polymers which resulted in the brittle nature of solution-casted films. A great increase in the backbone length led to a weak rubbery plateau in the master curve of these comb polymers. However, the plateau modulus was much lower than that of the linear polystyrenes. When the molecular weight of polystyrene branches was close to the $M_c$, even the comb polymer with a very short backbone length showed a clear rubbery plateau. Recently McKenna et al.\textsuperscript{17} systematically investigated the effect of branch length and backbone length on the rheological behavior of densely branched comb polymers with a polynorbornene backbone and polylactide branches. They observed two plateaus in master curves of the comb polymers, which were explained by the hierarchical relaxation process of branches.
and backbone. Despite the large molecular weight, little evidence of entanglement was found for branches and for the whole comb polymer. They further pointed out that the lower modulus plateau was due to the relaxation of the backbone instead of entanglements, which reflected the molecular orientation of these stiffened comb polymers.

2.4.2 Surface dynamics in thin films

The free surfaces of liquids display thermally stimulated height fluctuations of very small amplitude. Theoretical studies\textsuperscript{205, 206} of films of viscoelastic fluids that describe the phenomena using hydrodynamic continuum models find that for sufficiently high viscosity the fluctuations are overdamped capillary waves with relaxation times, $\tau$, that are functions of the film viscosity, liquid surface tension, film thickness, and wavelength of the capillary wave. Pioneering work by Kim et al.\textsuperscript{18} experimentally verified the validity of the hydrodynamic continuum theory (HCT) for describing surface dynamics of films of linear polystyrene ($M_n = 123,000$ g/mol) utilizing X-ray Photon Correlation Spectroscopy (XPCS). The authors have shown that for linear polystyrene films the dependence of $\tau$ on in-plane wave vector $q_{||}$ and thickness $h$ can be represented well by the expression derived by Jäckel\textsuperscript{206} for the HCT applied under a no-slip boundary condition at the substrate surface:

$$\frac{\tau}{h} = \frac{2\eta [\sinh(q_{||}h) \cosh(q_{||}h) + q_{||}^2h^2]}{\gamma q_{||}h[q_{||}h][\cosh(q_{||}h) - q_{||}h]}.$$  \hspace{1cm} (2.11)
where \( \eta \) is the zero shear viscosity of the bulk melt and \( \gamma \) the surface tension. They reported good agreement between the film viscosities inferred from the XPCS data and literature values for bulk viscosities for temperatures sufficiently above \( T_g \). They found no evidence for an inhomogeneity in viscosity with depth for polystyrene film thicknesses ranging from 84 to 333 nm. Later, Jiang et al.\(^{207}\) reported a substrate confinement effect on linear polystyrene films of thickness approaching the radius of gyration (\( R_g \)) of a single unperturbed chain using XPCS. To explain the suppressed surface dynamics observed for films with thicknesses of \( 4R_g \) or thinner it was necessary to modify the HCT for overdamped capillary waves\(^{206}\) to include a finite elastic modulus, \( \mu \), in the film, presumably due to pinning of chains by physisorption to the substrate,

\[
\tau(q_{||}) = \frac{\tau_0(q_{||})}{1 + \tau_0(q_{||})(\mu/\eta)},
\]

where

\[
\tau_0(q_{||}) = \frac{2\eta[\cosh^2(q_{||}h) + q_{||}^2h^2]}{\gamma q_{||} [\sinh(q_{||}h)\cosh(q_{||}h) - q_{||}h]}. \tag{2.13}
\]

These XPCS results for very thin films stand in provocative contrast to the conclusions of works claiming the existence of a mobile layer on the surface. Ellipsometry measurements of \( T_g \) in polymer thin films by Keddie, Jones and Cory\(^{208}\) revealed a thickness-dependent reduction of \( T_g \) in thin films. Torkelson and Ellison\(^{209}\) observed faster dynamics on the surface of a supported PS film and the existence of a gradient in \( T_g \) through the film by a fluorescence/multilayer technique. Ediger et al.\(^{210}\) reported the observation of a mobile layer with thickness of 4-7 nm for supported thin films of various
polymers including polystyrene at $T = T_{g,\text{bulk}}$, by temperature-ramping anisotropy measurements\textsuperscript{211} of rotational mobility of a dispersed fluorescent dye molecule. Tsui et al.\textsuperscript{212} measured the effective viscosity of polystyrene thin films coated on silicon substrate by power spectral density analysis of AFM images of dewetting films. Their results showed that the film viscosity decreased with decreasing film thickness, which could be well explained by the existence of a surface mobile layer with a constant thickness of less than 2.3 nm.

The effect of architecture on surface dynamics of polymer thin films was investigated by Foster et al.\textsuperscript{24, 25} using XPCS. They found that while the hydrodynamic continuum theory was able to describe the surface height fluctuations of thin films of unentangled macrocyclic polystyrene melts as well as linear polystyrene melts, it did not fully capture the behavior of end-branched polystyrene thin films. The film viscosities of the macrocyclic polystyrene melts derived from the XPCS measurements matched well with bulk viscosities measured by rheometry. However, a remarkable discrepancy between bulk viscosity and film viscosity inferred from XPCS experiments existed in the end-branched polystyrene thin films. For cyclic polymers and some end-branched polymers, the variations of thickness normalized surface relaxation time, $\tau/h$, with temperature normalized by $T_{g,\text{bulk}}$ collapsed to a single curve. Green and coworkers\textsuperscript{213, 214} found that thin film dynamics in star-shaped polymer melts was dependent on architecture details, such as the length of the arm and number of arms. In contrast to linear polystyrenes, the $T_g$ measured by ellipsometry for films of an 8-arm star with arm
molecular weight of 10k increased as the thickness decreased once it was below 60 nm. Positron annihilation lifetime spectroscopy measurements of that star polystyrene melt suggested $T_g$ at the surface was as much as 8 °C higher than in the bulk. On the other hand 8-arm stars with longer arms showed a decrease in film $T_g$ with decreasing film thickness.

2.5 Characterization techniques

Basic principles of several important characterization techniques used in this work are introduced in this section.

2.5.1 Small angle neutron scattering (SANS)

Neutron scattering is a powerful, non-invasive technique for condensed matter investigations in general, because neutrons do not change the investigated sample by depositing energy into it. Neutrons are scattered by the nuclei in the probed sample through nuclear interactions between the neutrons and the nuclei, and the ability of a nucleus to scatter neutrons is quantified as the scattering length of the nucleus. Neutron scattering lengths vary irregularly with atomic numbers and are independent of wave vector transfer $q$. This feature of neutron scattering is used to advantage in deuterium labeling, which is based on the fact that the scattering lengths for hydrogen and deuterium are widely different ($b_H = -3.74 \times 10^{-15}$ m and $b_D = 6.67 \times 10^{-15}$ m, respectively). The negative sign for $b_H$ means that the wave function of the scattered neutrons is out of
phase with respect to that of the incident neutrons. Neutrons also exhibit high penetration (low absorption) for most elements, which makes neutron scattering ideal for probing bulk samples. A SANS experiment measures the intensity of the scattered neutrons at varying small scattering angles ($2\theta$), from which information about the sample structure is inferred. Typical values of scattering angles are from $0.2^\circ$ to $2^\circ$, which correspond to length scales from 10 Å to several hundred Å for the investigated structures.\(^{215}\)

In an elastic collision, the total momentum and energy are conserved when a neutron is scattered by a particle. The momentum transfer is given as

$$\frac{h}{2\pi} q = \frac{h}{2\pi} (k_f - k_i),$$

(2.14)

where $k_i$ is the wave vector of the incident neutrons, $k_f$ is that of the scattered neutrons, and $h$ is Planck’s constant. The scattering vector or wave vector transfer $q$ is defined as $q = k_f - k_i$. The relationships among $q$, $k_i$ and $k_f$ for elastic scattering are presented in Figure 2.5. Since SANS is an elastic scattering technique, the magnitude, $k$, of the incident and scattered neutrons is $k = |k_i| = |k_f| = 2\pi / \lambda$, where $\lambda$ is the wavelength. The magnitude of $q$ is thus given as

$$|q| = \frac{4\pi \sin \theta}{\lambda},$$

(2.15)

![Figure 2.5 Relationships among $q$, $k_i$ and $k_f$ for elastic scattering.](image-url)
The reciprocal of $|q|$ is related to the length scale probed in real space, which is a controllable variable in a SANS experiment. The raw intensity data collected by a 2-dimensional detector are azimuthally averaged and converted to absolute coherent scattering intensity, $I(q)$, using the measured direct beam intensity.

The SANS curve for a single-phase binary isotopic polymer blend does not present distinct features like peaks. Therefore, modeling is necessary to obtain useful information about molecular structures and thermodynamic interactions in such a system. In this case, $I(q)$ is given as:

$$ I(q) = \frac{(b_1 - b_2)^2}{V} S(q), $$

where $V$ is a reference volume, and $b_i$ is the scattering length for component $i$ summed over the reference volume. $S(q)$ is the structure factor of the blend, from which information about the molecular structure and thermodynamic interactions can be inferred. The Random Phase Approximation (RPA) model developed by deGennes\textsuperscript{216} is a mean field theory to describe thermodynamics of polymer mixtures in the homogeneous phase region. The structure factor for an incompressible, isotropic binary blend in the RPA theory is given as:

$$ S^{-1}(q) = \frac{1}{\phi_1 N_1 S_1(q)} + \frac{1}{\phi_2 N_2 S_2(q)} - 2 \chi_{\text{eff}}, $$

where $\Phi_i$ is the volume fraction of component $i$, $N_i$ is the number of segments per chain for polymer $i$, $S_i(q)$ is the structure factor for component $i$, and $\chi_{\text{eff}}$ is the effective
exchange interaction parameter representing the exchange interaction between molecules on a per segment basis.

The structure factor for linear polymers of Gaussian statistics has the form of the well-known Debye function, $D(x)$:

$$S_{\text{linear}}(q) = D(x_{\text{linear}}) = \frac{2(e^{-x_{\text{linear}}} - 1 + x_{\text{linear}})}{x_{\text{linear}}^2},$$

where $x_{\text{linear}} = q^2 R_{g,\text{linear}}^2$ and $R_{g,\text{linear}}^2 = N_{\text{linear}} a^2/6$. $N_{\text{linear}}$ is the number of segments in the linear chain and $a$ is the statistical segment length. For polymers with different architectures such as star, pom-pom, and comb, different structure factors must be developed to describe each type of chain architecture. The structure factor for densely branched comb polymers studied in this work will be discussed and developed in detail in Chapter IV.

2.5.2 X-ray and neutron reflectometry (XR and NR)

X-ray or neutron reflectivity provides information about the composition depth profile of thin planar samples including layer thicknesses, and surface and interfacial widths. A XR or NR experiment measures the specular reflectivity as a function of the scattering wave vector perpendicular to the reflecting surface, $q_z$. Therefore structures in the direction perpendicular to the sample surface are probed.

When radiation is incident on the interface between two materials, part of the incident beam is reflected at the interface and the rest is transmitted through it. The relative
intensities of the reflected and refracted beams are decided by the refractive indices of the two materials. For X-rays and neutrons, the complex refractive index, \( n \), of a material is given as:

\[
n = 1 - \delta + i \beta, \tag{2.19}
\]

where \( \delta \) is the real part and \( \beta \) is the imaginary part of the \( n \). For X-rays,

\[
\delta = \frac{\lambda^2}{2\pi} r_e \rho_e \quad \text{and} \quad \beta = \frac{\lambda}{4\pi} \mu_x, \tag{2.20}
\]

where \( \lambda \) is the wavelength of the incident beam, \( r_e = 2.818 \times 10^{-15} \text{ m} \) is the classical electron radius, \( \rho_e \) is the electron density of the material, and \( \mu_x \) is the measured X-ray mass absorption coefficient. For neutrons, an analogous form of the complex refractive index applies, with

\[
\delta = \frac{\lambda^2}{2\pi} \left( \frac{b}{V} \right) \quad \text{and} \quad \beta = \frac{\lambda}{4\pi} \mu_n, \tag{2.21}
\]

where \( b/V \) is the neutron scattering length density of the material, and \( \mu_n \) is the material’s neutron absorption coefficient. \( \delta \) of most polymers is on the order of \( 10^{-6} \) for both X-rays and neutrons. The imaginary part of the \( n, \beta \), arises only for materials absorbing X-ray or neutrons. Absorption of neutrons is sufficiently small that \( \beta \) is negligible in most cases, except for materials containing isotopes of Li, B, Cd, or Gd. (However, incoherent scattering, which can be appreciable with H containing materials, is sometimes modeled using an effective absorption coefficient.) With CuK\(_\alpha\) X-rays, \( \beta \) for most materials is about 1/100 to 1/1000 of \( \delta \).

The electron density, \( \rho_e \), can be calculated as
\[
\rho_e = \frac{\rho N_A \sum b_i}{MW},
\]  
(2.22)

where \(N_A\) is the Avogadro’s number, \(MW\) is the molecular weight of a reference volume of material, \(b_i\) is the scattering length for a single atom in the reference volume, which is identical to the atomic number when far from an absorption edge, the sum is taken over the reference volume and \(\rho\) is the mass density. Similarly, the neutron scattering length density, \(b/V\), of a polymer can be calculated as

\[
\frac{b}{V} = \frac{\rho N_A \sum b_i}{MW},
\]  
(2.23)

where \(\rho\) is the mass density of the polymer, \(MW\) is the molecular weight of a repeating unit of the polymer, and \(b_i\) is the scattering length of element \(i\) in the repeating unit of the polymer.

X-ray scattering detects the variation in electron density in the sample, while neutron scattering detects the variation in neutron scattering length density. Electron density varies monotonically through the periodic table, but neutron scattering length density does not. Isotopes, though they have the same atomic number, can have largely different neutron scattering lengths. One can deliberately deuterate one component in the sample in order to provide enough contrast for neutron scattering measurements, due to the particularly large difference between the scattering lengths of hydrogen (\(b_H = -3.74 \times 10^{-15}\) m) and deuterium (\(b_D = 6.67 \times 10^{-15}\) m).

The geometry of a typical reflectometry experiment is shown in Figure 2.6. In this specular reflection geometry, the reflected angle, \(\theta\), is identical to the incident angle, \(\theta_0\),
and the angle of refraction, \( \theta_1 \), is given by Snell’s law:

\[
n_0 \cos \theta_0 = n_1 \cos \theta_1 .
\]

(2.24)

Figure 2.6 Scheme of neutron beam reflection and refraction at an interface.

If \( n_1 \) is less than \( n_0 \), \( \theta_1 \) will be less than \( \theta_0 \). This means that \( \theta_1 = 0 \) when \( \theta_0 \) reaches a critical value, \( \theta_c \), which can be calculated as

\[
\theta_c = \sqrt{2\delta} .
\]

(2.25)

Since \( \delta \) for polymers is usually \( 10^{-6} \), \( \theta_c \) is on the order of milliradians. For \( \theta_0 < \theta_c \), the total external reflection condition is reached, which means the incident beam will be entirely reflected in the absence of absorption. Above \( \theta_c \), only a portion of the incident beam intensity will be reflected and the rest is refracted. The reflectivity, \( R \), is defined as the ratio of the reflected intensity \( (I_r) \) to the incident intensity \( (I_0) \).

Changes in the direction of the refracted beam can be described by changes in the
component of the wave vector normal to the surface, \( k_{z,i} \). The second subscript denotes in which medium the quantity is calculated. For the case of the incident medium, \( k_{z,0} \) is given by

\[
k_{z,0} = 2\pi \sin \theta_0 / \lambda.
\]  

(2.26)

The value of \( k_z \) inside a one layer sample, \( k_{z,1} \), is calculated as:

\[
k_{z,1} = \left( k_{z,0}^2 - k_{c,1}^2 \right)^{1/2},
\]  

(2.27)

where \( k_{c,1} \) is the value of \( k_{z,0} \) with \( \theta_0 = \theta_c \) for medium 1. The \( k_z \) in layer \( i \) of a multilayer system is found from a generalized form of Eq. 2.27, namely

\[
k_{z,i} = \left( k_{z,0}^2 - k_{c,i}^2 \right)^{1/2}.
\]  

(2.28)

The reflection coefficient, \( r \), is the ratio of the reflected field amplitude to the incident field amplitude. For a smooth, sharp interface between layers \( i \) and \( i+1 \), it is given as:

\[
r = \frac{k_{z,i} - k_{z,i+1}}{k_{z,i} + k_{z,i+1}}.
\]  

(2.29)

The reflectivity \( R \) is the absolute square of \( r \) and by Fresnel’s law it can be given as:

\[
R = \frac{I_r}{I_0} = \frac{k_{z,0}^2 - k_{z,1}^2}{k_{z,0}^2 + k_{z,1}^2} = \frac{k_{z,0}^2 - \sqrt{k_{z,0}^2 - k_{c}^2}}{k_{z,0}^2 + \sqrt{k_{z,0}^2 - k_{c}^2}}.
\]  

(2.30)

For \( k_{z,0} \gg k_{z,c} \), the equation can be approximated as

\[
R \approx \frac{1 - \left( 1 - \left( \frac{k_{z,c}}{k_{z,0}} \right)^2 \right)^2}{1 + \left( 1 + \left( \frac{k_{z,c}}{k_{z,0}} \right)^2 \right)^2} \approx \frac{1}{16} \left( \frac{k_{z,c}}{k_{z,0}} \right)^4 = \frac{1}{16} \left( \frac{q_{z,c}}{q_{z,0}} \right)^4,
\]  

(2.31)

where \( q_{z,0} = 2k_{z,0} \) is the magnitude of the scattering wave vector in the direction perpendicular to the surface. Eq. 2.31 shows that for an ideal interface with no roughness, the reflectivity curve decays as \( q_z^{-4} \) at sufficiently large \( q_z \).
In a multilayer system, a beam refracted at the 0-1 interface may be reflected at other interfaces as well. Constructive or destructive interference takes place between the beam reflected at a deeper interface and the beam reflected at the surface because of the path difference between the two beams. Therefore in principle, information on the surface and interfaces within the sample can be inferred from the measured intensity.

Figure 2.7 shows an example of neutron reflectivity data obtained for a film on a substrate. The reflectivity $R$ is plotted as function $q$ on a semi-log scale. The reflectivity curve of a simple film sample usually exhibits three basic features. The first is the first rapid drop from the total reflection ($\log R = 0$), which occurs at a critical value of $q$ called $q_c$, or critical angle. The value of $q_c$ corresponding to this large drop is determined by the larger of scattering length densities of the substrate and the film. A second feature of the reflectivity curve is the decrease in envelop of the reflectivity with $q$, which is proportional to $q^{-4}$ for a smooth sample. The reflectivity decays more rapidly than $q^{-4}$ for samples with rough surface or interfaces. The reflectivity curve of a thin film sample may also show oscillations, the third feature, about the general trend of decreasing reflectivity. This pattern of oscillations is called Kiessig fringes, which is the result of interference between radiation reflected from the air/film interface and that reflected from the film/substrate interface. The amplitude of these fringes is proportional to the difference in scattering length densities between the thin film and the substrate, or the SLD contrast. Layer thickness may be estimated from the spacing between successive fringes at $q \gg q_c$ by
\[ d \approx \frac{2\pi}{\Delta q}, \quad \tag{2.32} \]

where \( \Delta q \) is the difference in \( q \) between successive minima or maxima in the reflectivity curve.

![Reflectivity curve by NR and model fit for an isotopic PS blend film on Si substrate.](image)

Reflectometry does not directly measure the chemical composition profile, because the measured reflectivity curve does not include phase information. In order to obtain a scattering length density depth profile, reflectivity curves from candidate models for the sample structure must be calculated and compared with the experimental curve. The
models are adjusted until a “best fit” between the calculated and experimental curve is found. In the non-linear regression process, the goodness of a fit is evaluated by the objective function given by

\[
\chi^2 \equiv \frac{1}{n+1} \sum \left\{ \frac{1}{\sigma_i^2} [R_m - R_c]^2 \right\},
\]

(2.33)

where \( R_m \) and \( R_c \) are the measured and calculated reflectivity at one value of \( q \), \( \sigma_i^2 \) is the variance and \( n \) is the total number of points from the experimentally measured reflectivity curve that is being fitted. A 3-layer model is the basis for describing the surface and interface segregation from which the analysis starts. With appropriate convolution of the interfaces with smearing functions, the scattering length density profile takes on the shape expected for interfacial segregation at both interfaces. The \( b/V \) values, thicknesses of the three layers, and the roughnesses for the air/film and film/substrate interface, are the parameters used for the fitting. A lower value of \( \chi^2 \) means that the calculated curve is closer to the experimental one. It is possible that calculated curves from several different models all show good agreement with the same experimental curve. In this case models that are mathematically possible, but not physically realistic, are excluded based on known sample information such as overall composition in the blend, or film thickness measured by ellipsometry. Finally, the scattering length density profile from the best fit is converted to a concentration depth profile according to the known scattering length densities of the two components in the blend.
In summary, XR and NR are powerful tools for studying the surface segregation in thin films. They provide rich information about the concentration depth profile inside the film without destruction, although this information is obtained indirectly by data fitting. XR and NR measurements are usually carried out with a relatively large footprint (cm$^2$) on the sample. Therefore, there is no lateral resolution.

2.5.3 X-ray photon correlation spectroscopy (XPCS)

XPCS measures the intensity-time autocorrelation function for a range of $q$, from which dynamics of a system can be inferred. Information about surface dynamics is obtained when the scattering observed occurs at the surface. More specifically, one can study thermal height fluctuation on the surface by measuring the variation of scattering intensity for a range of $q_{||}$, the in-plane wave vector, with time.

The geometry of a typical XPCS experiment with scattering on the surface is shown in Figure 2.8. $\theta_i$ and $\theta_f$ are the incident angle and angle of the scattered radiation with respect to the surface. For out-of-plane scattering an additional angle, $\psi$, between the plane of the incident beam (xz plane) and the plane of the scattered beam should be specified. The wave vector transfer, $q$, is dependent on the incident angle and angle of the scattered radiation. The in-plane scattering vector $q_{||} = q_x + q_y$ is the projection on the sample plane. The magnitude of the x, y and z components of $q$ are given by

$$q_x = k \left( \cos \theta_f \cos \psi - \cos \theta_i \right),$$

(2.34)
\[ q_y = k \cos \theta_r \sin \psi, \]  
\[ q_z = k \left( \sin \theta_r + \sin \theta_f \right). \]  

The directions x and y are equivalent because the sample is assumed to be isotropic.

Figure 2.8 Geometry of the XPCS experiment.

“Speckle pattern” refers to the 2-D pattern of intensity as a function of \( q_{||} \), which results from the scattering of a coherent X-ray beam on a surface with height fluctuations. The evolution of the speckle pattern with time is related to the dynamics of the surface at length scales determined by \( q_{||} \). The typical \( q_{||} \) range of XPCS measurement for this work is from \( 10^{-4} \, \text{Å}^{-1} \) to \( 10^{-3} \, \text{Å}^{-1} \), and the time window of XPCS measurement in this work is
from $10^{-1}$ sec to $10^{3}$ seconds, depending on the setup details of the instrument and the contrast of the probed system. Measuring a system with dynamics faster than the time window of XPCS experiment results in time-averaged speckle patterns. The basic principles of XPCS are the same as those of the more commonly known “dynamic light scattering” with visible light.\textsuperscript{217} The difference is that XPCS probes much smaller length scales and it can be used to study nontransparent materials.

The variation of intensity as a function of time collected in the XPCS measurement is quantified using a normalized intensity-intensity time autocorrelation function $g_2(q,t)$.\textsuperscript{218}

\[
g_2(q,t) = \frac{\langle I(q,t')I(q,t'+t) \rangle}{\langle I(q,t') \rangle^2}, \tag{2.37}
\]

where $I(q,t')$ is the scattering intensity at wave vector $q$ at time $t'$, angular brackets refer to ensemble averages over time $t'$, and $t$ is delay time. The function $g_2(q,t)$ is related to the normalized intermediate scattering function, $f(q,t)$, as

\[
g_2(q,t) = 1 + \beta f^2(q,t), \tag{2.38}
\]

where $\beta$ is a factor representing the degree of spatial coherence of the scattered field. It can be simplified as the ratio of the coherent volume to the illuminated sample volume, but a more accurate expression can be found in the literature.\textsuperscript{218, 219} In the ideal case with a totally coherent incident beam, $\beta = 1$. In the real XPCS measurement, $\beta$ is much smaller than 1. $\beta$ should be a sample-independent parameter only related to the coherence of the incident beam and infinite detector acceptance.\textsuperscript{220} In this work, however, $\beta$ is treated as a fitting parameter and we have not attempted to gain much information from it. The
normalized intensity autocorrelation of sequential 2-D speckle patterns is first calculated pixel-by-pixel. This calculation is then followed by an appropriate averaging over all pixels corresponding to the same narrow range of $q_{||}$. Figure 2.9 shows an example of an experimental autocorrelation function $g_2(q,t)$ as a function of time delay for a PS film of thickness 82 nm at 120 °C. The solid curve represents a single exponential decay function,

$$g_2(q,t) = 1 + \beta e^{-\frac{2t}{\tau}},$$  \hspace{1cm} (2.39)

found to often represent well the $g_2$ behavior for the overdamped surface fluctuations on polymer melt surfaces. This functional form has been fit to the experimental data using a regression in order to extract the value of $\tau$ that is the relaxation time of the film surface structure at a particular value of $q_{||}$.

Figure 2.9 An example of experimental autocorrelation function $g_2(q,t)$ as a function of time delay.
time delay for a PS film of thickness 82 nm at 120 °C. The solid line is a fit according to Eq. 2.39.

2.5.4 Static time of flight secondary ion mass spectrometry (STOF-SIMS)

Secondary ion mass spectrometry (SIMS) is a mass spectrometry-based analytical technique, which is used to directly obtain information about chemical composition of a surface. In a typical SIMS experiment (Figure 2.10), a beam of an energetic primary ion, such as Ar$^+$, is focused onto a solid sample surface under ultrahigh vacuum. The primary ions impact the sample surface and transfer energy and momentum to the sample in the so-called “collision cascade” process. The interaction of the primary ion beam with the sample generates neutral species, secondary electrons, and secondary ions desorbed from the sample surface. The secondary ions from the sample surface are subsequently analyzed by a mass spectrometer. A variety of primary ions are available, including the conventional atomic ions$^{221}$ (Ga$^+$, Cs$^+$, or Ar$^+$) and the emerging cluster ions$^{222}$ (C$_{60}^+$, Au$_3^+$, SF$_5^+$, or Bi$_3^+$). The primary ion energy may vary from 1 to 50 keV.$^{223}$ SIMS experiments can be performed in two modes: static and dynamic modes. In the static mode, the dosage of primary ion beam is kept low ($< 10^{12}$ ions/cm$^2$)$^{224}$ to minimize damage to the sample surface, so that only species from the top few atomic layers are sampled. In the dynamic mode, a high dosage of the primary ion beam is used for sputtering material away from the sample. Dynamic SIMS is often used to measure
composition depth profiles. SIMS is also used for chemical imaging of a sample surface by mapping intensities of selected ions on the surface.

Figure 2.10 Description of the processes when a primary ion beam impacts a sample surface.

Static SIMS is an extremely surface sensitive technique. It has been shown by molecular dynamics simulations\textsuperscript{225, 226} that in SIMS experiments the incident kinetic energy of prime ions is dissipated primarily in the near surface region and most sputtered molecular ions are generated within 10 Å underneath the surface. The SIMS detection
limits for most elements are between $10^{13}$ and $10^{18}$ atoms/cm$^3$. The SIMS secondary ion yield, defined as the number of ionized atoms sputtered by each incident ion, varies significantly for various elements. It is influenced by several factors, including the properties of the incident ions (i.e. energy and mass) and properties of the sample (i.e. ionization potential and electron affinity). Moreover, the secondary ion yield for a particular element heavily depends on its chemical environment in the sample, or its matrix. All the above features of secondary ion yield complicate the task of quantitative measurements of surface composition with static SIMS. However, the enormous sensitivity to surface species makes static SIMS a powerful technique for characterizing the chemical composition of surfaces. Surface analysis with static SIMS has been proved useful in identifying surface chemistry of polymer materials. Because the energy transferred from primary ions to individual molecules in the sample is high enough to cause fragmentation, small fragments instead of intact macromolecules are detected by STOF-SIMS. Figure 2.11 shows an example of a STOF-SIMS spectrum for a blend of hydrogenous PS and deuterated PS. The characteristic peak for hydrogenous PS is at $m/z = 91$ ($C_7H_7^+$) and for deuterated PS is at $m/z = 98$ ($C_7D_7^+$). The relative amounts of hydrogenous and deuterated PS can be estimated based on the area ratio of these two peaks.
Figure 2.11 STOF-SIMS spectra for hydrogenous PS (top) and deuterated PS (bottom).

In dynamic SIMS, materials are sputtered away by a high-dosage primary ion beam from the sample surface, continuously exposing buried molecular layers for SIMS analysis. The depth resolution for dynamics SIMS is around 10 nm in general. Due to the high dosage of the primary ion beam and the resulting secondary ions and electrons, a net electric charge is created at the sample surface, which is known as sample charging. Positive sample charging is usually compensated by injection of electrons with a flood gun. The ability of depth profiling with dynamic SIMS has proved to be useful in the study of surface segregation. Schwarz et al.\textsuperscript{227} used dynamic SIMS to study surface segregation in isotopic blends of linear PS. Tanaka et al.\textsuperscript{162} combined dynamic SIMS with NR to obtain depth profiles of binary polymer blend films in their studies of the chain end chemistry effect on surface segregation. Recently, the use of low energy cluster ion
beams ($C_{60}^+$, $Au_3^+$, $SF_5^+$, or $Bi_3^+$) has emerged in SIMS for polymeric materials.\textsuperscript{222} Compared to conventional atomic beams ($Ga^+$, $Cs^+$ or $Ar^+$), cluster ion beams have the advantages of surface-localized damage and significantly enhanced sputtering yield, which makes them ideal for depth profiling polymeric materials. Successful examples of depth profiling have been reported for PMMA, PEG and PLA.\textsuperscript{222} However, there are still many more polymers that have not been depth profiled, including PS. Recently new progresses have been made toward successful depth profiling of PS, with the use of low energy $Cs^+$\textsuperscript{228,229} or $O_2^+$\textsuperscript{230} ions and $C_{60}^+$ ions at glancing angle.\textsuperscript{231}
CHAPTER III

EXPERIMENT

In this chapter we discuss the techniques for synthesizing well-defined comb polystyrenes with living anionic polymerization at first (Section 3.1-3.3). Then we consider general characterization techniques for molecular structures and bulk properties (Section 3.4). Finally we describe methods of sample preparation and characterization techniques for the studies of thermodynamics and surface dynamics.

3.1 Inert Atmosphere Techniques

The high reactivity of organolithium compounds towards water, oxygen, and carbon dioxide necessitates the implementation of an inert gas or high vacuum atmosphere. Air- and moisture-sensitive reagents as well as reagents coming in contact with these compounds must be purified and handled under an inert atmosphere or high vacuum.

3.1.1 High Vacuum Techniques

A high vacuum line (Figure 3.1) provided the most effective experimental method to exclude impurities from the reaction system. The high vacuum line was
used to dry, degas, purify, and transfer solvents and reagents into reactors and ampules.

High vacuum ($10^{-4}$ torr) was obtained with an Edwards RV-8 direct drive pump coupled with a silicone oil diffusion pump. Vacuum pressure was qualitatively measured using a Tesla coil. When the pressure is greater than ~$10^{-4}$ torr, the Tesla coil produces a bluish discharge along with noise, due to ionization/excitation of gaseous nitrogen. The qualitative measurement of a quiet line was a requirement to confirm the absence of leaks in the reactors, ampules, and other apparatus connected to the vacuum line.

![Figure 3.1](image_url)  

**Figure 3.1** Schematic of the high vacuum line used in this work.

The vacuum line was constructed with an upper and a lower manifold, both made from Pyrex® (borosilicate) glass, with airtight control of flow via Rotaflo® stopcocks. The vacuum line contained an inlet for nitrogen gas, used to provide a positive nitrogen
atmosphere for injection of reactive chemicals into a flask or reactor connected to the vacuum line. Two connections with thick-wall glass and grease traps were used for attachment of ampules and reactors directly via hand-blown, all-glass connections. Four connections with standard-taper, 24/40 ground-glass joints were used for attachment of flasks to the vacuum line.

3.1.2 Schlenk Line Techniques

A Schlenk line was used for air- and moisture-sensitive reactions that were not carried out under vacuum, in the dry box, or using a nitrogen-filled balloon. A standard two-manifold system, with one manifold under positive nitrogen pressure and one under vacuum, was used in this case. With this system, reactions could be placed under vacuum, then purged with nitrogen by simply changing the position of the Schlenk line valve. This is advantageous for reactions where control of the atmosphere is important, but not as critical as in anionic polymerization.

3.1.3 Glove Box Techniques

The transfer and handling of air/moisture sensitive material was performed in a Vacuum Atmospheres dry box (Model HE-193). An inert atmosphere was maintained by recirculation of argon via a Vacuum Atmospheres Omni Train inert gas purification system. This system maintained equilibrium oxygen and water concentrations below 1 ppm, and the atmosphere was tested prior to use by placing a few drops of a
(Cp$_2$TiCl$_2$)$_2$ZnCl$_2$ complex dissolved in toluene onto weighing paper. Upon exposure to oxygen or water (>5 ppm), the complex changes from green to yellow as described by Sekutowski and Stucky.$^{238}$

3.2 Reagents

Reagents were used as received unless purity or reactive impurities presented complications in achieving the desired results. Oxygen and water must be removed from solvents used in anionic polymerization.

3.2.1 Reagents Used as Received

sec-Butyllithium (FMC, ~1.5M in cyclohexane, after double titration$^{239}$).

n-Butyllithium (FMC, ~1.5M in cyclohexane, after double titration$^{239}$).

Calcium hydride (Acros Organics, 93%, 0-20 mm grain size).

Dibutylmagnesium (FMC Lithium Division, 15 wt% in heptane).

Sodium dispersion (Alfa, 50 wt% in paraffin oil).

Lithium metal (FMC, 98% stabilized with Na).

Dimethoxy-2-phenylacetophenone (DMPA, Acros Organics, 99%).

1H,1H,2H,2H-perfluoro-1-decanethiol (Aldrich, 97%).

Mercaptoacetic acid (Acros Organics, 97%).

2-Mercaptoethanol (Aldrich, 99+%).

1,10-phenanthroline (Sigma-Aldrich, 99+%).
3.2.2 Solvents.

Solvents used in anionic polymerization must be purified in order to remove impurities such as dissolved oxygen and water.

3.2.2.1 Purification of Hydrocarbon Solvents

Benzene (EMD, ACS grade), cyclohexane (EMD, ACS grade), toluene (EMD, ACS grade) and heptane (EMD, 99%) were stirred over freshly-crushed calcium hydride in a flask on the vacuum line overnight. The solvents were cooled to -78 °C in an isopropyl alcohol (IPA)/dry ice bath, degassed, and warmed repeatedly to remove air and hydrogen gas generated during the drying process. In order to further dry the solvents, the resulting solutions were vacuum transferred into a second flask containing sodium dispersion. The solvents were again subjected to several freeze, degas, thaw cycles before final distillation into storage flasks containing poly(styryl)lithium and equipped with Rotaflo® stopcocks. The orange color of the poly(styryl)lithium was used as an indication of purity. Solvents were distilled directly from these flasks, as needed, through the high vacuum line.240

3.2.2.2 Tetrahydrofuran and Diethyl Ether

Tetrahydrofuran (EMD, ACS grade) (THF) and diethyl ether (EMD, ACS grade) were stirred over freshly-ground calcium hydride for 24 h with frequent degassing on the high vacuum line using a dry ice/isopropyl alcohol bath for cooling. They were vacuum
transferred onto sodium mirrors in a 2-L flask equipped with a Rotaflo® stopcock. This step was repeated until the sodium mirror maintained its integrity. The purified THF and diethyl ether were distilled directly from the sodium mirror into ampules and reactors, as needed.

3.2.3 Styrene

Styrene was stirred over freshly ground calcium hydride with periodic degassing using liquid nitrogen. A Rotaflo®-equipped flask was evacuated, tested for leaks, and then filled with a positive nitrogen atmosphere. 1,10-Phenanthroline (~100mg) and 2 mL of dibutylmagnesium were added and the flask was evacuated. The dried, degassed styrene was distilled into the Rotaflo®-equipped flask. A bright purple color served as an indication of active butylmagnesium complexed with phenanthroline. Purified styrene was stored in the refrigerator and transferred into ampoules via short-path vacuum distillation as needed. Purification of deuterated styrene (Cambridge Isotope Laboratories, Inc.; D8; 98%) followed the same procedure.

3.2.4 Initiators

The polymerizations of styrene and diene monomers were initiated with sec-butyllithium or 4-pentenyllithium. Other initiators, such as n-butyllithium and dibutylmagnesium, were used for purification purposes.
3.2.4.1 sec-Butyllithium

 sec-Butyllithium (FMC Lithium Division, ~1.5M in cyclohexane/heptane) was used, as received, after Gilman double titration with allyl bromide to determine the concentration of carbon-bound lithium. The amount of total base (carbanionic and non-carbanionic lithium species) was determined by injecting 1.0 mL of sec-butyllithium solution into three crimp-cap bottles, each containing 10 mL of freshly distilled cyclohexane in the dry box. The bottles were sealed, removed from the dry box, quenched with 10 mL of distilled water, and titrated with standardized 0.1 N HCl solution using phenolphthalein as indicator. The amount of free base (non-carbanionic lithium species) was determined by quenching 3.0 mL of sec-butyllithium in each of three crimp-cap bottles with 1 mL of allyl bromide and then adding 10 mL of distilled water. These solutions were then titrated with 0.1 N HCl using phenolphthalein as indicator. Subtracting the averaged amount of free base (allyl bromide quench) from the averaged amount of total base (water quench) gave the concentration of alkyl lithium. The sec-butyllithium solution received was separated into 100-mL crimp-cap bottles with ca. 30 – 40 mL of solution per bottle to prevent contamination.

3.2.4.2 n-Butyllithium

 n-Butyllithium (FMC Lithium Division, ~1.5M in cyclohexane) was distributed into crimp-cap bottles in the glove box and used in excess, as needed, without further analysis or purification.
3.2.4.3 Dibutylmagnesium

Dibutylmagnesium (FMC Lithium Division, 17 wt% in heptane) was distributed into crimp-cap bottles in the glove box and used without further analysis or purification.

3.2.4.4 4-Pentenyllithium

A 250 mL, Morton-creased, glass reactor equipped with a fritted glass filter connected to an empty ampule and a stir bar, and with ampules of diethyl ether (5 mL), 5-bromo-1-pentene (1.4 mL, 0.012 mol), lithium metal (0.82 g, 0.12 mol; 10-fold excess), was placed under high vacuum. Heptane was distilled into the reactor and the reactor was separated from the vacuum line by flame sealing. The break-seals of the lithium metal and 5-bromo-1-pentene ampules were broken sequentially and the reaction was stirred at room temperature for 3 days. The reactor and diethyl ether ampule were cooled to 0 °C and the ampule break-seal was broken. The reaction was stirred for 24 h at 0 °C. The reactor was then connected to the vacuum line via a break-seal, solvent was removed by flash distillation and 30 mL of heptane was added by distillation. The mixture was transferred through the glass filter into the empty ampule that was then flame-sealed from the reactor. The product was 0.19 M 4-pentenyllithium in heptane (48%) as determined by double titration. The synthesized 4-pentenyllithium was immediately distributed into ampules in a drybox and stored in the freezer. The initiator was good for use within one month of synthesis.
3.2.5 Other Reagents

Purification procedures of reagents, including methanol, 5-bromo-1-pentene and 4-vinylbenzyl chloride are introduced in this section.

3.2.5.1 Methanol

Methanol (Fisher Scientific, ACS grade) was degassed three times on the vacuum line before being distilled into ampules which were then flame-sealed from the vacuum line.

3.2.5.2 5-Bromo-1-pentene

5-Bromo-1-pentene (Aldrich, 95%) was fractionally distilled under vacuum, stirred over calcium hydride, and then distilled into a calibrated, flame-sealed ampule.

3.2.5.3 4-Vinylbenzyl chloride

4-Vinylbenzyl chloride (Aldrich, >90%) was purified by passing through a column of activated basic alumina in cyclohexane, dried over calcium hydride, vacuum distilled into a sealed flask, distributed into ampules in a drybox, and the ampules were flame-sealed on the vacuum line.
3.3 Synthesis of polymers

Synthetic procedures of polymers, including \((p\text{-vinylbenzyl})\text{polystyrene,}\ 
\alpha\text{-4-pentenyl}\omega-(p\text{-vinylbenzyl})\text{polystyrene,}\) unfunctionalized combs and Comb-Vinyl are descripted in this section.

3.3.1 Synthesis of \((p\text{-vinylbenzyl})\text{polystyrene} \quad (M_n = 1600 \text{ g/mol, Macromonomer A1;} \\
M_n = 2500 \text{ g/mol, Macromonomer A2})

The procedure for synthesizing Macromonomer A2 with \(M_n = 2500 \text{ g/mol}\) is described below in detail to illustrate the synthesis of Macromonomers A1 or A2.

\textit{sec-Butyllithium (1.5 mL, 2.1 mmol, 1.43 M)} was added to the A part of an all-glass reactor (Figure 3.2) which consisted of two, connected reaction flasks. Reactor A was equipped with a styrene ampule (5.6 mL, 5.1 g, 0.049 mol) and a THF ampule (41.5 mL, 36.9 g, 0.51 mol). The other reactor (B) was equipped with an ampule containing 4-vinylbenzyl chloride (5.0 mL, 5.42 g, 35.5 mmol)/THF (15 mL). Benzene (60 mL) was distilled into the reactor A after flame-sealing the reactor to the vacuum line and evacuating. The reactor was then separated from the vacuum line by flame sealing and the break-seal of the styrene ampule was broken. After 3 h at room temperature, the break-seal of the THF ampule was broken and THF was added into reactor A. The 4-vinylbenzyl chloride/THF ampule was broken in reactor B. All glassware was cooled to \(-78 \degree\text{C}\) in an isopropyl alcohol/dry ice bath and poly(styryl)lithium in reactor A was slowly transferred into the 4-vinylbenzyl chloride/THF solution in reactor B. After the
poly(styryl)lithium solution was completely transferred, solvent was removed by distillation under reduced pressure and toluene was added to dissolve the polymer. The resulting solution in toluene was precipitated into cold methanol (10 times solution volume) three times. The sample was dried in a vacuum oven overnight to afford a white powder.

Figure 3.2 Reactor for synthesizing Macromonomers A1 and A2.
To synthesize Macromonomer A1 with $M_n = 1600$ g/mol, the following reagents were used: sec-butyllithium (6.0 mL, 8.6 mmol, 1.43 M); styrene (14.8 mL, 13.5 g, 0.13 mol); 4-vinylbenzyl chloride (12.0 mL, 12.9 g, 84.4 mmol); THF (70 mL); benzene (70 mL).

3.3.2 Synthesis of $\alpha$-4-pentenyl-$\omega$-(p-vinylbenzyl)polystyrene ($M_n = 2300$ g/mol, Macromonomer B)

4-Pentenyllithium (6.0 mL, 1.1 mmol, 0.19 M) was added to the A part of an all-glass reactor (Figure 3.3) which consisted of two, connected reaction flasks. Reactor A was equipped with a styrene ampule (3.1 mL, 2.8 g, and 0.027 mol), THF ampule A (0.5 mL, 0.4 g, 6.2 mmol), and a THF ampule B (22 mL, 19.6 g, 0.27 mol). The other reactor (B) was equipped an ampule containing 4-vinylbenzyl chloride (2.6 mL, 2.82 g, 18.4 mmol)/THF (8 mL). Benzene (30 mL) was distilled into the reactor after flame-sealing the reactor to the vacuum line and evacuating. The reactor was then separated from the vacuum line by flame sealing and the break-seals of the THF ampule A and styrene ampule were broken sequentially. After 3 h at room temperature the break-seal of THF ampule B was broken and THF was added into reactor A. The 4-vinylbenzyl chloride/THF ampule was broken in reactor B. All glassware was cooled to -78 °C in an isopropyl alcohol/dry ice bath and the $\alpha$-4-pentenylpoly(styryl)lithium in reactor A was slowly transferred into the 4-vinylbenzyl chloride/THF solution in reactor B. After the $\alpha$-4-pentenylpoly(styryl)lithium solution was completely transferred, solvent was removed by distillation under reduced pressure and toluene was added to dissolve the
polymer. The resulting solution in toluene was precipitated into cold methanol (10 times solution volume) three times. The sample was dried in a vacuum oven overnight to afford a white powder.

![Figure 3.3 Reactor for synthesizing Macromonomer B.](image)

3.3.3 Synthesis of unfunctionalized combs and Comb-Vinyl

A series of well-defined unfunctionalized comb polystyrenes with sec-butyl branch ends were synthesized with living anionic polymerization using the same procedure
described in Section 3.3.3.1. These unfunctionalized combs have various lengths of branches (M = 15 or 24), various number of branches (P), and constant distance between adjacent branches (L = 1). The combination of M and P is used to identify each comb in the following sections. The procedure for synthesizing the comb polystyrene with partially 4-pentenyl branch chain ends (Comb-Vinyl) is described in Section 3.3.3.2.

3.3.3.1 Unfunctionalized combs

The syntheses of the unfunctionalized comb polymers with various branch lengths (M) and numbers of branches (P) share the same procedure, which is illustrated in detail by the following example of the synthesis of M24P50 with $M_n = 130,000$ g/mol:

Macromonomer A2 (1.00 g) was placed in a flask equipped with a Rotoflo® stopcock. Benzene (10 mL) was distilled into the flask to dissolve the macromonomer after the flask was attached to the vacuum line and evacuated. The reactor was then removed from the vacuum line. In a drybox freshly diluted sec-butyllithium (0.0143 M in benzene) was added dropwise into the flask with the benzene solution of macromonomer until a faint yellow color was observed. Then a calculated amount of diluted sec-butyllithium (0.6 mL, 0.008 mmol, 0.0143 M) was immediately injected into the flask and the solution became orange. The polymerization was quenched by methanol after 12 h at room temperature. Polymer product was collected by precipitation of the solution into methanol and then freeze-dried from benzene. Polymerization conditions for preparing unfunctionalized combs are summarized in Table 3.1.
Table 3.1 Polymerization conditions for preparing unfunctionalized combs.

<table>
<thead>
<tr>
<th>Comb Type</th>
<th>Macromonomer Type</th>
<th>Amount (g)</th>
<th>Amount (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M15P34</td>
<td>A1</td>
<td>1.0</td>
<td>1.6</td>
</tr>
<tr>
<td>M15P105</td>
<td>A1</td>
<td>0.9</td>
<td>0.4</td>
</tr>
<tr>
<td>M24P14</td>
<td>A2</td>
<td>1.0</td>
<td>2.4</td>
</tr>
<tr>
<td>M24P28</td>
<td>A2</td>
<td>1.0</td>
<td>1.2</td>
</tr>
<tr>
<td>M24P50</td>
<td>A2</td>
<td>1.0</td>
<td>0.6</td>
</tr>
</tbody>
</table>

3.3.3.2 Comb-Vinyl ($M_n = 74,000$ g/mol)

The procedure for preparing Comb-Vinyl was identical to that for synthesizing unfunctionalized combs described above. Macromonomer A2 (0.76 g, 0.30 mmol) and Macromonomer B (0.24 g, 0.10 mmol) dissolved in distilled benzene (10 mL) were well mixed in a flask equipped with a Rotoflo® stopcock after the flask was attached to the vacuum line and evacuated. After titration of impurities with sec-butyl lithium in a dry box until a faint orange color was observed, the calculated amount of diluted sec-butyl lithium (1.1 mL, 0.016 mmol, 0.0143 M) was added. Termination and work-up followed the procedure described for unfunctionalized combs.

3.3.4 Functionalization of Comb-Vinyl using thiol-ene “click” chemistry\textsuperscript{115}

Comb-Vinyl prepared in the previous step was used as the precursor for functionalized comb polystyrenes. We adopted the following nomenclature in this work. The comb containing branches with hydroxyl end functionalities was denoted as "Comb-OH". The comb with carboxylic acid functionalities on the branch ends was named "Comb-COOH"
and the comb with perfluorooctadecyl functional groups on the branch ends was termed "Comb- C_{8}F_{17}".

3.3.4.1 Comb-OH

Comb-Vinyl \( (M_n = 74,000 \text{ g/mol}, 0.7 \text{ g}, 85 \mu\text{mol vinyl}) \), 2-mercaptoethanol (24 mg, 307 \( \mu\text{mol} \)), and DMPA (4.1 mg, 16 \( \mu\text{mol} \)) were dissolved in 4 mL of THF. After irradiation with stirring for 1 h under a UV lamp with \( \lambda = 365 \text{ nm} \) at room temperature, the solution was precipitated into cold methanol three times. The sample was dried in a vacuum oven overnight to obtain a white powder (Comb-OH, 0.63 g; yield 90 %). It was further fractionated using toluene-methanol mixed solvents to obtain monodispersed product (0.48 g).

3.3.4.2 Comb-COOH

Comb-Vinyl \( (M_n = 74,000 \text{ g/mol}, 0.50 \text{ g}, 61 \mu\text{mol vinyl}) \), mercaptoacetic acid (22 mg, 239 \( \mu\text{mol} \)), and DMPA (3.6 mg, 14 \( \mu\text{mol} \)) were dissolved in 3 mL of THF. After irradiation with stirring for 1 h under a UV lamp with \( \lambda = 365 \text{ nm} \) at room temperature, the mixture was directly precipitated into aqueous NaOH solution (40 mL, pH = 10). The solid was collected, dissolved again in THF, and precipitated into aqueous HCl solution (40 mL, pH = 1). After precipitation again into distilled water (40 mL), the sample was collected by filtration and dried in a vacuum oven overnight to give a white powder.
(Comb-COOH, 0.32 g; yield 64%). Attempt to fractionate Comb-COOH was unsuccessful due to its good solubility in methanol.

3.3.4.3 Comb-C₈F₁₇

Comb-Vinyl ($M_n = 74,000$ g/mol, 0.45 g, 55 μmol vinyl), 1H,1H,2H,2H-perfluoro-1-decanethiol (110 mg, 229 μmol), and DMPA (3.3 mg, 13 μmol) were dissolved in 2.5 mL of THF, followed by irradiation with stirring for 1 h under a UV lamp with $\lambda = 365$ nm at room temperature. The solution was precipitated into cold hexanes/methanol mixed solvent (v/v = 1/30) three times. The sample was dried in a vacuum oven overnight to give a white powder (Comb-C₈F₁₇, 0.36 mg; yield 81%). It was further fractionated using toluene-methanol mixed solvents to obtain monodispersed product (0.25 g).

3.4 General characterization

Details of general characterization techniques, including size exclusion chromatography, NMR spectroscopy, MALDI-TOF mass spectrometry, differential scanning calorimetry and rheometer, are described in this section.

3.4.1 Size Exclusion Chromatography

Size exclusion chromatographic analyses (SEC) for the polymers were performed using a Waters 150-C Plus instrument equipped with three HR-Styragel columns [100 Å, mixed
bed (50/500/10³/10⁴ Å), mixed bed (10³, 10⁴, 10⁶ Å)] and a triple detector system. The three detectors included a differential refractometer (Waters 410), a differential viscometer (Viscotek 100) and a laser light scattering detector (Wyatt Technology, DAWN EOS, λ = 670 nm). THF was used as eluent with a flow rate of 1.0 mL/min at 30 °C. Samples were prepared in THF (10 mg/mL) and passed through a 0.45 μm Teflon filter before analysis. Results were analyzed using Wyatt ASTRA software (version 4.73.04, Viscotec Corp). The intrinsic viscosity measurements were performed using the Viscotek viscometer described above and the results were analyzed using the Omni SEC software (Version 4.3.1.246).

3.4.2 ¹H, ¹³C and ¹⁹F solution NMR spectroscopy

¹H, ¹³C and ¹⁹F solution NMR spectra were obtained on a Varian 500 spectrophotometer (500 MHz) using 40 mg of polymer dissolved in 1 mL of CDCl₃ (Cambridge Isotopes). For ¹H solution NMR measurements, the pulse width (PW) is set as 90°, delay time (d1) is set as 8 s and scan number (nt) is set as 32. For ¹³C solution NMR measurements, PW = 90°, d1 = 1 s and nt = 20,000. For ¹⁹F solution NMR measurements, PW = 30°, d1 = 1 s and nt = 32.

3.4.3 MALDI-TOF Mass spectrometry

MALDI-TOF/TOF mass spectra were recorded on a Bruker Ultraflex-III
MALDI-TOF/TOF mass spectrometer (Bruker Daltonics, Bullerica, MA) equipped with a Nd: YAG laser (355 nm). Solutions of DCTB (2-[(2E)-3-(4-tertbutylphenyl)-2-methylprop-2-enylidene]malononitrile) (20 mg/mL) (Alfa Aesar, 99+%), polymer sample (10 mg/mL), and silver trifluoroacetate (10 mg/mL) (Aldrich, 98%) were prepared in THF (Aldrich, 99.9%). These solutions were mixed in the ratio of matrix:cationizing salt:polymer (10:1:2), and 0.5-1.0 μL of the mixture was applied to the MALDI sample target and allowed to dry. To minimize polymer fragmentation, the intensities of the laser pulses were attenuated and adjusted to obtain the optimal signal intensity. Mass spectra were measured in the positive reflectron mode. The instrument was calibrated prior to each measurement with external PMMA standards at the molecular weight under consideration.

3.4.4 Differential Scanning Calorimetry (DSC)

The bulk glass transition temperature, $T_g$, of each polymer or blend was determined with DSC (TA DSC Q2000) equipped with a liquid nitrogen refrigeration cooling system. Each blend sample for DSC analysis was prepared by freeze-drying a 10 wt% benzene solution of that polymer blend. Sample size was 5-10 mg. A heating cycle was carried out from 20 °C to 150 °C at a heating rate of 10 °C /min, then the temperature was held at 150 °C for 5 min and then the sample was cooled to 20 °C at 10 °C /min. Data collected from a second heating scan were used to determine $T_g$. 

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3.4.5 Mechanical rheometry

The bulk rheology of the polymer melt was measured using an Anton Paar Physica MCR 301 rheometer with parallel plates. The measurements were performed in shear oscillatory mode using 8 mm diameter parallel disk geometry with a 1 mm gap over the angular frequency range of 0.01-100 s\(^{-1}\) and temperature range of 105-145 °C.

3.5 Preparation of samples for measurements of surface dynamics and thermodynamics

Procedures of sample preparation for small angle neutron scattering (SANS), neutron reflectivity (NR) and x-ray photon correlation spectroscopy (XPCS) measurements are described in this section.

3.5.1 Samples for SANS measurements

For SANS measurement of blends containing 50 vol% hydrogenous comb polymers with the deuterated linear analogues were prepared by dissolution of the polymer in toluene. Solutions were filtered three times with 0.45 μm filters (Whatman, PTFE) and then directly cast into films in Teflon beakers, allowing 3 days in a fume hood for evaporation of the solvent. The films were then dried under roughing vacuum at 70 °C for 7 days to ensure removal of the excess toluene. The dried polymer blend films were pressed inside 0.8 mm thick stainless steel rings with an outer diameter of 25.4 mm and an inner diameter of 19.1 mm. To obtain transparent, bubble-free films, the samples were pressed at 120 °C under 3000 kg between pieces of Mylar sheet.
3.5.2 Samples for surface segregation studies

Each film sample for NR and STOF-SIMS measurements was made by dissolving an appropriate amount of hydrogenous comb polystyrene and deuterated linear polystyrene in toluene (EMD, 99.5%) at a total polymer concentration of 2 wt%, filtering the solution with a 0.45 μm filter (Whatman, PTFE) three times, and spin-casting at 2000 rpm onto a clean 3 inch diameter silicon wafer from which the native oxide had been etched using immersion in an 1% HF solution for 1 minute. Before casting the polymer solution, the HF-etched wafer surface was prewetted by spin-casting toluene onto it. The spun-cast films were annealed for 12 hrs in vacuum at 180 °C to remove residual solvent and reach thermodynamic equilibrium.

3.5.3 Samples for surface dynamics studies

Each thin film was spun-cast at 2000 rpm for 2 minutes from a toluene solution of comb polystyrene onto a clean silicon wafer from which the native oxide had been etched using immersion in an 1% HF solution for 1 minute. The spun-cast films were annealed for 12 hrs in vacuum at 150 °C to remove residual solvent and relax stress induced by spinning. The thicknesses of all the thin films at room temperature were measured using a Gaertner ellipsometer at a wavelength of 632.8 nm, assuming a two layer model and refractive indices of 1.589 for polystyrene and 3.875 for silicon.
3.6 Characterization of surface dynamics and thermodynamics

Bulk thermodynamics in comb/linear blends were characterized with small angle neutron scattering (SANS). The surface segregation in comb/linear blends was probed using a combination of neutron reflectivity (NR) and static time of flight secondary ion mass spectrometry (STOF-SIMS). The surface dynamics of comb polymers were characterized with x-ray photon correlation spectroscopy (XPCS). Details of these measurements are given in the following sections.

3.6.1 SANS

SANS measurements were performed on the NG3 30-m SANS instrument at the Cold Neutron Research Facility of the National Institute of Standards and Technology (Gaithersburg, MD). A scheme of the typical setup for a SANS experiment is shown in Figure 3.4. A neutron beam with a nominal wavelength, $\lambda$, of 6 Å and $\Delta\lambda/\lambda$ of 0.15 was used. Measurements were made at a sample-to-detector distance of 4.5 m with a detector offset of 20 cm and a 2 inch diameter beamstop, five neutron guides, and sample aperture of 1.27 cm, providing a range of values of the scattering vector $q$ of 0.007-0.14 Å$^{-1}$. The samples, sandwiched between 1 mm thick quartz windows, were placed in sample holders provided by the National Institute of Standards and Technology laboratory. The sample holders were then placed inside a seven-position aluminum sample changer with temperature control. Sample temperatures were varied from 120 to 180 °C in steps of 20 °C. This sample changer sat inside a stainless steel vacuum chamber that was
evacuated to 450 μmHg vacuum and then backfilled with nitrogen gas to obtain a slight positive pressure, and this positive pressure was maintained throughout the measurement by adjusting the nitrogen flow. Equilibration times of about 15 min were allowed after each temperature set-point was reached. Data were also collected for a blocked beam, for an empty quartz-windowed cell, and for an empty sample position in order to estimate the background and empty cell contributions. To correct for incoherent scattering, 100% hydrogenous linear polystyrene and 100% deuterated linear analogue samples were measured. A direct beam measurement was made with seven attenuators inserted to calculate the transmission of the samples. An isotopic polymer blend standard sample was measured for the converting raw data into absolute intensities. The raw data were azimuthally averaged and converted to absolute coherent scattering intensity as a function of $q$. Correcting data for background, empty cell scattering, and transmission coefficient and reduction to absolute intensity were facilitated by use of a NIST-developed data analysis protocol running within the IGOR Pro environment.
NR measurements were performed on the NG7 horizontal reflectometer at NIST in Gaithersburg, MD. A schematic of the typical setup for a NR experiment is shown in Figure 3.5. The incident neutron beam has a nominal wavelength, $\lambda$, of 4.75 Å and resolution ($\Delta\lambda/\lambda$) of 0.15. The range of scattering vector, $q_z$, typically accessible for thin polymer films is from 0 to 0.201 Å$^{-1}$. The slit gaps were increased with $q_z$ to maintain a roughly constant beam footprint size and to achieve higher incident beam intensity at larger values of $q_z$ where the reflection is far weaker. The beam width was fixed at 35 mm. Background scattering was measured on each side of the specular peak and the background under the specular signal was estimated by linear interpolation. The incident beam intensity was measured independently for each setting of the slits for normalization of intensities to reflectivity. Reflectivity was determined by subtracting the background.
intensity from the raw reflected intensity and then dividing by the incident beam intensity for the appropriate setting of the slits for each value of $q_z$. To obtain a composition depth profile, reflectivity curve was calculated from a candidate model of the film structure, compared to the experimental data, and then the parameters of the model (thickness, roughness, and SLD) were adjusted until the “best fit” relative to a least squares error criterion was found. The parameter regression was constrained using a “mass balance” criterion of conservation of overall mass ratio of hydrogenous and deuterated species known to have been in the original blend. Models envisioning variations of the mass ratio for the sample overall of larger than 2% above or below the presumed mass ratio for deuterated linear polystyrene were excluded. Data reduction, including background subtraction and incident beam normalization, and fitting were conducted using the REFLPAK software package provided by NIST.

Figure 3.5 Schematic of the horizontal setup of the NG7 NR instrument at NIST.
3.6.3 STOF-SIMS

STOF-SIMS analysis was performed using a PHI Trift V nanoTOF instrument equipped with an Au$^+$ ion gun. The Au$^+$ beam energy was 30 keV, and the spatial resolution was 1 $\mu$m. The raster area of the Au$^+$ beam was $200 \times 200 \, \mu m^2$. Sample charging was compensated by an electron flood gun operating at 30 eV. The relative concentrations of deuterated and hydrogenous polystyrenes were obtained from the ratio of the $C_7H_7^+$ and $C_7D_7^+$ signals at 91.1 and 98.1 Da.

3.6.4 XPCS

Surface height fluctuation dynamics were measured using XPCS at beam line 8-ID-I at the Advanced Photon Source (APS) with a coherent monochromatic x-ray beam ($E = 7.5$ keV). The instrumental geometry is illustrated in Figure 3.6. With the incident angle (0.14°) below the critical angle of total external reflection for PS (0.16° at this wavelength), the x-ray beam only penetrates into the film to a depth of 9 nm, which is much less than the film thicknesses (>50 nm) studied here, ensuring that scattering from the height fluctuations of the vacuum/polymer surface overwhelmingly dominates the scattering. This setup makes it possible to collect data at values of the in-plane wave vector $q_{||}$ up to $10^{-3} \, \AA^{-1}$. The size of the beam was $20 \times 20 \, \mu m^2$ and intensity was typically about $5 \times 10^9$ photons/sec. The surface fluctuation dynamics were measured at temperatures between 105 °C and 145 °C for each comb polystyrene sample.
To minimize x-ray beam damage, the exposure time on a spot was limited to a certain amount (Table 3.2) and then the sample was shifted to illuminate a fresh spot. Measurement of the reflectivity curve before and after each XPCS measurement provided the film thickness and preliminary evaluation of whether the sample had been damaged by radiation. All data sets were ultimately checked for beam damage by comparing the relaxation times obtained by correlating different subsets of all the frames in each data set and discarding suspect frames. The off-specular diffuse scattering image from thin film surface was captured by a charge coupled device (CCD) located 3345 mm downstream of the sample and its time evolution was recorded at a set frequency. One example of the instantaneous diffuse scattering pattern, known as the “speckle pattern”, is shown in Figure 3.7.
Table 3.2 Total X-ray exposure time (seconds) on a spot during measurements of M24P14, M24P28, and M24P50 at different temperatures.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>M15P34</th>
<th>M15P105</th>
<th>M24P14</th>
<th>M24P28</th>
<th>M24P50</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>41nm</td>
<td>55nm</td>
<td>82nm</td>
<td>84nm</td>
<td>176nm</td>
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<td>105</td>
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<td>140</td>
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<td></td>
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<tr>
<td>145</td>
<td></td>
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</table>

Three modes were used to collect the off-specular diffuse scattering: static, full frame, and kinetic modes. The whole area of the CCD camera was used to collect the speckle pattern as a function of time for the “full frame mode” and to collect time averaged scattering patterns in “static modes”; in contrast, only 1/13 of the CCD active area was used to capture each frame for measurements using “kinetic mode”. Examples of the scattering patterns captured on the CCD camera using full frame and kinetic modes are shown in Figures 3.7 (a) and (b). For the static mode the time averaged scattering intensity was simply collected for a time long enough to obtain the pattern with good counting statistics. Analysis of the static structure factor can, in principle, provide information on the intrinsic properties of the films, for instance, surface tension and surface roughness. For the dynamics measurements (full frame and kinetic modes), speckle patterns were collected sequentially in time. In general, full frame mode was used.
for measuring slow surface fluctuations (500 s < \tau < several thousand seconds) and kinetic mode was used for measuring fast surface fluctuations (0.1<\tau<500 s). For measuring the largest relaxation times (e.g. several thousand seconds), or for measuring moderate relaxation times under high temperature conditions for which radiation beam damage is a concern, the time between adjacent frames was increased by inserting a time with no data collection, termed "sleep time". During sleep time, a fast beam shutter was kept closed to eliminate X-ray beam exposure. The setting of sleep time allows one to extend the window of accessible relaxation times without exceeding the X-ray exposure limit. Since the exposure per frame and total exposure per spot can become very short in this case, the dynamics are measured at multiple spots on the sample and the correlation functions from these multiple spots are averaged to obtain a correlation function with improved statistics. When operating in kinetic mode, the active area of the detector is cut into several regions (the default is 13). This is done to be able to measure for shorter times otherwise not accessible due to the finite readout time of the detector, which is 1.8 seconds for the detector used here. By dividing the area of the detector into several slices, the shortest time between frames can be reduced to 0.050 second. Reducing both the time per frame and the time between frames extended the time window of the XPCS measurement of relaxation times down to the order of 0.1-1 sec. However, the $q_\parallel$ range probed is sacrificed here due to the use of only a small portion of the CCD camera to collect the speckle pattern.
Figure 3.7 CCD images of speckle patterns collected using (a) full frame and (b) kinetic modes.

The sample's surface dynamics were characterized by calculating the normalized intensity-intensity time autocorrelation function:

\[ g_2(q,t) = \frac{\langle I(q,t')I(q,t'+t) \rangle}{\langle I(q,t') \rangle^2}, \] (3.1)

where \( I(q, t') \) is the scattering intensity at wave vector \( q \parallel \) and time \( t' \), and angular brackets refer to ensemble averages over time \( t' \) and \( t \) is the delay time. Calculation of values of the autocorrelation function was carried using a MATLAB-based XPCS Analysis Program developed by Zhang Jiang and Michael Sprung of Argonne National Laboratory and made available to users by the 8-ID-I beamline staff.
CHAPTER IV
SYNTHESIS OF COMB POLYSTYRENES

Synthesis of comb polystyrenes via the “graft-through” strategy is described in this chapter. Comb polystyrenes with only sec-butyl groups at branch chain ends are prepared by homopolymerization of Macromonomer A1 or A2. Comb-Vinyl, which is comb polystyrene with both sec-butyl and vinyl groups at branch chain ends, is prepared by copolymerization of Macromonomers A2 and B. Comb-Vinyl is then used as the precursor for synthesizing combs with functionalized branch chain ends utilizing thiol-ene “click” chemistry.

4.1 Synthesis of unfunctionalized comb polystyrenes

Comb polystyrenes with extremely high branching density were prepared by living anionic homopolymerization of polystyrene macromonomers with \( \omega \)-styril end groups, as shown in Scheme 4.1. Since sec-butyllithium was used as the initiator for synthesizing Macromonomers A1 and A2, the resulting comb polystyrenes did not possess functional groups at branch chain ends.
Scheme 4.1 Reaction pathway for the synthesis of unfunctionalized comb polystyrenes. (a) synthesis of Macromonomers A1 and A2; (b) synthesis of comb polystyrenes by homopolymerization of Macromonomers A1 or A2.

4.1.1 Synthesis of \(\omega-(p\)-vinylbenzyl\)polystyrene (Macromonomers A1 and A2).

\(\omega-(p\)-Vinylbenzyl\)polystyrene was prepared by living anionic polymerization using the procedure described by Asami and coworkers\textsuperscript{53} with a slight modification of the reaction of poly(styryl)lithium (PSLi) with 4-vinylbenzyl chloride (VBC). PSLi initiated by sec-butyllithium in benzene was slowly added into 18 molar equivalents of VBC in THF at \(-78\ \text{°C}\) as shown in Scheme 4.1 (a). The reaction conditions used, including amount of VBC, reaction temperature, solvent, and addition mode, were based on previous investigations.\textsuperscript{53, 70, 241} The characteristic red color of the PSLi solution in THF
disappeared in seconds once it was added to the VBC solution. The excess VBC was removed from the macromonomer samples by precipitation into methanol 3 times. Cold methanol was used to decrease the solubility of the macromonomers with low molecular weight. The resulting macromonomer had a sec-butyl group at the $\alpha$-end and a polymerizable $p$-vinylbenzyl group at the $\omega$-end. Its structure and purity were thoroughly characterized by SEC, NMR, and MALDI-TOF mass spectrometry. The SEC chromatograms of both Macromonomers A1 and A2 (Figure 4.1) exhibit symmetric, monomodal distributions and analysis of the chromatograms yielded $M_n = 1600$ g/mol (calcd. $M_n = 1600$ g/mol) with PDI = 1.08 for Macromonomer A1 and $M_n = 2500$ g/mol (calcd. $M_n = 2500$ g/mol) with PDI = 1.08 for Macromonomer A2. The $^1$H NMR spectra of Macromonomers A1 and A2 in Figure 4.2 clearly show characteristic peaks for vinyl protons from the $p$-vinylbenzyl group ($H_a, 2 \text{ H}, \delta 5.2 \text{ and } 5.7 \text{ ppm}$) and methyl protons from the sec-butyl initiator fragment ($H_c, 6 \text{ H}, \delta 0.5 - 0.8 \text{ ppm}$), with an integral ratio of $H_a : H_c = 2 : 6.8$ for Macromonomer A1 and $H_a : H_c = 2 : 6.8$ for Macromonomer A2, which is close to the expected ratio of $H_a : H_c = 2 : 6$. No proton peaks from VBC (sharp peaks at $\delta 4.5, 5.3 \text{ and } 5.8 \text{ ppm}$) were observed in either spectrum, indicating that excess VBC was effectively removed in the precipitation step. The MALDI-TOF mass spectra (Figure 4.3) confirmed the uniformity and well-defined structure of Macromonomers A1 and A2 with one narrow distribution of peaks corresponding to the proposed structure. For Macromonomer A1, a representative monoisotopic mass peak at $m/z$ 1321.68 corresponds to the 10-mer of ($p$-vinylbenzyl)polystyrene,
C₄H₉-(C₈H₈)₁₀-C₉H₉•Ag⁺, with calculated monoisotopic mass \[57.0704(C₄H₉) + 10 \times 104.0626(C₈H₈) + 117.0704(C₉H₉) + 106.9051(Ag⁺)] = 1321.67 Da. For Macromonomer A2, a representative monoisotopic mass peak at \(m/z\) 2154.15 corresponds to the 18-mer of (p-vinylbenzyl)polystyrene, C₄H₉-(C₈H₈)₁₈-C₉H₉•Ag⁺, with calculated monoisotopic mass \[57.0704(C₄H₉) + 18 \times 104.0626(C₈H₈) + 117.0704(C₉H₉) + 106.9051(Ag⁺)] = 2154.17 Da. Overall, the results from SEC, NMR, and MALDI-TOF mass spectrometry support the efficient synthesis of Macromonomer A1 and A2 with controlled molecular weight, narrow PDI, and high styril chain end functionality.
Figure 4.1 SEC chromatograms of Macromonomer A1 and A2 and corresponding comb polystyrenes (before and after fractionation) for (a) M24P14, (b) M24P28, (c) M24P50, (d) M15P34 and (e) M15P105.
Figure 4.2 $^1$H NMR spectra of (a) Macromonomer A1, M15P34, M15P105; (b) Macromonomer A2, M24P14, M24P28, and M24P50.
4.1.2 Homopolymerization of macromonomers

Comb polystyrenes with extremely high branching density were prepared by living anionic polymerization of macromonomers with \(\omega\)-styryl end groups. Since polystyrene
macromonomers are solids, their purification in order to meet the demanding standards of living anionic polymerization is challenging. Impurities can also originate from glassware used as the reactor and from the solvent used for polymerization. These trace impurities significantly undermine or even completely disable the living anionic polymerization by quenching initiators and terminating growing macro anions, which is especially problematic when a high degree of polymerization is desired. In this work, for purification purposes the benzene solution of macromonomers in the polymerization reactor was titrated with diluted sec-butylithium initiator in a drybox filled with argon. Once impurities present in macromonomers and the reactor had been neutralized by sec-butylithium, a faint yellow color appeared due to the formation of poly(styryl)lithium macroanions in the initiation step. Then the calculated amount of sec-butyllithium initiator was immediately added into the reactor to start the polymerization of macromonomers. It is also noteworthy that the excess VBC was efficiently removed from the macromonomers prior to their polymerization.

The SEC chromatograms of macromonomers and their homopolymerization products are compared in Figure 4.1; molecular weights were determined using SEC coupled with a light scattering detector. In all the cases, the peak for the macromonomer has disappeared and a new peak at a lower retention volume has appeared, indicating successful polymerization. SEC analysis of the peaks corresponded to each comb are summarized in Table 4.1, with comparison to the calculated $M_n$. A shoulder next to the
main peak of M24P14 or M15P34 was observed at higher retention volume, while this shoulder was not so obvious for the other combs with larger degrees of polymerization. It is possible that a small fraction of the macromonomers could have been initiated, and even polymerized into macroanions with a low degree of polymerization ($M_n < 35000$ g/mol) before the titration was completed. However, these macroanions were soon terminated by remaining impurities to form products corresponding to the shoulder. These polymeric impurities were readily removed after a fractionation process, indicated by the disappearance of shoulders in SEC chromatograms for fractionated combs in Figure 4.1. The fractionation process also shifted the main peak to lower retention volume in SEC chromatograms by selectively removing polymers with lower molecular weights, therefore the combs exhibit higher $M_n$ values after fractionation.

Table 4.1 Summary of SEC analysis of comb polystyrenes.

<table>
<thead>
<tr>
<th></th>
<th>Calcd. $M_n$</th>
<th>SEC before frac. $M_n$</th>
<th>PDI</th>
<th>SEC after frac. $M_n$</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>M15P34</td>
<td>44,000</td>
<td>49,000</td>
<td>1.12</td>
<td>56,000</td>
<td>1.08</td>
</tr>
<tr>
<td>M15P105</td>
<td>157,000</td>
<td>135,000</td>
<td>1.12</td>
<td>170,000</td>
<td>1.07</td>
</tr>
<tr>
<td>M24P14</td>
<td>29,000</td>
<td>23,000</td>
<td>1.30</td>
<td>37,000</td>
<td>1.08</td>
</tr>
<tr>
<td>M24P28</td>
<td>58,000</td>
<td>62,000</td>
<td>1.11</td>
<td>69,000</td>
<td>1.04</td>
</tr>
<tr>
<td>M24P50</td>
<td>116,000</td>
<td>122,000</td>
<td>1.10</td>
<td>130,000</td>
<td>1.04</td>
</tr>
</tbody>
</table>

Polymerization of macromonomers was also confirmed by evidence from $^1$H NMR characterization. The peaks for protons from the $p$-vinylbenzyl group of both macromonomers ($H_a$, 2 H, $\delta$ 5.2 and 5.7 ppm) disappeared in the $^1$H NMR spectra of the
resulted comb polystyrenes (Figure 4.2) due to polymerization. The broad peak at δ 0.5 - 0.8 ppm was attributed to methyl protons in sec-butyl groups originating from the macromonomers (H₆, 6 H, δ 0.5 - 0.8 ppm).

It is concluded from the characterization results by SEC and ¹H NMR analyses that impurities present in the reactions were efficiently removed with this titration purification procedure, and thus relatively high degrees of polymerization (Mₙ = 170,000 g/mol; Xₙ = 105) for the resulting comb polymers were achieved. It is also noteworthy that combs prepared with this method also exhibited narrow molecular weight distributions after fractionation.

4.1.3 Physical properties of unfunctionalized comb polymers

Physical properties of unfunctionalized comb polymers after fractionation are summarized in Table 4.2.

Table 4.2 Molecular characteristics of comb polystyrenes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total Mₙ (g/mol)a</th>
<th>PDIa</th>
<th>Mₚ</th>
<th>Pc</th>
<th>Ld</th>
<th>Rₕ (nm)e</th>
<th>[η]/(ml/g)f</th>
<th>g²g</th>
<th>T₉,bulk (°C)h</th>
</tr>
</thead>
<tbody>
<tr>
<td>M24P14</td>
<td>37,000</td>
<td>1.08</td>
<td>24</td>
<td>14</td>
<td>1</td>
<td>3.6</td>
<td>7.6</td>
<td>0.27</td>
<td>82</td>
</tr>
<tr>
<td>M24P28</td>
<td>69,000</td>
<td>1.04</td>
<td>24</td>
<td>28</td>
<td>1</td>
<td>5.0</td>
<td>10.6</td>
<td>0.25</td>
<td>82</td>
</tr>
<tr>
<td>M24P50</td>
<td>130,000</td>
<td>1.04</td>
<td>24</td>
<td>50</td>
<td>1</td>
<td>6.0</td>
<td>13.8</td>
<td>0.20</td>
<td>90</td>
</tr>
<tr>
<td>M15P34</td>
<td>56,000</td>
<td>1.08</td>
<td>15</td>
<td>34</td>
<td>1</td>
<td>4.0</td>
<td>6.9</td>
<td>0.20</td>
<td>74</td>
</tr>
<tr>
<td>M15P105</td>
<td>170,000</td>
<td>1.07</td>
<td>15</td>
<td>105</td>
<td>1</td>
<td>7.0</td>
<td>12.0</td>
<td>0.15</td>
<td>80</td>
</tr>
</tbody>
</table>
\(^a\) Molecular weight and polydispersity index determined by SEC coupled with refractometer and light scattering detector (± 10 %).

\(^b\) Number of styrene repeat units in a branch.

\(^c\) Number of branches.

\(^d\) Number of styrene repeat units between adjacent branches.

\(^e\) Hydrodynamic radius by dynamic light scattering in THF at 30 °C (± 10%).

\(^f\) Intrinsic viscosity determined by SEC coupled with differential viscometer in THF at 30 °C (± 10%).

\(^g\) Branching factor: \(g' = \frac{[\eta]_{\text{branch}}}{[\eta]_{\text{linear}}} (± 0.01); \) Intrinsic viscosity determined in THF at 30 °C.

\(^h\) Bulk glass transition temperature determined from 2nd heating scan at 10 °C / min (± 1 °C).

Comparison of the \(R_h\) values for combs with the same branch length (either \(M = 24\) or \(M = 15\), Figure 4.4) shows that they increase slowly with molecular weight. These combs fall into the transition region between a nearly constant \(R_h\) with changing \(P\) for fixed \(L\) and \(M\) at low values of \(P\) and a more rapid change in \(R_h\) with \(P\) for higher values of \(P\).\(^{29}\)
Figure 4.4 Log-log plot of hydrodynamic volume $R_h$ versus weight-average molecular weight $M_w$ for comb polystyrenes M24P14, M24P28, and M24P50 in THF at 30 °C.

The intrinsic viscosity of a comb polystyrene is substantially lower than that of a linear polystyrene of similar molecular weight (Figure 4.5) due to the highly branched structure of combs. Tsukahara et al.\textsuperscript{28} established a crossover in the intrinsic viscosity from $[\eta] \sim M_w^0$ for low P to $[\eta] \sim M_w^{0.75}$ (consistent with the behavior of linear chains) at high P, for comb polymers with fixed L and M. In this study, $[\eta] \sim M_w^{0.50 \pm 0.05}$ is observed for comb polystyrenes in THF at 30 °C. It appears that these comb polystyrenes are in the crossover between the star-like behavior identified for low P and the bottlebrush-like behavior at high P.
Figure 4.5 Log-log plot of intrinsic viscosity [$\eta$] versus weight-average molecular weight, $M_w$, for linear PS (squares), comb PS with $M = 24$ (circles) and comb PS with $M = 15$ (triangles) in THF at $30^\circ$C.

Plots of storage ($G'$) and loss ($G''$) moduli near the terminal regime for comb polystyrenes obtained from rheometry measurements are shown in Figure 4.6. In the master curves of all comb polystyrenes the value of $G'$ is below the value of $G''$ for all frequencies, so the comb chains are not entangled, even though the total molecular weight is beyond the critical entanglement molecular weight $M_c \sim 28k$. This is consistent with the behavior seen by McKenna et al.\textsuperscript{17} for well-defined copolymer combs with polynorborene backbone and polylactide branches. Master curves for M15P105 in Figure
4.6(b) indicate that it is closer to entanglement than are the other combs, due to its shorter branch length ($M = 15$) and large number of branches ($P = 105$). For our PS combs the relaxation time becomes longer and the terminal flow region moves to lower frequency as the number of branches increases while the length of branch is kept constant. This result, which has been observed for other combs with different chemical composition and architecture details,$^{16,17}$ is expected, since in the terminal regime the whole comb chain relaxes and the size of the whole molecule matters.
Figure 4.6 Master curves of dynamic storage modulus, $G'$, (open squares) and loss modulus $G''$ (open triangles) as a function of frequency for (a) comb polystyrenes with branch length $M = 24$, referenced to 145 °C; (b) comb polystyrenes with branch length $M = 15$, referenced to 115 °C.
$T_g$s of combs in Table 4.2 varied with the architecture details. In general, $T_g$s of combs with shorter branches were lower, which would be expected according to the free volume theory. The variation of $T_g$ with number of branches was more complicated. For combs with $M = 24$, $T_g$ was constant at 82 °C when $P$ increased from 14 to 28, while it increased to 90 °C when $P$ was further increased to 50. For combs with $M = 15$, $T_g$ increased from 74 to 80 °C as $P$ increased from 34 to 105. There are only a limited amount of examples in the literature regarding $T_g$ variation with architecture details for densely branched comb polymers. Tsukahara et al.\textsuperscript{16} found that $T_g$ is independent of the number of branches when the branch length is constant for comb polymers with PS branches and PMMA backbone, which is different from our observation. More data points will be needed in order to draw decisive conclusions about the architecture dependence of $T_g$.

4.2 Synthesis of comb polystyrenes with functionalized branch chain ends

In this work a new, general method has been investigated for the preparation of well-defined, comb polystyrenes with controlled, variable amounts and types of branch chain-end functionalities by combining living anionic polymerization and thiol-end “click” chemistry as outlined in Scheme 4.2. 4-Pentenyllithium has been investigated as the initiator for the preparation of well-defined $\alpha$-vinyl-, $\omega$-styryl-functionalized macromonomers (Macromonomer B) after termination with vinylbenzyl chloride (Scheme 4.2). It was envisioned that these vinyl-functionalized macromonomers could be anionically copolymerized with different amounts of $\omega$-styryl-functionalized
macromonomers (Macromonomers A2, initiated by sec-BuLi) to form well-defined, comb polystyrenes (Comb-Vinyl) with varying amounts of $\omega$-vinyl functionality on branches. Subsequent photoinitiated, thiol-ene “click” reactions of substituted thiols with the pendant vinyl groups would then be used to introduce diverse functionalities.

Scheme 4.2 Reaction pathway for the synthesis of functionalized comb polystyrenes. (a) synthesis of Macromonomer A2; (b) synthesis of Macromonomer B; (c) synthesis of Comb-Vinyl by copolymerization and subsequent functionalization by thiol-ene “click” chemistry.
4.2.1 Synthesis of α-4-pentenyl-ω-(p-vinylbenzyl)polystyrene (Macromonomer B).

Living polymerization with a functional initiator ensures that every chain will have the functional group at the initiating, α, chain end. The initiator 4-pentenyllithium was prepared using the procedure described by Takano and coworkers by reacting lithium metal with 5-bromo-1-pentene in heptane. 4-Pentenyllithium was then used to initiate the polymerization of styrene in benzene in the presence of six equivalents of THF. As found in previous research, addition of Lewis base was required to promote dissociation of the primary alkyl lithium initiator in hydrocarbon solvent and thus increase the rate of initiation relative to propagation, which was necessary to obtain a narrow molecular weight distribution product. The reaction of the resulting α-4-pentenylpoly(styryl)lithium with VBC followed the end-capping procedure for preparing Macromonomer A1 and A2 described before.

The resulting product exhibited a symmetric monomodal distribution as shown in Figure 4.7 and analysis of the SEC yielded $M_n = 2300$ g/mol (calcd. $M_n = 2500$ g/mol) with PDI = 1.06. The $^1$H NMR spectrum of the product is shown in Figure 4.8. Compared to that of Macromonomer A1 or A2, besides the peaks assignable to vinyl protons from the ω-(p-vinylbenzyl) group (H_a, 2 H, δ 5.2 & 5.7 ppm), new peaks appear in the $^1$H NMR spectrum which are attributable to protons from the 4-pentenyl initiator fragment (H_d, 1 H, δ 5.7 ppm, and H_e, 2 H, δ 4.9 ppm). The resonance peak for H_a overlaps with the peak for H_d at δ 5.7 ppm, which results in an integration ratio of 1.8:1.0:2.0 for peaks from vinyl protons at δ 5.7, 5.2 and 4.9 ppm, as expected. Characteristic vinyl carbons
could also be observed in the $^{13}$C NMR spectrum (Figure 4.9) at $\delta$ 114.0 and 139.0 ppm for $\alpha$-4-pentenyl group and at $\delta$ 112.7 and 135.0 ppm for the $\omega$-(p-vinylbenzyl) group, which are in good agreement with values reported in the literature$^{54,97,115}$. Thus, both $^1$H and $^{13}$C NMR spectral analyses confirmed the structure of Macromonomer B as $\alpha$-4-pentenyl-$\omega$-(p-vinylbenzyl)polystyrene. The MALDI-TOF mass spectrum of Macromonomer B is shown in Figure 4.10. Only one mass distribution is detected, with a representative monoisotopic peak at $m/z$ 2270.43 corresponding to the 19-mer of $\alpha$-4-pentenyl-$\omega$-(p-vinylbenzyl)polystyrene, $C_5H_9$-$\left(C_8H_8\right)_{19}$-$C_9H_9\cdot Ag^+$, with calculated monoisotopic mass $[69.0704(C_5H_9) + 19 \times 104.0626(C_8H_8) + 117.0704(C_9H_9) + 106.9051(Ag^+)] = 2270.24$ Da. Therefore, the MALDI-TOF mass spectrometry results combined with the SEC and NMR results are consistent with efficient synthesis of Macromonomer B with controlled $M_n$, narrow PDI and high $\alpha$-vinyl, $\omega$-styryl chain end functionality. This $\alpha$-vinyl functionalized macromonomer provided a unique ability to prepare comb polymers (polymacromonomers) with functionalized branch chain ends via a variety of post-polymerization functionalization reactions.
Figure 4.7 SEC overlays of the chromatograms for Macromonomer A2, Macromonomer B, Comb-Vinyl, and functionalized comb polystyrene before and after fractionation for:

(a) Comb-OH; (b) Comb-COOH; (c) Comb-C$_8$F$_{17}$. 
Figure 4.8 $^1$H NMR spectrum of Macromonomer B.

Figure 4.9 $^{13}$C NMR spectrum of Macromonomer B.
4.2.2 Synthesis of Comb-Vinyl

The strategy of living anionic polymerization of Macromonomer A1 or A2 purified by the sec-BuLi titration procedure, as demonstrated by the successful synthesis of unfunctionalized combs, was extended to copolymerization of Macromonomers A2 and B for the preparation of Comb-Vinyl as the precursor for comb polymer with functionalized branch ends. The vinyl branch ends were introduced into the comb polymer through the incorporation of Macromonomer B. By simply varying the ratio of Macromonomers A2 and B in the mixture before copolymerization, one can precisely control the fraction of
vinyl branch ends in Comb-Vinyl, and therefore the degree of functionalization in the final product. Since Macromonomers A2 and B have the same styrene repeating unit, the same \( p \)-vinylbenzyl end group for polymerization, and similar molecular weights (2500 g/mol vs. 2300 g/mol), the reactivity ratios for copolymerization of the two macromonomers should be close to unity, which is helpful for controlling the fraction of functionalizable vinyl chain ends and for achieving their random distribution in Comb-Vinyl. For this work, Comb-Vinyl was prepared from a mixture of Macromonomers A2/B = 76/24 (w/w).

Figure 4.7 shows the SEC chromatogram of the polymerization product. Complete conversion of both macromonomers was indicated by the disappearance of peaks for Macromonomers A2 and B. A new monomodal peak, corresponding to the polymerization product Comb-Vinyl, appeared at a retention volume lower than both macromonomers. SEC analysis of the peak yielded \( M_n = 74000 \text{ g/mol} \) with \( \text{PDI} = 1.09 \), slightly higher than the calculated \( M_n = 64000 \text{ g/mol} \). A small amount of polymeric impurities (\( M_n < 25000 \text{ g/mol} \)), presumably generated during the titration, is present as a small shoulder next to the peak of Comb-Vinyl at higher retention volume. Yield of Comb-Vinyl is nearly 100% from polymerization of Macromonomers A2 and B.

The \(^1\text{H} \) NMR spectrum of the resulting Comb-Vinyl is shown in Figure 4.11a. Comparison of \(^1\text{H} \) NMR spectra for the two macromonomers (Figures 4.2b and 4.8) with Comb-Vinyl (Figure 4.11a) shows that the peaks for protons from the \( p \)-vinylbenzyl groups (\( H_a, 2 \text{ H}, \delta 5.2 \) and 5.7 ppm)\(^{54,97} \) disappeared due to polymerization; peaks for
protons from the 4-pentenyl initiator fragment of Macromonomer B (H_d, 1 H, δ 5.7 ppm, and H_e, 2 H, δ 4.9 ppm) and protons from the methyl groups from the sec-butyl initiator fragment of Macromonomer A2 (H_c, 6 H, δ 0.5 - 0.8 ppm) remained. The integral ratio of H_e and H_c from NMR analysis is 2.0:18.5 in the comb, which is close to the calculated ratio of 2.0:17.5 based on the weight ratio of Macromonomers A2 / B (76 / 24) before polymerization. The ^13C NMR spectrum of Comb-Vinyl is shown in Figure 4.12a. The most important observation is that peaks for carbons from the p-vinylbenzyl group (δ 112.7 and 135.0 ppm, see Figure 4.9) are gone, while peaks for carbons from the α-4-pentenyl group remain at δ 114.0 and 139.0 ppm.

Based on the SEC and NMR results, it is confirmed that Macromonomers A2 and B were successfully copolymerized by living anionic polymerization and that the α-4-pentenyl groups from Macromonomer B remained intact during the polymerization. These results once again demonstrate that the pre-polymerization titration of impurities using sec-BuLi is an excellent method for anionic polymerization of macromonomers to form well-defined comb polymers.
Figure 4.11 $^1$H NMR spectra of (a) Comb-Vinyl, (b) Comb-OH, (c) Comb-COOH, and (d) Comb-C$_8$F$_{17}$.
Figure 4.12 $^{13}$C NMR spectra of (a) Comb-Vinyl, (b) Comb-OH, (c) Comb-COOH, and (d) Comb-$C_8F_{17}$. 
4.2.3 Functionalization of Comb-Vinyl using thiol-ene chemistry.

Comb-Vinyl made by copolymerization of Macromonomers A2 and B possesses pendent vinyl groups to which chain end functionalities can be added. Thiol-ene “click” chemistry is an efficient and versatile process for functionalizing vinyl groups, making it ideal for bringing diverse functionalities to vinyl-functionalized combs. Three commercially available thiols with various functionalities were used: 2-mercaptoethanol, mercaptoacetic acid, and 1H,1H,2H,2H-perfluoro-1-decanethiol. Previous work reported successful functionalizations of short linear model polystyrenes by thiol-ene “click” reactions. Herein a similar procedure was followed to functionalize Comb-Vinyl, except that a higher concentration ([thiol] : [C=C] = 3.9 : 1 vs. 1.1 : 1) and a longer reaction time (1 h vs. 15 min) were used, due to the larger steric hindrance effect expected for comb versus linear polymers. Major small molecule impurities, including excess thiol, initiator residue, and disulfide byproduct, were readily removed by simple precipitation with no need for chromatographic separation. Fractionation was further applied here in order to remove polymeric impurities.

The SEC spectra of the functionalized combs are shown in Figure 4.7. The peak corresponding to each of the three functionalized combs overlapped with the peak of Comb-Vinyl very well, indicating the absence of side reactions causing molecular weight increases in the thiol-ene “click” reactions with all three thiols. For Comb-OH and Comb-C$_8$F$_{17}$, polymeric impurities were removed by fractionation and thus better defined peaks were obtained after fractionation. However, attempts to fractionate Comb-COOH
were unsuccessful. The strongly polar carboxyl groups at the branch chain ends greatly increased the solubility of Comb-COOH in methanol; therefore a solution of Comb-COOH in mixed toluene/methanol solvent formed a stable emulsion that could not be readily separated into two clear layers. This observation supported the successful functionalization of Comb-Vinyl with carboxyl groups.

The \(^1\)H NMR spectra of functionalized combs are shown in Figures 4.11b, 4.11c, and 4.8d. The peaks assignable to protons of the \(\alpha\)-4-pentenyl group (H\(_d\), 1 H, \(\delta\) 5.7 ppm, and H\(_e\), 2 H, \(\delta\) 4.9 ppm) completely disappeared, which indicates complete reaction within 1 hour. Complete reaction is also supported by the disappearance of the vinyl sp\(^3\) carbon signals at \(\delta\) 114.0 and 139.0 ppm in the \(^{13}\)C NMR spectra of all three functionalized combs (Figures 4.12b, 4.12c, and 4.12d). A broad peak attributed to methyl protons from the sec-butyl initiator fragment (H\(_c\), 6 H, \(\delta\) 0.5 - 0.8 ppm) was still observed. Due to the formation of thiol ether bonds, characteristic resonance peaks appeared in the \(^1\)H NMR spectra as well. For Comb-OH, three peaks for methylene protons from the functionalized chain end can be clearly identified at \(\delta\) 2.4 ppm for \(-SCH_2\)– (H\(_h\)), \(\delta\) 2.7 ppm for \(-SCH_2CH_2O\)– (H\(_g\)), and \(\delta\) 3.7 ppm for \(-SCH_2CH_2O\)– (H\(_i\)), respectively (Figure 4.11b).\(^{115}\) The integral ratio of proton peaks by \(^1\)H NMR analysis is H\(_f\) : H\(_g\) : H\(_c\) = 2.0 : 1.9 : 18.1, which is close to expected values of 2.0 : 2.0 : 18.5 based on the composition of Comb-Vinyl. For Comb-C\(_8\)F\(_{17}\), the two peaks at \(\delta\) 2.4 ppm and 2.7 ppm in Figure 4.11d were attributed to protons (H\(_i\) and H\(_j\)) of the two methylene groups on each side of the thiol ether linkage.\(^{115}\) The chemical shift of the methylene protons near CF\(_2\)
(–SCH$_2$CH$_2$CF$_2$–) could not be clearly identified since it overlapped with peaks from the polystyrene backbone protons in the $^1$H NMR spectrum. $^{19}$F NMR signals from the long perfluorinated alkyl chain were clearly observed as a singlet peak at – 80.7 ppm corresponding to methyl fluorines [CF$_3$–(CF$_2$)$_7$–], and multiple peaks from – 121 to – 126 ppm attributed to methylene fluorines [CF$_3$–(CF$_2$)$_7$–] in the $^{19}$F NMR spectrum of Comb-C$_8$F$_{17}$ (Figure 4.13). For Comb-COOH, the methylene protons (H$_i$) between the carbonyl group and sulfur (–CH$_2$SCH$_2$COOH) were observed at $\delta$ 3.2 ppm while the other methylene protons (H$_k$) near sulfur (–C$_H$$_2$SCH$_2$COOH–) were evidenced by characteristic peaks at $\delta$ 2.6 ppm (Figure 4.11c). The integral ratio of protons from thiol-functionalized chain ends and sec-butyl chain ends by $^1$H NMR analysis was H$_i$ : H$_c$ = 2.0 : 23.6, which differed from the expected ratio of 2.0 : 18.1. The reason for the lower than expected fraction of thiol-functionalized chain ends in Comb-COOH may be that lower molecular weight combs with branch chain ends functionalized with carboxyl groups are more soluble in polar solvents, which means that they are more likely to be removed from the products during precipitation. This explanation was supported by the fact that there was a lower yield of polymers after purification for Comb-COOH (64%) than for Comb-OH (90%) and Comb-C$_8$F$_{17}$ (81%). TLC analysis of the purified Comb-OH, Comb-COOH, and Comb-C$_8$F$_{17}$ exhibited only one spot at the bottom of silica gel plate, consistent with a high yield of functionalized combs (unfunctionalized polymers < 2%).

The combination of evidence from $^1$H, $^{13}$C and $^{19}$F NMR spectra as well as TLC
analysis shows that pendent \( \alpha \)-4-pentenyl groups of Comb-Vinyl were efficiently functionalized with OH, COOH or C\(_8\)F\(_{17}\) groups by thiol-ene “click” reactions. No evidence for side reactions was observed and impurities were easily removed. Therefore well-defined comb polystyrenes with controlled amount and type of functionalized branch ends were successfully prepared using these methods.

Figure 4.13 \(^{19}\)F NMR spectrum of Comb- C\(_8\)F\(_{17}\).
CHAPTER V

BULK THERMODYNAMICS OF UNFUNCTIONALIZED COMB/LINEAR
POLYSTYRENE BLENDS

Bulk thermodynamics in blends containing deuterated linear PS with molecular weight of 36k (dLPS36k) and one of the five unfunctionalized combs (M24P14, M24P28, M24P50, M15P34 and M15P105) were studied by DSC and SANS. DSC measurements provided qualitative information about blend miscibility (Section 5.1), while SANS was used to quantitatively measure the effective bulk thermodynamic interaction parameter, $\chi_{\text{eff}}$, of a blend (Section 5.2).

5.1 Bulk miscibility of comb/linear polystyrene blends by DSC

In this section study of the bulk miscibility of comb/linear polystyrene blends by DSC is described. Since the $T_g$s of each comb studied here is distinctly lower than the $T_g$ of its linear counterpart in the blend, one expects to observe two separate endothermic transitions in the DSC curve if bulk phase separation occurs in the blend. DSC curves for 50/50 (comb/linear, v/v) blends of combs with deuterated 36k linear PS (dLPS36k) are shown in Figure 5.1. For each 50/50 blend containing M24P14 ($T_g = 82 \, ^\circ\text{C}$) or M24P28
(\(T_g = 82 \, ^\circ\text{C}\)) comb, there is only one glass transition, at a temperature intermediate between the \(T_g\)s of the corresponding comb and dLPS36k (\(T_g = 104 \, ^\circ\text{C}\)). \(T_g = 96 \, ^\circ\text{C}\) for the 50/50 M24P14/dLPS36k blend and \(T_g = 96 \, ^\circ\text{C}\) for the 50/50 M24P28/dLPS36k blend. This indicates that M24P14 and M24P28 are miscible with dLPS36k in the bulk at 50/50 composition at temperatures near the \(T_g\). The exact temperature for which the miscibility is probed is not well-defined. However, one should be cautious to draw the same conclusion from the DSC result for M24P50 (\(T_g = 90 \, ^\circ\text{C}\)). Since the glass transition (\(T_g = 97 \, ^\circ\text{C}\)) is broader in its 50/50 blend with dLPS36k and the \(T_g\) difference between M24P50 and dLPS36k is relatively small, it is possible that DSC did not clearly resolve two separate glass transitions for M24P50 and dLPS36k, if bulk phase separation took place.

For M15P34 (\(T_g = 74 \, ^\circ\text{C}\)) and M15P105 (\(T_g = 80 \, ^\circ\text{C}\)) combs with shorter branches, 50/50 blends with dLPS36k were immiscible at temperatures in the neighborhood of \(T_g\), as indicated by the presence of two distinct glass transitions in each DSC curve. \(T_{g,1} = 83 \, ^\circ\text{C}\) and \(T_{g,2} = 102 \, ^\circ\text{C}\) for the 50/50 M15P34/dLPS36k blend. \(T_{g,1} = 82 \, ^\circ\text{C}\) and \(T_{g,2} = 103 \, ^\circ\text{C}\) for the 50/50 M15P105/dLPS36k blend. The two \(T_g\)s were slightly closer in the M15P34/dLPS36k blend than in the M15P105/dLPS36k blend. The first \(T_g\) in M15P34/dLPS36k blend was shifted higher by 9 \(^\circ\text{C}\) from the \(T_g\) of pure M15P34, while this shift was only 2 \(^\circ\text{C}\) in the M15P105/dLPS36k blend. These results indicate that miscibility was improved by decreasing number of branches in the comb.
Figure 5.1 DSC curves for 50/50 blends of various combs with dLPS36k.

Decreasing the comb content in blends corresponds to moving into a portion of the phase diagram where a single phase is stable, as shown in Figure 5.2. It is necessary to decrease the M15P34 content from 50 vol% to 10 vol% in order to obtain a miscible blend with dLPS36k. To obtain a miscible blend between M15P105 and dLPS36k, the comb content must be further reduced to 5 vol%.
Figure 5.2 DSC curves for blends with various comb compositions between M15P34 or M15P105 and dLPS36k.

According to these DSC results, the architecture details of combs greatly affect their miscibility with the linear component. Decreasing branch number and increasing branch length improve the miscibility between comb and linear polystyrenes, in agreement with the results reported by Tsukahara et al. \(^{246}\)

5.2 Bulk thermodynamics in comb/linear polystyrene blends characterized by SANS

Quantitative comparison of bulk miscibility of different combs with the linear analog was performed using SANS measurements of 50vol% blends of comb and dLPS36k at
temperatures of 120 to 180 °C. As shown previously, SANS data for miscible blends of branched and linear PS can be fit reasonably well with structure factors derived for the corresponding architectures in the incompressible random phase approximation (RPA). If Gaussian statistics are assumed for both the branched and linear chains, the measured intensity is given by

\[
\frac{(b_{\text{linear}} - b_{\text{comb}})^2}{V} I(q) = \frac{1}{\bar{\phi}_{\text{linear}} N_{\text{linear}} S_{\text{linear}}(q)} + \frac{1}{\bar{\phi}_{\text{comb}} N_{\text{comb}} S_{\text{comb}}(q)} - 2 \chi_{\text{eff}},
\]

(5.1)

where \( V \) is a reference segment volume, \( \phi_i \) is the volume fraction of species \( i \), \( N_i \) is the number of segments per chain, \( b_i \) is the scattering length for component \( i \) defined over the reference volume, \( S_i \) is the structure factor for component \( i \), and \( \chi_{\text{eff}} \) is the effective segment-segment exchange interaction parameter representing the strength of interaction between molecules on a per segment basis. To account for change in molar volume with temperature, the value of 5.5 × 10^{-4} K^{-1} for the thermal expansion coefficient was used.

The structure factor for a linear polymer with the Gaussian statistics is the well-known Debye function, \( D(x) \):

\[
S_{\text{linear}}(q) = D(x_{\text{linear}}) = \frac{2(e^{-x_{\text{linear}}} - 1 + x_{\text{linear}})}{x_{\text{linear}}^2},
\]

(5.2)

where \( x_{\text{linear}} = q^2 R_{g,\text{linear}}^2 \) and \( R_{g,\text{linear}}^2 = N_{\text{linear}} a^2 / 6 \). \( N_{\text{linear}} \) is the number of segments in the linear polymer and \( a \) is the statistical segment length.

The structure factor of a comb polymer can be obtained by considering the correlations between the segments. As shown in Figure 5.3 there are three types of correlations in a
comb polymer: (1) between two segments in the same tooth and in the backbone, which is described by $S_1$; (2) between segments in two different teeth, $S_2$; (3) between one segment in a tooth and another segment in the backbone, $S_3$.

![Figure 5.3](image1.png)

Figure 5.3 Structure of a comb polymer and the possible interactions among various portions of the chain.

$S_1$ is simply derived using Debye’s function:

$$S_1(q) = PM^2D(x_M) + ((P-1)L)^2D(x_{(P-1)L}),$$

(5.3)

where $x_M = Ma^2q^2/6$ and $x_{(P-1)L} = (P-1)La^2q^2/6$. $M$, $P$ and $L$ are the three parameters describing the architecture of a comb. It must be noted that we simplify the calculation of $S_1$ by assuming that the segmental length of the backbone equals that of each branch. $S_2$ is given as:

$$S_2(q) = 2\sum_{i=2}^{P}\sum_{j=1}^{i}M^2F(x_M)^2E(x_{(i-j)L}),$$

(5.4)
where $F(x) = \frac{1-e^{-x}}{x}$, $E(x) = e^{-x}$, and $x_{(i-j)L} = (i-j)La^{2}q^{2}/6$. $S_{3}$ is written as:

$$S_{3}(q) = 2MF(x_{M})((\sum_{i=1}^{P}(i-1)LF(x_{(i-1)L}))+ (P-1)LF(x_{(P-1)L})).$$  \hspace{1cm} (5.5)$$

The structure factor of a comb is then obtained by combining the three contributions above:

$$S_{\text{comb}}(q) = \frac{S_{1}(q) + S_{2}(q) + S_{3}(q)}{N_{\text{comb}}^{2}},$$  \hspace{1cm} (5.6)$$

where $N_{\text{comb}} = (P-1)L + PM$ is the total number of segments per comb.

The SANS curves for blends containing M24P14 and M24P28 are compared with that for the reference linear/linear isotopic blend in Figures 5.4 and 5.5. The much larger $\chi$ parameters and larger chain sizes in the blends with the combs are evidenced by the much higher intensities at low $q$ for those blends. The SANS curves for both of these comb blends were reasonably well fit with the RPA model using the comb structure factors derived above. The only parameters varied to fit the experimental SANS curve were the statistical segment length $a$ and $\chi_{\text{eff}}$. The intensity at low $q$ decreased as the temperature increased for both combs, which is characteristic of upper critical solution temperature (UCST) behavior.
Figure 5.4 Experimental SANS curves with a fit to the RPA model for the 50 vol% M24P14/dLPS36k blend and 50 vol% linear/linear isotopic blend at 120 °C and 180 °C.

Figure 5.5 Experimental SANS curves with a fit to the RPA model for the 50 vol% M24P28/dLPS36k blend and 50 vol% linear/linear isotopic blend at 120 °C and 180 °C.
However, the SANS curve for the blend containing 50 vol% M24P50 could not be fit with the RPA model as well, as shown in Figure 5.6. The intensities calculated with the RPA model were somewhat lower than the experimental values at the lowest values of $q$. In this case it was difficult to capture the shape and magnitude of the experimental SANS curve by only varying $a$ and $\chi_{\text{eff}}$. There are two obvious possible reasons for the difference between the theory and experiment. One possible reason for the poorer fitting is the blend has just reached a point of bulk phase separation in the 50 vol% M24P50/dLPS36k blend, which would be consistent with the broad glass transition observed for its DSC curve shown in Figure 5.1. A second possibility is that non Gaussian behavior of the combs is manifested for the longest one in this series. The structure factor derivation assumes Gaussian statistics. The fit is definitely better at 180 °C, which could be consistent with the miscibility improving into the single phase regime with the increase in temperature. However, one problem with the suggestion that the sample may be phase separated at some temperatures measured is that in that case phase decomposition into two phases would most likely have taken place over the time used to measure the sample at several temperatures. Once a sample begins to phase demix its structure factor changes continually with time and the shape diverges from that characteristic of a single phase. The rate of the changes in scattering depends on the viscosity of the blend. The measurements were done beginning at 120 °C and moving up in temperature. If the equilibrium state of the sample had been phase separation for a temperature of, say 160 °C, the phase separated structure of the sample would have been
evolving as instrument adjustments were made. The sample was equilibrated at various
 temperatures and the measurements for multiple samples were made at 120, 140, and
160 °C, which was a process requiring about 5 hours. These considerations argue against
the problem of being phase segregation for at least temperatures above about 140°C.

Figure 5.6 Experimental SANS curves with a fit to the RPA model for the 50 vol% M24P50/dLPS36k blend and 50 vol% linear/linear isotopic blend at 120 °C and 180 °C.

Bulk phase separation was clearly observed for blends containing 50 vol% M15P34
and M15P105, indicated by two distinct glass transitions in their DSC curves shown in
Figure 5.1. Attempts to fit their SANS curves with the RPA model were unsuccessful.
The shapes of SANS curves for blends containing 50 vol% M15P34 or M15P105 are different from that of the two miscible blends containing 50 vol% M24P14 and M24P28, as shown in Figure 5.7. At 120 °C the curve for M24P50 blend was below the curve for M24P28 blend in most range of $q$. However, the intensity for M24P50 blend increased sharply as $q$ decreased and finally surpassed the intensity for M24P28 blend at the lowest values of $q$ measured. The curves for the M15P34 blend and the M15P105 blend, marked by abruptly increasing intensity at low $q$, were distinctly different from curves of blends containing the other combs. The non-RPA shapes of the SANS curves and the DSC characterization for the 50 vol% M15P34 blend and M15P105 blend indicate bulk phase separation in the sample. Therefore, the RPA model for miscible blends could not describe their SANS curves.

Figure 5.7 Experimental (symbol) and calculated (solid line) SANS curves for the linear isotopic blend and blends of 50 vol% comb PS with dLPS36k at 120 °C.
SANS data at low \( q \) region (0.007-0.02 Å\(^{-1}\)) for the five comb/linear blends at 120 °C were examined with the Guinier plot of \( \ln (I) \) vs. \( q^2 \) in Figure 5.8. Experimental SANS curves were well fitted with the RPA model in the Guinier plot for the linear isotopic blend and the blend containing M24P14 or M24P28 as the comb component. It was seen more clearly in the Guinier plot that the calculated SANS curve based on the RPA model for the M24P50/dLPS36k blend deviated from the experimental curve. The RPA model was unable to capture the abrupt change of slope at low \( q \) Guinier region observed for M15P34/dLPS36k and M15P105/dLPS36k blends.

Figure 5.8 Guinier plot of experimental (symbol) and calculated (solid line) SANS curves for the linear isotopic blend and blends of 50 vol% comb PS with dLPS36k at 120 °C.
The temperature dependences of $\chi_{\text{eff}}$ for the miscible blends shown in Figure 5.9 are represented well by the relationship:

$$\chi_{\text{eff}} = \frac{A}{T} + B,$$

(5.7)

where $A$ and $B$ are constants. The values of these constants, as well as the values of statistical segment lengths found from the best fits are summarized in Table 5.1. All the comb blends have $\chi_{\text{eff}}$ values almost an order of magnitude higher than the values seen for linear chain blends with end-branched star chains of similar molecular weights,\textsuperscript{19-21, 247} which is consistent with the theoretical prediction of Fredrickson et al.\textsuperscript{22} The temperature independent, entropic contribution to $\chi_{\text{eff}}$ is also seen to be much more important than the enthalpic contribution in keeping with expectations, and the general magnitude of $\chi_{\text{eff}}$ values observed here is also in line with the value reported for a less well-defined comb blend with six, wider spaced branches.\textsuperscript{19} The variations in $\chi_{\text{eff}}$ with comb architecture are quite strong. The large increase in $\chi_{\text{eff}}$ going from M24P14 to M24P28 is reasonable, but the subsequent decrease in $\chi_{\text{eff}}$ from M24P28 to M24P50 is in doubt. However, it should be noted that SANS curves for the blend containing 50 vol% M24P50 were fitted poorly with the RPA model due to possible bulk phase separation. A simple estimate of the critical value of $\chi$ for each comb blend, according to Flory-Huggins theory for asymmetric linear/linear blends, is also listed in Table 5.1. The fact that the $\chi_{\text{eff}}$ values for the blends containing 50 vol% of M24P14 or M24P28 are less than the $\chi_c$ values for those blends is consistent with the fact that those fits to the RPA are good. The value of $\chi_c$ for the M24P50 blend is close to the experimental values suggesting that blend could be
close to or beyond phase separation, and indeed the fit with the miscible RPA model to
that blend is much less good than are the fits for the other two lower molecular weight
comb blends (figures of merit for fits provided in Appendix C). This is in agreement with
the theory by Fredrickson et al.\textsuperscript{22} as well, which predicted that phase separation should be
readily expected for comb/linear homopolymer blends in practice. It is concluded based
on the results present in this work that the tendency to demixing from its linear analog is
stronger for a densely grafted comb with shorter branch length and larger number of
branches. Both the DSC and SANS results indicate that bulk miscibility in the
comb/linear blends increases in the following order: M15P105 < M15P34 < M24P50 <

Table 5.1 Statistical Segment Length and $\chi_{eff}$ Parameters for Isotopic Blends.

<table>
<thead>
<tr>
<th></th>
<th>$\chi_c \times 10^3$</th>
<th>$a$ (Å)\textsuperscript{b}</th>
<th>$\chi_{eff} = A/T + B$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>120 °C</td>
<td>140 °C</td>
</tr>
<tr>
<td>M24P14</td>
<td>5.92</td>
<td>7.2</td>
<td>7.2</td>
</tr>
<tr>
<td>M24P28</td>
<td>4.50</td>
<td>6.3</td>
<td>6.3</td>
</tr>
<tr>
<td>M24P50</td>
<td>3.60</td>
<td>7.8</td>
<td>7.9</td>
</tr>
<tr>
<td>M15P34</td>
<td>4.92</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>M15P105</td>
<td>1.41</td>
<td>--</td>
<td>--</td>
</tr>
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</table>

\textit{a} $\chi_c = \frac{1}{2} \left( \frac{1}{\sqrt{N_{comb}}} + \frac{1}{\sqrt{N_{linear}}} \right)^2$

\textit{b} Statistical segment length using segment volume = 100 cm\textsuperscript{3}/mol (±0.3 Å).
Figure 5.9 Temperature dependence of interaction parameter for blends of 50vol% comb PS (M24P14 (triangle), M24P28 (square), M24P50(circle)) with dLPS36k derived from the SANS data assuming that the single phase RPA structure factor is appropriate.

Calculations of \( \chi_e \) values with the Gaussian field theory by Fredrickson et al.\textsuperscript{22} were made by Renfeng Hu and Dr. David T. Wu (Department of Chemical Engineering, Colorado School of Mines) for 50 vol% comb/dLPS36k blends. This theory considers that in an athermal blend the correlated composition fluctuations on intermediate length scales lead to an entropic contribution to the excess free energy of mixing. The subscript of \( \chi_e \) denotes the entropic origin of this contribution to the exchange interaction parameter. For the purpose of this approximate comparison the segment length is taken to be 6.2 Å.
for all the polymers, although the experimental values of segment length are larger for the combs. Structure factors of all the polymers used in the calculation are the same ones used in the experimental determination of $\chi_{\text{eff}}$ with SANS. The values of all other molecular parameters (N, M, L and P) and blend parameters ($\Phi_i$) are taken to be those from the experimental determination of $\chi_{\text{eff}}$.

The isotopic contribution to the $\chi_{\text{eff}}$ value at 120 °C was estimated by fitting the data from the linear/linear isotopic blend. The value of $\chi_{\text{eff}}$ for that blend was about $2 \times 10^{-4}$, which was significantly lower than the measured $\chi_{\text{eff}}$ values for the comb/linear blends. This contribution has been subtracted from the $\chi_{\text{eff}}$ values determined by fitting the SANS curves at 120 °C for blends containing combs with $M = 24$ before making the comparison in Figure 5.10 between calculated and experimental $\chi_e$ values. The calculated $\chi_e$ values were of the same order of magnitude as the measured $\chi_e$ values. The theory predicted that the $\chi_e$ values should increase monotonically with the number of branches (P), which was true for the measured $\chi_e$ values as P increased from 14 to 28. However, the measured $\chi_e$ value decreased when P increased from 28 to 50. It should be noted that the measured $\chi_{\text{eff}}$ values for the blend containing 50 vol% M24P50 were inaccurate because its SANS curves were poorly fitted with the RPA model. It is possible that error in those $\chi_{\text{eff}}$ values is substantial.
Figure 5.10 Comparison between $\chi_e$ values (circle) calculated from the theory of Fredrickson et al.\textsuperscript{22} and $\chi_e$ values (square) determined by fitting SANS curves at 120 °C for blends of dLPS36k and comb with $M = 24$.

For the two blends where fitting to the miscible blend structure factor is clearly satisfactory, different values of the statistical segment length are found. Plotting experimental and calculated SANS curves in a log-log scale in Figure 5.11 revealed that the RPA models, which fitted the experimental data at low $q$ reasonably well, did not capture the high-$q$ part of the SANS curves. Since information about statistical segmental length $a$ mostly lies in the SANS data at high $q$, the values of $a$ in Table 5.1 determined
by fitting the SANS curves with RPA models could be inaccurate. One possible explanation for the poor fitting at high $q$ is related with the validity of the assumption of Gaussian statistics for the comb chains. With the extremely dense branching for these comb chains in this case, it is possible that the chain conformation of the backbone or of a branch does not follow Gaussian statistics any more. Thus, it is expected that the RPA model with a comb structure factor taking into account the non-Gaussian behavior of the comb chain will provide an improved fit with the SANS data. More accurate values of $a$ could be extracted from such fits.

Figure 5.11 Log-log plot of experimental (symbol) and calculated (solid line) SANS curves for the linear isotopic blend and blends of 50 vol% comb and dLPS36k at 120 °C.
In summary, the values of $\chi_{\text{eff}}$ for the comb/linear blends are large as compared to $\chi_{\text{eff}}$ values for blends of end branched stars and linear polymers, and therefore phase separation occurs readily. Results from SANS measurements sensitive to the $\chi_{\text{eff}}$ value and DSC measurements sensitive to the presence of phase separated domains are consistent with each other about the compatibility of a blend at temperatures probed in this work. For the blends that are clearly in a single phase state $\chi_{\varepsilon}$ values determined from the SANS data are in reasonable agreement with $\chi_{\varepsilon}$ values calculated from the theory of Fredrickson et al.\textsuperscript{22} without using any adjustable parameters. However, the structure factor assuming Gaussian statistics for the comb component does not fit the SANS data uniformly well even over the modest $q$ range measured here. Deviations at high $q$ region suggest that corrections accounting for non-Gaussian behavior of the comb may be necessary.
CHAPTER VI

SURFACE SEGREGATION OF COMB/LINEAR POLYSTYRENE BLENDS

In this chapter, the surface segregation in blends of unfunctionalized comb and linear chains as measured using NR and STOF-SIMS measurements are discussed first. The unfunctionalized combs discussed here include M24P14, M24P28, M24P50, M15P34 and M15P105. In the second part the surface segregation of three comb polystyrenes with functionalized branch ends (Comb-OH, Comb-COOH and Comb-C₈F₁₇) in blends with linear polystyrenes is discussed.

6.1 Surface segregation of unfunctionalized comb/linear polystyrene blends

NR measurement as a non-invasive technique was performed to study the surface segregation behavior in thin films of comb/dLPS36k blends. That strong enrichment at the surface was present in the thin film of 20 vol% M24P28/dLPS36k blend was indicated by the “beating” pattern in its reflectivity curve shown in Figure 6.1. This beating reflects the presence of a relatively well-defined layer of thickness ca. 50 Å in the sample, while the more narrowly spaced fringes indicate an overall film thickness of
roughly 800 Å estimated by a simple calculation of $2\pi/\Delta q_{\text{max}}$ without fitting, where $\Delta q_{\text{max}}$ is the fringe period at $q >> q_c$.

Figure 6.1 Neutron reflectivity curves of 20 vol% (square), 12 vol% (triangle) and 6 vol% (reverse triangle) M24P28/dLPS36k blends. Neutron reflectivity curve of the unannealed (circle) 20 vol% M24P28/dLPS36k blend is also shown. Solid lines are the fits to the corresponding experimental curves.

More quantitative information about the comb concentration depth profile in the thin film blend was obtained by fitting the reflectivity curve with a 2-layer model for the film structure. Details of the model parameters are shown in Table 6.1. The depth profile for
20 vol% M24P28/dLPS36k in Figure 6.2 shows that the concentration of M24P28 increased monotonically from 0.20 to 0.95 volume fraction as the surface was approached from the bulk, indicating strong surface segregation of combs in the film. It is noteworthy that the estimated decay length of segregation in the thin film blend is 62 Å, which is determined as the depth where the tangent at half maximum of the surface segregation crosses with the line corresponding to bulk comb volume fraction. This value of decay length of segregation is of the order of the size of a M24P28 comb molecule \( (R_h = 54 \text{ Å}) \).

The similarity between the length scale of segregation and size of a comb chain has been predicted by the theory of Wu and Fredrickson.\textsuperscript{175} These theories also predicted that the maximum in the concentration depth profile should occur near the surface.\textsuperscript{175} It was found that this more complicated depth profile shape was not necessary for fitting the NR data measured here and resolving this feature with NR would be challenging for molecules of this size, so whether such a sub-surface maximum is present remains an open question.
Table 6.1 Model parameter values for annealed and unannealed 20 vol% M24P28/dLPS36k blend.

<table>
<thead>
<tr>
<th>Fit parameter</th>
<th>annealed</th>
<th>unannealed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Error in mass balance closure (%)</td>
<td>0.2</td>
<td>1.4</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>3.0</td>
<td>4.0</td>
</tr>
<tr>
<td>$\Phi_{H}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>air</td>
<td>0.95±0.05</td>
<td>0.92±0.05</td>
</tr>
<tr>
<td>bulk</td>
<td>0.16±0.02</td>
<td>0.19±0.02</td>
</tr>
<tr>
<td>substrate</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Decay length (Å)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>air</td>
<td>62±3</td>
<td>52±3</td>
</tr>
<tr>
<td>substrate</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Roughness (Å)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>air</td>
<td>3±1</td>
<td>2±1</td>
</tr>
<tr>
<td>substrate</td>
<td>1±1</td>
<td>2±1</td>
</tr>
<tr>
<td>Film thickness (Å)</td>
<td>798±2</td>
<td>805±2</td>
</tr>
<tr>
<td>Surface excess (Å)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>air</td>
<td>33±3</td>
<td>25±3</td>
</tr>
<tr>
<td>substrate</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

Figure 6.2 Comb concentration depth profiles of annealed 12h at 180 °C (solid) and unannealed (dash) 20 vol% M24P28/dLPS36k blends.
STOF-SIMS measurements confirm the presence of strong surface segregation observed by NR in the comb/linear blends. While NR provides information about the concentration depth profiles in the films from fitting data, STOF-SIMS provides direct information on the chemical composition at the film surface. Figure 6.3 shows the fragmentation spectrum of the 20 vol% M24P28/dLPS36k blend. Fragments of interest are $C_7H_7^+$ ($m/z$ 91) from the hydrogenous comb PS and $C_7D_7^+$ ($m/z$ 98) from the deuterated linear PS. The fact that the intensity for the $C_7H_7^+$ peak ($m/z$ 91) is nearly one order of magnitude higher than that for the $C_7D_7^+$ peak ($m/z$ 98) suggests that the hydrogenous comb PS is highly enriched at the surface in its blend with deuterated 36k linear PS. Calibration to obtain absolute concentrations is very challenging, since adding an internal standard, for example, can affect the surface segregation of the blend being studied and thus change the surface composition. However, the ratio of the peak areas for those two characteristic fragments, $I_{91} / (I_{91} + I_{98})$, is related to the surface concentration of comb PS. (The contributions from other isotopic species are extremely small.) For the 20 vol% M24P28/dLPS36k blend, the value of $I_{91} / (I_{91} + I_{98})$ is 0.96, which is very close to the surface comb concentration of 95 vol% derived by fitting its neutron reflectivity curve. The values of $I_{91} / (I_{91} + I_{98})$ from STOF-SIMS and the surface comb concentrations from NR for all of the comb/linear blends studied here are summarized in Table 6.2 and agree well with each other. Results from both characterization techniques evidence strong surface segregation of the combs in the linear matrix in all cases.
Figure 6.3 STOF-SIMS spectra for (a) pure M24P28; (b) pure dLPS36k; (c) annealed 20vol% M24P28/dLPS36k; (d) unannealed 20vol% M24P28/dLPS36k.
An interesting finding of this study is the limited effect of annealing on the surface segregation of the combs. Comb concentration depth profiles for unannealed and annealed 20 vol% M24P28/dLPS36k blends are compared in Figure 6.2. The profile from the unannealed blend was fitted with a 2-layer model, for which the details are shown in Table 6.1. A very substantial fraction of the surface segregation already occurs during the very short time (several seconds) in spin-casting when sufficient solvent is present for the chains to move. Once most of the solvent is gone, the film vitrifies. With other types of blend films containing branched and linear PS that have been studied, this time is insufficient for substantial surface segregation to take place. Thus, here the thermodynamic driving force for surface enrichment by the comb must be large and the

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Table 6.2 Summary of Surface Segregation in Comb/Linear Blends.

<table>
<thead>
<tr>
<th>Component 1</th>
<th>Component 2</th>
<th>Bulk Fraction (v/v)</th>
<th>Surface Fractions NR (±0.05)</th>
<th>STOF-SIMS (±0.05)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M24P14</td>
<td>dLPS36k</td>
<td>22/78</td>
<td>0.84</td>
<td>0.84</td>
</tr>
<tr>
<td>M24P28</td>
<td>dLPS36k</td>
<td>20/80</td>
<td>0.92</td>
<td>0.90</td>
</tr>
<tr>
<td>M24P28</td>
<td>dLPS36k</td>
<td>20/80</td>
<td>0.95</td>
<td>0.94</td>
</tr>
<tr>
<td>M24P28</td>
<td>dLPS36k</td>
<td>12/88</td>
<td>0.95</td>
<td>0.96</td>
</tr>
<tr>
<td>M24P28</td>
<td>dLPS36k</td>
<td>6/94</td>
<td>0.85</td>
<td>0.85</td>
</tr>
<tr>
<td>M24P50</td>
<td>dLPS36k</td>
<td>21/79</td>
<td>--</td>
<td>0.97</td>
</tr>
<tr>
<td>M15P34</td>
<td>dLPS36k</td>
<td>20/80</td>
<td>--</td>
<td>0.99</td>
</tr>
<tr>
<td>M15P34</td>
<td>dLPS36k</td>
<td>10/90</td>
<td>1.00</td>
<td>0.98</td>
</tr>
<tr>
<td>M15P34</td>
<td>dLPS36k</td>
<td>7/93</td>
<td>0.98</td>
<td>0.98</td>
</tr>
<tr>
<td>M15P105</td>
<td>dLPS36k</td>
<td>20/80</td>
<td>--</td>
<td>1.00</td>
</tr>
<tr>
<td>M15P105</td>
<td>dLPS36k</td>
<td>10/90</td>
<td>--</td>
<td>0.99</td>
</tr>
<tr>
<td>M15P105</td>
<td>dLPS36k</td>
<td>6/94</td>
<td>1.00</td>
<td>0.98</td>
</tr>
</tbody>
</table>

* unannealed blends.
mobility of the combs in the solution as it dries must be high. For the chains to segregate additionally, the film must be heated above the pertinent $T_g$. Annealing at more than 75 °C above $T_g$ for 12 h only increased the surface segregation of the combs slightly, in this case increasing the surface volume fraction of comb from 0.92 to 0.95, as shown in Table 6.2. The rapid surface segregation of combs in these blends makes them attractive for practical applications because it could eliminate the need for a costly annealing process.

The dependence of surface segregation on bulk concentration of the comb PS in the blend was examined by comparing M24P28/dLPS36k blends with comb concentrations of 6, 12 and 20 vol%. Neutron reflectivity curves and the corresponding fits with 3-layer models for the 12 and 6 vol% blends are shown in Figure 6.1. No clear beating patterns were observed in the reflectivity curves of 12 and 6 vol% blends, indicating segregation behaviors different from that of the 20 vol% blend. There proved to be some ambiguity in determining the best fit. The NR curves for the 12 and 6 vol% blends apparently can be fitted with a 3-layer model with either a “rough” or “smooth” surface. Details of these models are shown in Table 6.3. Models with “rough” sample surfaces provide slightly better fits (smaller $\chi^2$ values) to experimental NR data than models with “smooth” sample surfaces do. SLD depth profiles of models for blends with various bulk compositions are compared in Figure 6.4. It is clearly seen that the amount of hydrogenous M24P28 segregated to the surface region of the blend decreases as the bulk composition of M24P28 in the blend decreases. The surface roughness of the sample in a “rough” model
is 13-14 Å for the best fit to the experimental NR curve as shown in Table 6.3, which is a lot larger than the roughness determined for the same sample using AFM. This requires that the broad surface regions of the SLD depth profiles for the “rough” models in Figure 6.4 not be interpreted solely as resulting from roughness. In Figure 6.5, the concentration depth profiles for the 12 and 6 vol% M24P28/dLPS36k blends that have been derived from the SLD depth profiles of the “rough” models show strange shapes. The surface comb volume fraction obtained from the concentration depth profile of the “rough” model is in good agreement with the surface yield fraction measured with STOF-SIMS as shown in Table 6.2. However, the surface comb volume fraction from the “smooth” model is lower than the surface comb fraction from STOF-SIMS measurement. It should be pointed out that determining the exact surface composition is not among the strengths of the NR technique. The strength of NR lies in providing the magnitude of the surface excess and the depth over which the segregation occurs. The values of surface excess for the “rough” and “smooth” models for the same bulk comb composition are similar to each other, as are also the depths over which segregation is seen. A clear increasing trend is observed for surface excess of comb as the bulk comb composition increases from 6 to 20 vol% in Figure 6.6(a). The theory of Wu and Frederickson is a linear response, which anticipates that the surface comb composition will increase linearly with the increase in bulk comb composition. However, linear response is not clearly seen here. This is likely due to the fact that already at 6 vol% bulk composition the response is quite large. The surface comb composition is much above the bulk composition. Even at 6
vol% bulk composition the system is already in the nonlinear response regime. It is possible to reach linear response regime by decreasing bulk comb concentration further below 6 vol%.

Table 6.3 Model parameter values of annealed 12 and 6 vol% M24P28/dLPS36k blends.

<table>
<thead>
<tr>
<th>Fit parameter</th>
<th>12vol% “Rough”</th>
<th>12vol% “Smooth”</th>
<th>6vol% “Rough”</th>
<th>6vol% “Smooth”</th>
</tr>
</thead>
<tbody>
<tr>
<td>Error in mass balance closure (%)</td>
<td>1.0</td>
<td>1.5</td>
<td>1.3</td>
<td>1.2</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>2.9</td>
<td>3.9</td>
<td>3.7</td>
<td>4.2</td>
</tr>
<tr>
<td>$\Phi_{H}$</td>
<td>0.95±0.05</td>
<td>0.80±0.05</td>
<td>0.85±0.05</td>
<td>0.50±0.05</td>
</tr>
<tr>
<td>air</td>
<td>0.09±0.01</td>
<td>0.09±0.01</td>
<td>0.06±0.01</td>
<td>0.06±0.01</td>
</tr>
<tr>
<td>bulk</td>
<td>0.24±0.05</td>
<td>0.13±0.05</td>
<td>0.22±0.05</td>
<td>0.40±0.05</td>
</tr>
<tr>
<td>substrate</td>
<td>52±3</td>
<td>57±3</td>
<td>52±3</td>
<td>54±3</td>
</tr>
<tr>
<td>Decay length (Å)</td>
<td>22±2</td>
<td>44±3</td>
<td>14±2</td>
<td>20±2</td>
</tr>
<tr>
<td>substrate</td>
<td>13±1</td>
<td>3±1</td>
<td>14±1</td>
<td>4±1</td>
</tr>
<tr>
<td>Roughness (Å)</td>
<td>5±1</td>
<td>6±1</td>
<td>5±1</td>
<td>10±1</td>
</tr>
<tr>
<td>air</td>
<td>23±2</td>
<td>26±3</td>
<td>17±2</td>
<td>14±1</td>
</tr>
<tr>
<td>substrate</td>
<td>1±1</td>
<td>1±1</td>
<td>1±1</td>
<td>2±1</td>
</tr>
<tr>
<td>Film thickness (Å)</td>
<td>783±2</td>
<td>783±2</td>
<td>838±2</td>
<td>836±2</td>
</tr>
<tr>
<td>Surface excess (Å)</td>
<td>1±1</td>
<td>1±1</td>
<td>1±1</td>
<td>2±1</td>
</tr>
<tr>
<td>air</td>
<td>1±1</td>
<td>1±1</td>
<td>1±1</td>
<td>2±1</td>
</tr>
<tr>
<td>substrate</td>
<td>20 vol%</td>
<td>12 vol%</td>
<td>6 vol%</td>
<td></td>
</tr>
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</table>
Figure 6.4 SLD depth profiles of models with the best fits to NR data for 20 (red), 12 (blue) and 6 (black) vol% M24P28/dLPS36k blends. Solid lines represent for depth profiles of models with “rough” surfaces, and dotted lines represent for depth profiles of models with “smooth” surfaces.

Figure 6.5 Comb concentration depth profiles of models with the best fits to NR data for 20 (red), 12 (blue) and 6 (black) vol% M24P28/dLPS36k blends. Solid lines represent for depth profiles of models with “rough” surfaces, and dotted lines represent for depth profiles of models with “smooth” surfaces.

The variation in surface composition with bulk composition is shown in Figure 6.6(b). Increasing the bulk composition of M24P28 from 6 to 12 vol% has a clear impact on its
surface concentration, regardless of the model used to fit the NR data, while an additional increase to 20 vol% in the bulk had little further impact according to the SIMS results and NR fitting with a “rough” model. This trend is obvious when directly comparing the STOF-SIMS spectra of these blends in Figure 6.7.

Figure 6.6 Dependence of surface segregation on bulk composition for the M24P28/dLPS36k blend. (a) Surface excess vs. bulk comb volume fraction; (b) Surface comb volume fraction (NR) vs. bulk comb volume fraction (NR, rough model, smooth model, STOF-SIMS).
comb volume fraction vs. bulk comb volume fraction.

Figure 6.7 STOF-SIMS spectra for (a) 20 vol%, (b) 12 vol% and (c) 6 vol% M24P28/dLPS36k blend film.

Strong surface segregation of the comb component is observed in the other blends studied as well. Their neutron reflectivity curves and the corresponding fits are shown in Figure 6.8. Parameter values for the models are shown in Table 6.4. Surface comb fractions of 0.85 or greater are observed for all of the comb/linear blends listed in Table 6.2.
Figure 6.8 Neutron reflectivity curves of comb blends as marked in the legend. Solid curves are the fits to the corresponding experimental data.

Table 6.4 Model parameter values for annealed comb blends.

<table>
<thead>
<tr>
<th>Fit parameter</th>
<th>22vol% M24P14</th>
<th>10vol% M15P34</th>
<th>7vol% M15P34</th>
<th>6vol% M15P105</th>
</tr>
</thead>
<tbody>
<tr>
<td>Error in mass balance closure (%)</td>
<td>1.6</td>
<td>0.6</td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>4.5</td>
<td>4.0</td>
<td>2.7</td>
<td>3.2</td>
</tr>
<tr>
<td>$\varphi_H$</td>
<td>air</td>
<td>0.84±0.05</td>
<td>0.99±0.05</td>
<td>0.98±0.05</td>
</tr>
<tr>
<td></td>
<td>bulk</td>
<td>0.21±0.02</td>
<td>0.07±0.01</td>
<td>0.05±0.01</td>
</tr>
<tr>
<td></td>
<td>substrate</td>
<td>--</td>
<td>0.14±0.05</td>
<td>0.35±0.05</td>
</tr>
<tr>
<td>Decay length (Å)</td>
<td>air</td>
<td>54±3</td>
<td>40±3</td>
<td>46±3</td>
</tr>
<tr>
<td></td>
<td>substrate</td>
<td>--</td>
<td>33±1</td>
<td>24±2</td>
</tr>
<tr>
<td>Roughness (Å)</td>
<td>air</td>
<td>4±1</td>
<td>2±1</td>
<td>3±1</td>
</tr>
<tr>
<td></td>
<td>substrate</td>
<td>6±1</td>
<td>2±1</td>
<td>3±1</td>
</tr>
<tr>
<td>Film thickness (Å)</td>
<td>air</td>
<td>813±2</td>
<td>782±2</td>
<td>841±2</td>
</tr>
<tr>
<td>Surface excess (Å)</td>
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<td>25±3</td>
<td>28±3</td>
<td>28±3</td>
</tr>
<tr>
<td></td>
<td>substrate</td>
<td>--</td>
<td>1±1</td>
<td>2±1</td>
</tr>
</tbody>
</table>
Altering architectural details of the comb alters details of the surface segregation behavior, as shown in Figure 6.9. When the number of branches is increased from 14 to 28, keeping branch length constant at 24 (22 vol% M24P14/dLPS36k vs. 20 vol% M24P28/dLPS36k) the surface concentration of comb PS increases from 0.85 to 0.96. Also the length scale of the surface segregation increases. For M24P14 the length scale is 54±3 Å, and for M24P28 it is 62±3 Å.

Combs with shorter branch length exhibit stronger tendency to segregate to the surface and their bulk miscibilities with linear chains also decrease. The closest comparison for the effect of branch length is between M24P28 (M = 24) and M15P34 (M = 15). The comb with the shorter branch length has a few more arms (34 vs. 28), but somewhat lower molecular weight (56k vs. 69k). Despite the lower molecular weight, DSC measurement (Figure 5.2) shows that at a composition of 20 vol% comb, the blend with the shorter branch comb is phase separated. NR data from a blend of 20 vol% M15P34 cannot be fit well using a model for a miscible blend with surface enrichment and so the film is phase separated as well. STOF-SIMS measurement of the M15P34 blend film shows that its surface is fully covered by the comb. Lowering the bulk volume fraction of M15P34 in the blend from 20 vol % to 10 vol % leads to a DSC trace indicating bulk miscibility with 36k linear PS at this 10 vol% composition (Figure 5.2). The concentration depth profile for the 10 vol% M15P34 film blend from NR reveals a top layer consisting of pure hydrogenous M15P34 (Figure 6.9) and STOF-SIMS measurement confirms that the surface concentration of M15P34 is close to 100 vol%.
The flat shape of the composition profile near the surface and its sharp interface with the bulk suggest that this system may lie very close to the point for phase separation in the film, although the blend of this composition is miscible in the bulk according to the DSC measurement. When the film composition is decreased modestly to 7 vol%, the flat region at the surface in the composition depth profile disappears and the shape expected for surface enrichment in a single phase is recaptured. The surface concentration of M15P34 in the 7 vol% blend is also slightly lower than that in the 10 vol% blend, in agreement with SIMS measurements.

When the number of branches in the shorter branch comb is increased substantially from 34 to 105, stronger surface segregation of the comb is observed. With 6 vol% of M15P105 in the blend, the surface is once again enriched with nearly 100 vol% comb. Also the gradient between the surface enrichment layer and the bulk of the film becomes sharper again and the shape of the profile near surface is closer to being flat. The fact that a relatively small amount of comb is necessary to achieve a comb-rich surface layer provides an important advantage for their application as additives to modify surface properties without altering bulk properties.
The width of the interface between the comb-rich surface layer and the bulk is dependent on the comb architecture. The miscible blend films of longer branch combs have broader interfaces than do the blends containing the shorter branch combs. The slope of the interface in the case of the shorter branch combs is 2.2 times larger than that of the interface for the longer branch combs. For immiscible blend interfaces and chains of infinite size, Helfand\textsuperscript{146} finds the interface width to vary as $1/\sqrt{\chi}$. Consideration of the finite chain sizes modifies Helfand’s equation for interface width,\textsuperscript{249} but the scaling with $\chi$ is still similar. This suggests the value of $\chi$ for the blends with shorter branch combs may be about a factor of 4.8 larger than for the blends with longer branch combs.
Based on the $\chi$ value of miscible blend of the longer branch comb and dLPS36k available from fitting SANS data (Table 5.1), the $\chi$ value of blend of the shorter branch comb and dLPS36k is estimated to be of the order of $10^{-2}$, which is much larger than the critical value of $\chi$ estimated for phase separation to occur near a composition of 50 vol% ($\chi_c = 4.92 \times 10^{-3}$ for M15P34 and $\chi_c = 1.41 \times 10^{-3}$ for M15P105). For blends of much lower comb composition the $\chi$ value can be much larger than this without phase separation. For blends in which the length of comb branches is the same, but one is closer or farther from immiscibility, the interface width also varies. The interfacial width in the M15P34/dLPS36k blends increases as the blend moves farther from immiscibility by decreasing the comb concentration from 10 to 7vol%.

The concentration depth profile for the 20vol% M24P28/dLPS36k blend measured with NR may be compared with that calculated using the self-consistent field theory by Wu and Fredrickson. When only entropic surface potentials for ends and joints are taken into account, and reasonable values for the potentials for chain ends ($U_{\text{end}} = -0.31$ kT) and branch points ($U_{\text{joint}} = 0.19$ kT) are taken into account, the surface segregation predicted is significantly weaker than that measured with NR, as shown in Figure 6.10. A maximum in comb concentration is expected beneath the surface at a small depth corresponding to the size of the branches. The existence of such a maximum cannot be substantiated or disproved by the NR data at this level of resolution. Insisting that the experimental depth profile have a maximum below the surface substantially complicates the regression of the data (adds more fitting parameters), without improving the quality of
the fit and therefore we show the fitting result with the simpler depth profile shape.

The predicted length scale of surface segregation appears to be consistent with the experimental results. We take the distance from the surface to a point at which a tangent to the composition profile intersects a horizontal line of constant composition equal to that of the bulk as the length scale of surface segregation. For the M24P28 blend this length scale from NR is 62Å. With the parameter $a$ having a value of 6.2 Å the length scale of segregation from the calculation is also about 54 Å.

In order for the theory to properly capture the strength of the surface segregation, however, a more negative surface potential for chain ends ($U_{\text{end}} = -1.62 \, kT$) has to be accounted for, which may be due to an enthalpic contribution from the chemistry of the chain ends. Close examination of the chemical structures of the comb and linear PSs reveals a small chemical difference due to the sec-butyl group at the end of each branch and at one end of the linear chain. Although the surface energy difference between one styrene repeating unit and one sec-butyl group is very small, it may be amplified by the large number of branches ($P$) in the comb. This stronger surface attraction for ends may also indicate that the actual entropic preference of ends at the surface is larger than the prediction of the theory. Agreement between the calculated and measured depth profiles is greatly improved by taking the stronger surface attraction for ends ($U_{\text{end}} = -1.62 \, kT$) into account, while keeping the potential for the branch points ($U_{\text{joint}} = 0.19 \, kT$) the same. The experimental composition at the surface can be matched, the experimental surface excess (area under the curve) can be closely approximated, and the peak in the theoretical
depth profile near the surface disappears after the above modification.

Figure 6.10 Concentration depth profiles of the 20vol% M24P28/dLPS36k blend from NR measurement (black squares), calculations with (red curve) and without (blue curve) enthalpic surface attraction for ends ($U_{\text{end}}$). $\Delta\Phi$ is the difference between comb concentration at depth $z$ and bulk comb concentration. $z/a$ is depth $z$ normalized by segmental length $a$.

6.2 Surface segregation of functionalized comb/linear polystyrene blends

The branching effect and chain end chemistry effect on surface segregation have been studied simultaneously by blending branch end-functionalized comb polystyrenes with linear polystyrenes. Three branch end-functionalized combs, for which the synthesis was described in Section 4.2, with hydroxyl (Comb-OH), carboxyl (Comb-COOH) and
fluoroalkyl (Comb-C$_8$F$_{17}$) groups respectively, were selected for this study. A 25% portion of the branch ends in each of the three comb molecules was functionalized with the corresponding groups, and the rest of the branch ends were sec-butyl groups. The surface energies of end groups studied here may be estimated from the values of surface tensions of their analog compounds, which are 27.6±0.1 mN/m for γ(CH$_3$COOH), 22.4±0.1 mN/m for γ(CH$_3$CH$_2$OH), 18.1±0.1 mN/m for γ(CH$_3$CH$_2$CH(CH$_3$)CH$_2$CH$_3$), and 13.7±0.1 mN/m for γ(n-C$_8$F$_{18}$) at 20°C. Correspondingly the surface energies of the end groups studied here increase in this order: γ(C$_8$F$_{17}$) < γ(sec-butyl) < γ(OH) < γ(COOH). Architecture parameters for all three branch end-functionalized combs are the same with M = 22, L = 1 and P = 32 (close to the structure of M24P28 unfunctionalized comb) since they were prepared from the same precursor Comb-Vinyl. The surface segregation in blends containing 20 vol% of one of the three combs (Comb-OH, Comb-COOH or Comb-C$_8$F$_{17}$) and 80 vol% of dLPS36k was characterized by STOF-SIMS and contact angle measurements.

STOF-SIMS results for three functionalized comb/linear blends, shown in Figure 6.11, show strong surface segregation of the functionalized combs. The values of $I_{91}/(I_{91} + I_{98})$ for the three blends are 0.99 (Comb-C$_8$F$_{17}$), 0.91 (Comb-OH) and 0.98 (Comb-COOH) respectively. Comb-C$_8$F$_{17}$ almost completely covers the surface as expected, because its surface segregation is favored by both its comb architecture and the low surface energy C$_8$F$_{17}$ groups at its chain ends. The surface of a blend containing Comb-COOH or Comb-OH is also enriched by combs, despite the fact that -COOH or -OH groups of high
surface energy are attached to the combs. The sec-butyl groups at the rest 75% branch chain ends complicate the comparison between the branching effect and chain end chemistry effect on surface segregation of combs. According to the analysis in the previous section, enthalpic surface attraction for sec-butyl end groups may provide the driving force for surface segregation of unfunctionalized combs. As a result, the surface segregation of functionalized combs cannot be simply interpreted as the result of the branching effect prevailing over the chain end chemistry effect. The surface segregation of functionalized combs may also be a combining effect on surface segregation of the two different chain end chemistries at each comb molecule. Although the surface energy is higher for COOH groups than for OH groups, the surface concentration of Comb-COOH is higher than that of Comb-OH, as indicated by the comparison of their values of $I_{91} / (I_{91} + I_{98})$. This result could not be simply explained by the branching effect and chain end chemistry effect offsetting each other.
At first we expected the surface segregation of combs with COOH, OH and C$_8$F$_{17}$ groups at branch ends might cause changes in the macroscopically observable surface properties. Contact angles with water were thus measured for the functionalized comb/linear blends. As seen in Figure 6.12, only the blend with the Comb-C$_8$F$_{17}$ shows a contact angle that differs significantly from that of the blend with the unfunctionalized comb M24P28. The contact angle of the 20 vol% M24P28/dLPS36k blend is measured to be 86±2°, which is consistent with values of 86-88° reported for films of pure linear
The contact angle of 20 vol% Comb-$C_8F_{17}$/dLPS36k blend increases the most, up to 95±2°, which is anticipated since the higher F content leads to higher hydrophobicity and the fluorinated groups are preferred at the surface. The contact angles of the blends containing 20 vol% Comb-COOH and Comb-OH may be somewhat higher than that of the blend with unfunctionalized comb, though the differences are within the experimental uncertainties, even though the combs with hydrophilic COOH and OH groups at branch ends are enriched at the surface according to the STOF-SIMS results. To explain this seemingly contradictory surface segregation and contact angle results, we propose that the low surface energy $C_8F_{17}$ groups are directly exposed to air in the Comb-$C_8F_{17}$/dLPS36k blend, while the high surface energy COOH and OH groups are buried underneath the air/polymer surface in the Comb-COOH/dLPS36k and Comb-OH/dLPS36k blends, as illustrated in Figure 6.13. The increasing contact angles of blends containing Comb-COOH and Comb-OH may be explained by considering exactly where the functional groups reside. It should be noted that the percentages of chain segments containing functionalities in all the three branch end-functionalized combs were very small (<1 wt%). The chain end chemistry effect on macroscopic surface properties such as contact angles is expected to become stronger with higher concentration of functional groups present in the blend, either by increasing the volume fraction of functionalized combs, or by increasing the degree of functionalization per comb.
Figure 6.12 Contact angles for 20 vol% blends with dLPS36k containing (a) M24P28; (b) Comb-C$_8$F$_{17}$; (c) Comb-OH; (d) Comb-COOH.
Figure 6.13 Schematic illustration of the explanation for the seemingly contradictory surface segregation and contact angle results. For COOH and OH the functionalities are “buried” near, but underneath the surface, while for $C_8F_{17}$ the functionalities reside at the surface.
CHAPTER VII

SURFACE DYNAMICS OF COMB POLYSTYRENE THIN FILMS

Combs studied in this work exhibit not only unique surface segregation properties when blended with linear polymers as discussed in Chapter VI, but also interesting surface dynamic behaviors that are present in this chapter. Before starting to study the more complicated comb/linear blend system, we first investigate the surface fluctuation dynamics of thin films consisting of pure comb polymers.

7.1 Surface fluctuations and HCT theory

The surface fluctuations were characterized using the normalized intensity-intensity autocorrelation of the coherent surface scattering. The intensity autocorrelation function, $g_2(q||, t)$, is given by $g_2(q||, t) = \langle I(q||, t')I(q||, t + t) \rangle / \langle I(q||, t') \rangle^2$, where $I(q||, t')$ is the scattering intensity for in-plane wave vector $q||$ at time $t'$ and $t$ is the time delay. Kim\textsuperscript{18} et al. found that a single exponential decay describes the intensity autocorrelation for melts of linear PS at temperatures not too close to $T_{g,\text{bulk}}$. Plots of $g_2$ functions derived from XPCS measurements for a film of M24P50 comb polystyrene at 120 °C are shown for four values of $q||$ in Figure 7.1. The solid curves are fits corresponding to $g_2 = 1 +$
\[ \beta \exp(-2t/\tau), \] where \( \beta \) is the speckle contrast and \( \tau = \tau(q) \) is the relaxation time for equilibrium surface height fluctuations. Such single exponential functions fit the data from the comb polystyrene melts well.

Figure 7.1 Intensity-intensity autocorrelation functions obtained at four values of \( q \) for the M24P50 comb polystyrene at 120 °C. The solid curves are fits to the functional form \( g_2 = 1 + \beta \exp(-2t/\tau) \). The relaxation time, \( \tau \), at each value of \( q \) is shown in the legend.

The variations of the relaxation time with temperature and \( q \) for the M24P50 comb polystyrene film are summarized in Figure 7.2(a). Relaxation over larger length-scales (smaller \( q \)) is slower. As temperature increases, relaxation time decreases. Relaxation time decreases with increasing film thickness as well, as shown in Figure 7.2 (b). Kim and coworkers\(^{18} \) have shown that for linear polystyrene films the dependence of \( \tau \) on \( q \) and thickness \( h \) can be represented well by the expression derived by Jäckel\(^{206} \) for the HCT applied under a no-slip boundary condition at the substrate surface:
where $\eta$ is the zero shear viscosity of the bulk melt and $\gamma$ the surface tension. Figure 7.2 shows that the data from the film of M24P50 comb polystyrenes are described reasonably well by the HCT when the ratio of $\eta/\gamma$ is allowed to vary as a fit parameter. In Table 7.1 the values of $\eta/\gamma$ giving the best fits to the data are compared with the values calculated from values of $\eta$ known from rheometry measurements of bulk samples and values of $\gamma$ from linear analogs. We know that the value of $\gamma$ is slightly different for comb polymers, but on the log-log plots for which the key comparisons are being made here these errors are small. The best fit value of $\eta/\gamma$ generally is close to the corresponding bulk value based on rheometry and similar to the values determined for other film thicknesses, with the rheometry value being slightly higher for the case of the lowest temperature investigated.
Figure 7.2 (a) Temperature and $q_{\parallel}$ dependence of relaxation time for the M24P50 comb polystyrene film with thickness of 82 nm. (b) Thickness and $q_{\parallel}$ dependence of relaxation time for the M24P50 comb polystyrene film at 125 °C. The solid curves represent least-squares fits to the HCT expression, eq. (7.1).
Table 7.1 Values of $\eta/\gamma$ (s/nm) for M24P50 comb PS films from fits to eq. (7.1).

<table>
<thead>
<tr>
<th>$T \degree C$</th>
<th>Nominal Layer Thickness, nm</th>
<th>$55^b$</th>
<th>$82^b$</th>
<th>$176^b$</th>
<th>Bulk$^c$</th>
</tr>
</thead>
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<tr>
<td>115</td>
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<td>0.019</td>
<td>---</td>
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<tr>
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<td>0.00061</td>
<td>0.00052</td>
<td></td>
</tr>
<tr>
<td>145</td>
<td>0.00013</td>
<td>0.00012</td>
<td>---$^d$</td>
<td>0.00013</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ The uncertainty of $\eta/\gamma$ derived from XPCS is about $\pm$ 15%.

$^b$ Exact thickness at each temperature given in Table S2.

$^c$ Values derived using bulk viscosity measured by rheometry and surface tension values calculated using interpolation from data in ref. 19 and 20: $\gamma = 41.5 - 0.068t$ with $t$ in $\degree C$.

$^d$ The relaxation time was below 0.1 s, which was below the measurement limit.

Eq. (7.1) predicts thickness independence for a plot of $\tau/h$ versus $q_{\parallel}h$, a dimensionless scattering vector. Data collected from films of various thicknesses should collapse to a single master curve when plotted this way, if the assumptions of the theory hold. At the same temperature plots of $\tau/h$ versus $q_{\parallel}h$ for samples with various thicknesses collapse reasonably well to form a single curve, as shown in Figure 7.3, which confirms the universal scaling of relaxation time with thickness predicted by eq. (7.1). In fact, we have been able to achieve reasonably good fits to the $\tau/h$ versus $q_{\parallel}h$ data using the HCT for all of the comb polystyrenes studied here. It should be noted that the samples with nominal thicknesses of 41, 84 and 176 nm were measured during a different beam time than were the samples with thicknesses of 55 and 82 nm. The degree to which the data points for the 82 and 84 nm films agree with each other in Figure 7.3 demonstrates the reproducibility.
of the XPCS results. The values of $\tau/h$ for the film with thickness of 41 nm consistently lie above the average of the data from the other film thicknesses. We conjecture that 41 nm is close to a threshold value of thickness below which the confinement effect appears.

“Bulk” values of $\eta/\gamma$ (Table 7.1) were derived from bulk viscosities measured by rheometry and curves of $\tau/h$ versus $q/h$ were simulated using the “bulk” values of $\eta/\gamma$ based on eq. (7.1) and plotted in Figure 7.3 as well. The data points measured by XPCS fall slightly below the simulated curve at 115 °C, but at higher temperatures the simulations assuming the film viscosity equals the bulk viscosity match the experimental data reasonably well. The comparison between experimental results from XPCS and results from bulk rheology measurements is discussed in more detail in the next section.

Figure 7.3 Plot of $\tau/h$ versus $q/h$ for M24P50 comb polystyrene films with thicknesses 41, 55, 82, 84 and 176 nm at 115, 125, 135 and 145 °C. The curves are those predicted based on the HCT expression of eq. (7.1) for a film of viscous liquid with viscosity and surface tension equal to that of the bulk M24P50 polymer.
7.2 Comparison between XPCS film and bulk viscosity

Film viscosity can be derived from the value of the fitting parameter $\eta/\gamma$ if the surface tension at each temperature is known. Accurate measurement of surface tension for polymer melts with high molecular weight, especially for polystyrene, which is comparatively stiff, is difficult\textsuperscript{253}. Therefore, since the differences in surface tension values among polymers with various architectures are small for high molecular weight,\textsuperscript{182} for the present level of analysis it suffices to take the surface tensions of the comb polystyrenes to be approximately those of the linear analogs with similar molecular weight, for which surface tension data are available in the literature.\textsuperscript{254} Specifically we used the expression $\gamma = 41.5 - 0.068t$ with $t$ in °C to calculate the surface tension of the M24P50 comb polystyrene at each temperature. It has been demonstrated that the rate of change in $\gamma$ with temperature (-0.068 mN/m °C) varies little with the architecture of the polystyrene chain.\textsuperscript{182} For each of the other combs a comparable expression was found by considering the behavior of a linear chain with the same overall molecular weight. Figure 7.4 compares the temperature variation of bulk zero-shear viscosity with that of the XPCS-derived viscosity for the corresponding film. The film viscosities derived using the HCT and the bulk viscosities agree reasonably well, though there are some small distinctions.

The M24P14 chain looks the most like a end-branched star and for this architecture the viscosities derived from XPCS are above those from bulk rheometry, which is the same trend seen for end-branched stars,\textsuperscript{25} but with the effect here being much smaller than that
seen for end-branched stars of the same overall molecular weight. The data for 6star are shown for comparison. The differences between the XPCS-derived and bulk viscosities are smaller for any comb than for the 6star, though we note that the data here do not extend as close to $T_{g,bulk}$ as do the data for the end-branched chains in ref. 203. For the M24P50 comb, which looks more like an impenetrable bottle brush, the viscosities from bulk rheometry are essentially the same as those from XPCS. The similarity of the rheometry and XPCS-derived values provides support for the contention that the HCT is satisfactory for describing the surface dynamics of comb polystyrenes melts and that its assumption of a uniform viscosity through the depth of the film is sufficient for a good description of the films studied here. A key question of this contribution is why the HCT approach is sufficient for linear chains, cyclic chains, and these extremely highly branched chains when one is not able to predict the XPCS-derived film viscosities for melt films of less highly branched chains.

We conjecture that even though the chains with which we have worked are considered unentangled as regards their bulk dynamics, the manner in which neighboring chains can interpenetrate and therefore move past one another nonetheless influences the surface dynamics. The linear chains and cyclics move very readily past one another. Likewise, these very highly branched chains are so compact that they do not interpenetrate much and therefore they also move past one another readily. In the case of less densely branched chains, on the other hand, the branches of neighboring chains can interpenetrate
readily and increase the difficulty of moving past one another near an interface. This
effect appears to manifest itself more strongly when closer to $T_{g_{\text{bulk}}}$. 

When we consider the data for the combs with shorter branches (M=15) the overall
picture of the behavior of these densely branched chains becomes more complex. First,
for these shorter branch combs, deviations between the film and bulk viscosities are
larger for the longer comb, not the shorter comb. Secondly, the deviation increases with
temperature rather than decreasing with temperature as is the case with less densely
branched star-like chains. We note, though, that even at the highest temperature for the
longer comb the discrepancy is only about a factor of two, which is small compared to
the discrepancies seen for the less densely branched chains. For the case of M15P34 the
film and bulk viscosities are quite close, with a deviation just larger than the experimental
uncertainties observed at the highest temperature for which data were collected. For the
longer M15P105 comb, there is a clear deviation at every temperature and the increase in
the deviation with temperature is quite clear. We suggest that the shorter M15P34 comb
shows little deviation because the arms are so short that the chain still behaves much like
a linear chain, not at all like a star. We conjecture that the larger deviations for the longer
M15P105 comb result from the fact that the overall length is sufficiently large that the
melt is nearer entanglement than is the case for any of the combs with M= 24. That is, a
different mechanism, entanglement of the chain as a whole (as opposed to
interpenetration of side chains) is beginning to play a role. Nonetheless, that a
discrepancy could both increase with temperature for some architectures and decrease
with temperature for others suggests that the interplay between chain conformation, which is temperature sensitive, and the way in which the chains move past one another in the film may be quite complex, leading to various relationships between the bulk viscosity and viscosity in the thin film melt.

Figure 7.4 Comparison of film viscosities derived from XPCS data (filled symbols) for 80 nm thick films with bulk viscosities measured by rheometry (open symbols) as a function of temperature for 6star (circles) and combs: (a) M24P14 (triangles), M24P28 (stars) and M24P50 (squares); (b) M15P34 (triangles) and M15P105 (stars).
7.3 Effect of architecture on surface fluctuation

The impact of long-chain branching on bulk viscosity can be remarkable, with the viscosity of a melt of an unentangled comb chain being less than that of a melt of an unentangled linear chain with much lower molecular weight. This is due to the more compact nature of the comb chain and the fact that the bulk viscosity is dictated by the ease of movement of the chain as a whole through the surroundings, which can be viewed as a continuum. The XPCS results for the comb PS melts confirm that the surface dynamics can similarly be strongly impacted by long-chain branching in this extreme of high density branching. To illustrate this point we compare in Figure 7.5 the normalized relaxation times of linear PS chains of molecular weight 14,000 g/mol, for which $T_{g,\text{bulk}} = 93^\circ\text{C}$, and those of a melt film of M24P50 ($M_n = 130,000$ g/mol), for which $T_{g,\text{bulk}} = 90^\circ\text{C}$. Despite this large difference in molecular weights the relaxation times for the two types of chains are nearly the same at 130 and 140°C, so for a chain of given molecular weight, the surface fluctuations of the comb melt are much faster. At the lowest temperature probed, which is ca. 30°C from the $T_{g,\text{bulk}}$ for both chains, the surface fluctuations of the linear chain melt are noticeably slower, indicating that the surface fluctuations for the two types of chains have different temperature dependences.
Figure 7.5 Comparison of surface dynamics for films of M24P50 comb PS ($M_n = 130,000$ g/mol) and linear PS ($M_n = 14,000$ g/mol) at 120, 130 and 140 °C, measured by XPCS. The curves represent least-squares fits of data for the M24P50 comb polystyrene to the HCT.

It has been shown that for linear and cyclic chains of molecular weight of 14k and below, the variations of thickness normalized surface relaxation time, $\tau/h$, with temperature collapse to a single curve when differences in $T_{g,\text{bulk}}$, among the chains are accounted for by plotting as a function of $T-T_{g,\text{bulk}}$. That is, segmental mobility seems to be playing a very important role in determining surface fluctuations in those cases. A similar apparent collapse to a universal behavior has been seen for some branched chains, such as 6star, as well. In contrast to the behaviors seen for both the cyclics and end-branched chains the dependence of $\tau/h$ on $T-T_{g,\text{bulk}}$ appears to be distinct for each comb studied here.
Figure 7.6 addresses the question of whether the surface fluctuation behaviors for these different combs collapse to some kind of universal behavior if variations in \( T_{g,bulk} \) are taken into account. Data for \( \tau/h \) for both series of combs are shown as a function of \( T-T_{g,bulk} \). The surface fluctuation dynamics for the various combs are distinct, even though, for example, the \( T_{g,bulk} \) values for the M24P14 and M24P28 combs are the same within experimental uncertainty. The normalized relaxation times do not collapse to a universal function of \( T-T_{g,bulk} \) for either series of combs. We note as well, three other features of the data. First, the variation of \( \tau/h \) with overall molecular weight in the series of 3 \( M=24 \) combs is not monotonic at any value of relative temperature and the order of the three changes with \( T-T_{g,bulk} \). The surface of the melt of comb of intermediate length is the slowest at all values of \( T-T_{g,bulk} \). The surface of the melt of the longest comb is fastest at the lowest value of \( T-T_{g,bulk} \) and intermediate at the highest \( T-T_{g,bulk} \). Secondly, the temperature dependence for the most star-like comb, M24P14 is nearly the same as that of the 6 arm star. Thirdly, the shapes of the temperature dependences of the longer combs are qualitatively different from those of the shorter combs, the linears and the 6star. For example, the curve for the M24P50 crosses over that for the M24P14. Likewise the curve for M15P105 is coincident with the curve for M15P34 at lower \( T-T_{g,bulk} \), but deviates above it as \( T-T_{g,bulk} \) increases. Overall, the variation in temperature dependence with comb architecture seems very complex and we surmise from this limited comparison that the details of the branched architecture still play a role in determining the surface fluctuation dynamics, even in the limit of quite densely branched chains.
Figure 7.6 Comparison of surface dynamics at constant $q/h = 0.5$ for films of molecules with different architectures: end-branched star (6star), linear (LPS14k and LPS37k) and comb. Combs in the plots are (a) M24P14, M24P28 and M24P50; (b) M15P34 and M15P105.

Plotting the data in the form of an Angell plot as shown in Figure 7.7, in which $T_{g,bulk}$ is assumed to coincide with a viscosity of $10^{12}$ Pa·s. allows us to consider, in addition, the effect of chain architecture on fragility under confinement. As has been pointed out in ref. 203, the fragilities of the melt films of the branched chains having various star related
architectures are lower than the fragilities of the corresponding bulk melts, with the 6-end film melt being the strongest. In contrast, on a plot of this resolution, the fragilities of most of the film melts of the comb molecules can hardly be distinguished from those of the corresponding bulk melts. Only the fragilities of the M15P105 seem distinguishable. All of the comb materials are somewhat less fragile than the linear 37k PS.

Figure 7.7 Zero shear viscosities of combs compared to 6star from Ref. 203 and a 37k linear analog as a function of $T_g/bulk/T$ compared with values of $\eta_{film}$ from XPCS.

In this work the surface dynamics of melt films of comb polystyrenes with extremely high branching density have been investigated for the first time. For these particular
comb polymers, which did not show entangled chain dynamics in conventional bulk chain dynamics measurements, the films have surface fluctuations remarkably faster than those of films of linear chains of the same molecular weight. To our surprise, despite their highly branched structure, the surface height fluctuations of the comb polystyrene melts can be reasonably well described by the hydrodynamic continuum theory known to be appropriate for surface dynamics of linear and cyclic polystyrenes.\textsuperscript{18,24} The viscosities of the comb PS melt films derived from the XPCS measurement assuming the validity of the HCT match well with bulk viscosities measured by rheometry for three of the combs, while deviating somewhat for the other two. The largest deviation is seen for the comb (M15P105) that has shorter arms and is so long that its bulk rheology behavior appears to be close to that of an entangled melt. For this comb the deviation also grows with temperature, in contrast to the behavior seen for less highly branched chains.\textsuperscript{25} As with linear chains, if a surface layer of different mobility exists,\textsuperscript{212} its presence is not manifested in the dynamics of the surface fluctuations for these film thicknesses, since the surface fluctuations result from hydrodynamic flow in the entire film. Comparison of the dynamics of five comb polystyrenes with architectures lying along the continuum between star-like and bottlebrush-like chains demonstrates that while changes in $T_{g,\text{bulk}}$ with architecture play a role in determining the surface dynamics, those dynamics are also affected by details of the nonlinear architecture in a manner not yet fully elucidated.
CHAPTER VIII

CONCLUSION

This research leads to important conclusions in three topics related with the synthesis and properties of a class of highly branched comb polymers. There are two conclusions from the synthesis work. The first conclusion is that the successful synthesis of a series of well-defined highly branched comb polystyrenes with precise control of architecture details by living anionic polymerization of macromonomers provides unique possibilities for the incisive study of long-chain comb branching on bulk thermodynamics of blends. The backbone, branches and branch points of each of these combs all consist of styrene repeat units. The sec-butyl group at each branch end is only slightly different from a styrene repeat unit in terms of surface energy. This feature of the combs synthesized in this work is essential because it further reduces the chemical differences between the comb and linear components in blends and allows one to just focus on the effect of long-chain branching in the thermodynamics studies. A second conclusion from the synthesis work is that a new, general method for the efficient synthesis of well-defined, comb polystyrenes with controlled, variable amounts and types of branch end
functionalities (C₈F₁₇, OH and COOH) has been demonstrated by combining living anionic polymerization and thiol-ene “click” chemistry.

The second group of major conclusions from this work has to do with thermodynamics of comb/linear blends. Results from DSC and SANS measurements show that architecture details of the comb component strongly influence its bulk miscibility with the linear component in a blend. The comb architecture increases the value of the effective exchange interaction parameter measured by SANS, \( \chi_{\text{eff}} \), of its blend with linear polymer by an order of magnitude, relative to values of \( \chi_{\text{eff}} \) for a blend containing a branched component with less densely branched architecture, such as a 6-arm star. In fact, bulk phase separation is observed in the blend containing a comb with short branches of 15 styrene repeat units. It is surprising to see that the calculated values of \( \chi_{\text{es}} \), the entropic contribution to exchange interaction parameter, are close to the experimental values of \( \chi_{\text{es}} \), considering that this calculation needs only parameters of the molecules and blends from experiments and segment lengths as inputs. In principle, segment lengths are also available from experiments. Currently we consider simply one segment length for each comb architecture and obtain its value from the best fit to the corresponding SANS curve with a relatively wide \( q \) range. A more realistic and complex approach to obtain values of segment lengths of combs might be to allow one segment length for the branch and another segment length for the backbone of a comb architecture, and focusing on fitting the high \( q \) part of the SANS curve that is most sensitive to segment length.
NR and STOF-SIMS measurements indicate that combs strongly segregate to the surface of blends with linear polymers and more than 85 vol% of the surface region in the blend is occupied by combs. Thermal annealing is not necessary to achieve significant surface segregation in comb/linear blends. Good agreement between the experimentally measured concentration depth profile and the correspondingly calculated one using a self-consistent field theory by Wu and Fredrickson is found after increasing the surface attraction for ends. The stronger surface attraction for ends may have an enthalpic origin from the slight, but remaining chemical difference between comb and linear PS. However, it is more probable that the actual entropic driving force for surface segregation of combs is stronger than the theoretical prediction. When 25% of the branch ends of the comb component are functionalized with various chemical groups (C₈F₁₇, OH or COOH), combs are still preferred by the surface. This result may indicate that the effect of long-chain branching on surface segregation prevails over the effect of chain end chemistry under the current conditions. It can also be explained as the composite effect of different enthalpic surface attractions (or repulsions) for sec-butyl and the other branch ends. That is, while high energy ends tend to keep combs from the surface, the sec-butyl ends tend to drive the comb to the surface and the sum of these two effects determines the outcome. The contact angle with water does not decrease for the blend containing a comb with branch ends partially functionalized with hydrophilic OH or COOH groups, which is explained by a proposed structure for the blend surface with OH or COOH groups buried
underneath the surface. Measurements of the distribution of these functional branch ends near the surface are needed to confirm the proposed structure.

In the third part of this work the surface fluctuation dynamics of melt films of comb polystyrenes with extremely high branching density have been investigated with XPCS. For these particular comb polymers, which are not entangled according to bulk rheology measurements, their films have surface fluctuations remarkably faster than those of films of linear chains with similar molecular weight. Despite the chains’ highly branched structures, the surface height fluctuations of some of the comb polystyrene melts can be well described by the hydrodynamic continuum theory known to be appropriate for surface dynamics of linear\textsuperscript{18} and cyclic\textsuperscript{24} polystyrenes, but inappropriate for surface dynamics of less densely branched polymers\textsuperscript{25} including a 6-arm star. The viscosities of the comb PS melt films derived from the XPCS measurements assuming the validity of the HCT match well with bulk viscosities measured by rheometry for three of the combs, while deviating somewhat for the other two. The largest deviation is seen for the comb (M15P105) that has shorter branches and a number of branches so large that its bulk rheology behavior appears to be close to that of an entangled melt. For this comb the deviation also grows with temperature, in contrast to the behavior seen for less densely branched chains. Comparison of the dynamics of these five comb polystyrenes with architectures lying at the transition from star-like to bottlebrush-like chains demonstrates that while changes in $T_{g,\text{bulk}}$ with architecture play a role in determining the surface height
fluctuation dynamics, those dynamics are also affected by details of the nonlinear architecture in a complex manner.

There are several interesting topics not fully explored in this dissertation, which may be worth an investment of more effort in the future. One interesting topic is the effect of bulk comb concentration on surface segregation and the validity of the linear response theory. Current results on this topic suggest that the bulk comb concentration must be below 6 vol% in order to reach the linear response regime of the theory. We may also lower the bulk comb concentration in blends for SANS measurements to improve blend miscibility so that $\chi_{\text{eff}}$ values of blends of more comb architectures (e.g. M15P34) are available from fitting with the RPA model to the corresponding SANS curves. The current structure factor for comb architecture with only one segment length for the whole comb molecule can be improved by including two different segment lengths for a comb molecule: one for the backbone and one for the branch. This modification of structure factor is expected to yield better fitting with the RPA model to the SANS curves. Replacing sec-butyl groups with styrene-like units at the branch chain ends of a comb is synthetically challenging. However, its benefits could be significant, since athermal blends could be made with this new type of comb. In the study of surface segregation in functionalized comb/linear blends, the presence of sec-butyl groups at the branch chain ends complicated the comparison between branching effect and chain end chemistry effect on surface segregation. We can remove the influence of sec-butyl groups by
increasing the ratio of functional branch chain ends in a comb from the current value of 25 % to 100 %. XPS measurements may be helpful for determining the distribution of functional branch ends near the surface of a functionalized comb/linear blend.
REFERENCES


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227. Zhao, X.; Zhao, W.; Sokolov, J.; Rafailovich, M. H.; Schwarz, S. A.; Wilkens, B. J.; Jones, R. A. L.; Kramer, E. J. "Determination of the Concentration Profile at the


APPENDICES
APPENDIX A

SURFACE SEGREGATION AND BULK THERMODYNAMICS OF 6POM POLYSTYRENES

We have studied surface segregation with neutron reflectivity (NR) measurements and bulk thermodynamics with small angle neutron scattering (SANS) measurements for a series of pom-pom branched polymers. These pom-pom molecules, shown in Figure A.1 include 6pom0k, 6pom2k, 6pom4k, 6pom18k & 6pom34k, which have the same chemical structure details at the chain ends, branch points and center, while having various distances between branch points. We also synthesized a new linear analog, which has six sec-butyl groups at its ends and one double diphenylethylene (DDPE) initiator residue at the middle. It is considered to be superior to the traditional linear analog with only one sec-butyl group and without initiator residue because it matches all the chemical details of the pom-pom molecules except for having end branches.
A.1 Surface segregation

One objective of an NR study of surface segregation of these pom-pom molecules in blends with linear chains was to verify the effect of the sec-butyl groups at chain ends. We conjectured that the sec-butyl end groups, which have surface energy slightly below that of a styrene repeat unit, are favored at the surface, therefore contributing to the surface segregation of branched chains. In general we found surface segregations of these “pom-pom” branched polymers when blended with linear analogs were modest, which increased the difficulty in making clear comparisons among samples. Nonetheless useful conclusions could be drawn from comparisons between some specific pairs of samples.

Measurements of two specifically designed samples were conducted in order to serve this purpose. These two samples have the same branched polymer component, which is...
6pom0k, but different linear analogs. The novel linear analog has six sec-butyl end groups while the traditional one has only one. If those sec-butyl end groups play an important role in the surface segregation of branched chains, we expect to see a noticeable difference in the degree of segregation of 6pom0k molecules between the two samples. The comparison of the depth profiles of the two samples is shown in Figure A.2, in which the y axis is scattering length density (SLD) and the x axis is the depth from the air/film surface. In the blend the branched polystyrene is hydrogenous with SLD equaling to $1.41 \times 10^{-6} \text{Å}^{-2}$, while the linear polystyrene is deuterated with SLD equaling to $6.52 \times 10^{-6} \text{Å}^{-2}$. The SLD for the bulk of the film with 25 vol% of hydrogenous polymer would be expected to be roughly $5.3 \times 10^{-6} \text{Å}^{-2}$. In Figure A.2 we can see for the sample with the traditional linear analog, the SLD near the surface is always lower than the SLD of the bulk, which means the concentration of hydrogenous branched polystyrene is higher at the surface than its concentration in the bulk. In other words, the branched polymer 6pom0k enriches the sample surface when it is blended with the traditional linear analog with only one sec-butyl end groups. However, when 6pom0k is blended with the novel linear analog a slightly increase in SLD at the surface is observed, which indicates that the sample surface is in fact enriched by the novel linear analog with six sec-butyl end groups. This comparison result confirms our conjecture that chain end chemistry, sec-butyl end groups in this case, influences the surface segregation of branched polymers. If its effect is strong enough, it is able to offset the entropic preference of branched polymer on the surface.
Figure A.2 Comparison between the SLD depth profile of a sample with the novel linear analog and one with the traditional linear analog. The same branched polymer, 6pom0k, is used in both blends. Depth is recorded starting from the air/sample surface. The higher the SLD value is, the higher is the concentration of hydrogenous component, branched polymer in this case.

Another interesting comparison in this data set is between the behavior of 6pom34k and that of the traditional linear analog when they are blended with the same novel linear analog. 6pom34k has short arms and a long distance between the two branching points, closely resembling a linear chain in terms of its architecture. It is expected that its surface segregation behavior should resemble that of a linear chain as well. However, the sec-butyl end groups on 6pom34k will affect its surface segregation. Therefore, we
designed a comparison test such that the effect of the sec-butyl end groups is separated from the architecture effect. In Figure A.3 both samples, whether containing 6pom34k or the traditional linear analog, show enrichment of the deuterated novel linear analog on the surface and their depth profiles are similar to each other. (Both also show a depletion of the deuterated novel linear analog at the substrate interface.) The results indicate that while the architecture effect should favor the 6pom34k molecule at the surface, this effect is offset by the effect of the sec-butyl end groups that is more important. Thus, since both the 6pom34k and the novel linear analog have six sec-butyl end groups, the isotopic effect drives the deuterated molecule to slightly enrich the surface. This supports our assumption at the beginning. It is also evidence that surface segregation is affected by several factors including architecture and chain end chemistry. We note in passing that at the substrate interface the hydrogenous species is favored in both cases, but the interfacial excess of 6pom34k is greater than that of the traditional linear chain.
Figure A.3 Comparison of SLD depth profiles of samples containing 6pom34k or linear chains blended with the novel linear analog. Depth is recorded starting from the air/sample surface. Enrichment of the deuterated novel linear analog is observed for both samples indicated by higher SLD values near the surface than in the bulk.

We also observe an interesting nonmonotonic change of the degree of surface segregation with length of the center portion of the pom-pom for 6pom0k, 6pom2k and 6pom4k, as shown in Figure A.4. It should be noted that these three branched chains have the same chemical structure details, but the molecular weight of the linear section between branch points is varied from 0 to 4,000 g/mol. All three samples have the novel linear polystyrene as linear component. Instead of a monotonic change in surface segregation of the hydrogenous branched polymers, and thus in the SLD of the blends,
we see a more complicated trend. 6pom4k has a longer distance between its two branch points than does 6pom2k and 6pom2k shows more surface segregation than does 6pom4k. 6pom0k is expected to have even stronger surface segregation than has 6pom2k due to its shorter distance between branch points; however, the trend is reversed between them. In the blend of 6pom0k and the novel linear analog the surface is even enriched slightly by the deuterated linear component. We are not aware of any theories that can appropriately explain this finding yet. At this stage we conjecture that a combination of effects of not only the distance between branch points, but also the size of the whole branched polymer results in the nonmonotonic trend in degree of surface segregation with distance between branch points.

Figure A.4 Comparison of SLD depth profiles of different branched polymer components in blends with the novel linear analog. Depth is recorded from the air/sample surface.
A.2 Bulk thermodynamics

We use SANS to study the bulk thermodynamics of branched polymers blended with two different linear analogs, the traditional one and the novel one. The SANS curves for 50/50 blends of the pom-pom polymers with the traditional linear analog at 120 °C are shown in Figure A.5a and those for blends with the novel linear analog in Figure A.5b. The magnitude of the interaction parameter, $\chi$, primarily impacts the low Q portion of the curve and therefore its magnitude can be roughly compared just by visual inspection of the low Q portions of the curves for this special case in which the sizes of the components are so similar among the blends. However, the different pom-pom polymers do not have exactly the same values of $R_g$, so detailed modeling with the RPA expression is necessary to extract quantitative values of $\chi$. Roughly speaking, higher intensity at low Q indicates a larger value for $\chi$. When the branched polymers are blended with the traditional linear analog, their SANS curves substantially overlap each other and can hardly be differentiated, as shown in Figure A.5a. The value of absolute intensity at Q or 0.007 Å$^{-1}$ is between 27 and 34 cm$^{-1}$, depending on the pom-pom. The difference in SANS curves among the branched polymers is greatly enlarged as the linear counterpart in the blend is switched to the novel linear chain in Figure A.5b. Three blends still have values of absolute intensity at Q of 0.007 Å$^{-1}$ around 30 cm$^{-1}$, but blends for two chains have values greater than 37 cm$^{-1}$ and one has a value of about 16 cm$^{-1}$. This suggests that the enthalpy effect from the sec-butyl end groups contributes to the interaction parameter between the branched and linear polymer. Since the traditional linear analog has only one
sec-butyl end group while all pom-pom branched polymers have six ones, it is possible that Figure A.5a reflects the enthalpy effect of sec-butyl end groups more than it does the entropy effect from the architectures of the branched chains. The argument is also supported by Figure A.5b, which shows greater difference among various architectures when the effect of sec-butyl end groups is cancelled by using the novel linear analog having the same number of sec-butyl end groups as have the branched chains. Figure A.5b reveals that the magnitude of χ varies as 6pom2k > 6pom4k > 6pom0k. This trend, which is nonmonotonic in the length of the center linear section, resembles what we observe for the surface segregation behavior. SANS curves for 6pom0k, 6pom34k and linear in Figure A.5b are closely overlapped with each other and all three molecules show similar surface enrichment of deuterated novel linear analog in their blends as well. The association between surface segregation behavior and interaction parameter observed here might provide insight into interpreting the unique trend. The curve for 6pom18k in Figure A.5b is suspicious, because its intensity is much lower at low Q than that of other samples, even the linear/linear blend. The intensity is also lowest for the blend with 6pom18k in Figure A.5a, but the difference is not so striking. This abnormal low intensity could be caused by impurities or bubbles present in the sample.
Figure A.5 Comparison of SANS curves of blends with different branched polymer components at 120 °C mixed with (a) traditional linear analog; (b) novel linear analog.
APPENDIX B

THIN FILM SURFACE DYNAMICS OF 4-ARM STAR POLYSTYRENES WITH VARIOUS JUNCTION POINT FLEXIBILITIES

With the synthesis of a star polymer named “h4star”, we completed a series of 4-arm stars with a flexible butadiene core (4starwBD), 4-arm star without a flexible core (4starwoBD) and 4-arm star with a flexible ethylene core (h4star). Their structures are shown schematically in Figure B.1 and their molecular characterization summarized in Table B.1. Study of these three molecules provides an interesting comparison for addressing the effect of flexibility at a junction point on the dynamics of branched chains.

Figure B.1 Schematic drawings of three 4-arm stars with different core flexibilities.
Table B.1 Molecular weight characterization and butadiene unit determination for 4-arm stars and the precursor arms.

<table>
<thead>
<tr>
<th>Sample</th>
<th>No. of BD units per arm&lt;sup&gt;a&lt;/sup&gt;</th>
<th>$M_n$(arm)&lt;sup&gt;b&lt;/sup&gt; g/mol</th>
<th>$M_n$(star)&lt;sup&gt;b&lt;/sup&gt; g/mol</th>
<th>No. of arms&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
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<tr>
<td>4starw/BD</td>
<td>1.4</td>
<td>4,200</td>
<td>17,200</td>
<td>4.0</td>
</tr>
<tr>
<td>4starw/oBD</td>
<td>0</td>
<td>4,100</td>
<td>16,700</td>
<td>4.0</td>
</tr>
<tr>
<td>h4star</td>
<td>0</td>
<td>4,200</td>
<td>17,200</td>
<td>4.0</td>
</tr>
</tbody>
</table>

<sup>a</sup> Average of results from MALDI-TOF (±1%) and 1H NMR (±2%).

<sup>b</sup> Determined by SEC coupled with light scattering (±5%).

<sup>c</sup> Arm functionality calculated based on $M_n$ determined by SEC (±5%).

The hydrogenation of the butadiene units at the junction point of the previously synthesized 4-arm star 4starwBD is described in Figure B.2. The butadiene units in 4starwBD were completely hydrogenated to ethylene units in the sample denoted as “h4star”, as indicated by their NMR spectra in Figure B.3. Samples for XPCS were prepared by spin-casting onto etched silicon wafers to make films of about 90 nm thickness. This is sufficiently thick so that changes in $T_g$ of the film due to thickness should not be a strong factor.
Figure B.2 Scheme of hydrogenation of 4starwBD.

Figure B.3 NMR spectra of 4starwBD (left) and h4star (right). Complete hydrogenation is indicated by the disappearance of the protons at ca. $\delta$ 5.3ppm.

The XPCS results for the hydrogenated star are extremely interesting. The relaxation times are summarized in the form of $\tau/h$ vs. $1/T$ in Figure B.4(a) and in the form of $\tau/h$ vs. $T$ in Figure B.4(b). We find that the surface dynamics of the h4star are very similar to
those of 4starwBD in terms of relaxation time when normalized by film thickness. The surface dynamics of h4star and 4starwBD are significantly faster than those of the 4starwoBD. This result is expected since the core structures in both 4starwBD and h4star are more flexible. We hypothesized that this greater flexibility would result in faster dynamics of the whole molecule and therefore of the surface. On other hand, if segmental dynamics are important, then normalization of the temperature by $T_g$ should result in the data collapsing onto a single curve. In Figure B.5 the data points for LPS17k, 4starwBD and 4starwoBD do nearly collapse onto a single curve in such a plot. However, the data points for the h4star are an obvious exception. We note that although h4star and 4starwBD have similar surface dynamics, the experimentally determined bulk $T_g$ of h4star is 13 °C higher than that of 4starwBD. Presumably this $T_g$ increase is due to the somewhat stiffer linkage at the core after the double bonds are hydrogenated.
Figure B.4 Comparison of surface dynamics data of thin films, measured by XPCS, for three 4-arm stars and a linear analog of comparable molecular weight (a) in the form of $\tau/h$ vs. $1/T$; (b) in the form of $\tau/h$ vs. $T$. 

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$ (°C)</th>
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</thead>
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<tr>
<td>4starwBD</td>
<td>76</td>
</tr>
<tr>
<td>h4star</td>
<td>89</td>
</tr>
<tr>
<td>4starwoBD</td>
<td>86</td>
</tr>
<tr>
<td>LPS17k</td>
<td>95</td>
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</table>
Figure B.5 Normalized XPCS relaxation times vs. temperature normalized with the bulk glass transition temperature ($T_g$) of the molecule for the three 4-arm stars and linear analog. Values of $T_g$ are noted in the inset.

We consider here also a comparison of the bulk viscosity measured by conventional rheometry and the film viscosity inferred from the XPCS data using the HCT in Figure B.6. The bulk viscosity of 4starwBD is the lowest, as anticipated. At the same temperature, the bulk viscosity of h4star is higher than that of 4starwoBD, although h4star had flexible ethylene units at the junction point. The ethylene units are not as flexible as are the butadiene units. There is a discrepancy for each of the three 4 arm stars between the viscosity from rheometry and viscosity derived from XPCS. However, the discrepancies for 4starwBD and 4starwoBD, while similar, are both much larger than the discrepancy for h4star. Figure B.6 is plotted in a manner to facilitate analysis of the temperature behavior of the viscosity assuming an Arrhenius-type behavior. Therefore, activation energy ($E_a$) can be estimated from the slope of a linear fit to each data set and are summarized in Table B.2. The activation energies for the XPCS and bulk data sets of linear PS (LPS17k) are similar to one other, with $E_a = 286$ kJ/mol. Values of $E_a$ for the XPCS and bulk data sets of h4star and 4starwoBD are reasonably close to those of LPS17k, varying from 260 kJ/mol to 293 kJ/mol. For 4starwBD, the activation energies for the XPCS ($E_a = 333$ kJ/mol) and bulk ($E_a = 221$ kJ/mol) data sets are different and distinct from the values of $E_a$ for the other samples compared here. The value from the
XPCS data set is above those for all the other data sets, and the value from the bulk data set is below $E_a$ for all the other samples.

![Graph showing comparison of XPCS-derived and bulk viscosities at various temperatures for three 4-arm stars and the linear analog.]

Figure B.6 Comparison of XPCS-derived and bulk viscosities at various temperatures for three 4-arm stars and the linear analog.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_a$ (kJ/mol, ±10%)</th>
<th>XPCS</th>
<th>Bulk</th>
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<tr>
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<td>286</td>
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<tr>
<td>h4star</td>
<td>292</td>
<td></td>
<td>290</td>
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<tr>
<td>4starwBD</td>
<td>333</td>
<td>221</td>
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<tr>
<td>4starwoBD</td>
<td>293</td>
<td>260</td>
<td></td>
</tr>
</tbody>
</table>

| Table B.2 Activation energies ($E_a$) of various samples inferred from XPCS and bulk rheometry data sets in Figure B.6. |

Modification of junction point flexibility appears to affect the fragilities of star
polymers. The temperature dependence of XPCS-derived and bulk viscosities are presented in the form of an Angell plot in Figure B.7. The films of 4starwBD, 4starwoBD and linear PS exhibit fragility similar to one other. However, they are less fragile than the h4star film according to XPCS results. The fragilities of the melt films of 4starwBD and 4starwoBD are lower than the fragilities of the corresponding bulk melts. This discrepancy between film and bulk fragilities is much narrower in the case of h4star.

At present we have no explanation for the remarkable changes that come in the surface dynamics of the 4 arm star just from hydrogenating the double bonds in these linking units. It appears that tailoring of small features of the molecular structure of a branched chain may be used to control the surface dynamics. Further investigation will be needed, however, to clarify the relationship between the details of the linking flexibility and the surface dynamics.
Figure B.7 Angell plot of XPCS-derived and bulk viscosities at various temperatures for three 4-arm stars and the linear analog.
APPENDIX C

FIGURES OF EFFECTIVE EXCHANGE INTERACTION PARAMETERS FOR COMB/DLPS36K BLENDS AT VARIOUS TEMPERATURES

Table C.1 $\chi_{\text{eff}}$ for 50 vol% comb/dLPS36k blends at various temperatures measured by SANS.

<table>
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<tr>
<th>Comb</th>
<th>$\chi_c \times 10^3$</th>
<th>$\chi_{\text{eff}} \times 10^3$</th>
<th>$\chi_{\text{eff}} = A/T+B$</th>
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<td></td>
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<td>120 °C</td>
<td>140 °C</td>
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<td>4.30</td>
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<tr>
<td>M24P50</td>
<td>3.60</td>
<td>3.72</td>
<td>3.59</td>
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$^a$ Estimate of the critical value of the interaction parameter for a linear/linear blend with component molecular weights equal to those of the comb and linear in the comb/linear blend, $\chi_c = \frac{1}{2} \left( \frac{1}{\sqrt{N_{\text{comb}}} + \sqrt{N_{\text{linear}}}} \right)^2$.

$^b$ Values of $\chi_{\text{eff}}$ are obtained by fitting with a miscible RPA model to SANS curves.
APPENDIX D

BUFFERS FOR NEUTRON REFLECTIVITY MEASUREMENTS

Buffers for neutron reflectivity measurements performed on NG7 at NIST are described in this appendix.

D.1 Buffer for measuring main beam (or slit scan)

Table D.1 Main beam buffer

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D.2 Buffers for measuring background

Table D.2 Background + buffer

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$^a$ XM designates the offset from specular position for the position of motor No.13.
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$^a$ XM designates the offset from specular position for the position of motor No.13.

### D.3 Buffers for measuring a sample

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APPENDIX E

AFM ADHESION MAPPING MEASUREMENTS FOR POLYSTYRENE BLENDS

E.1 Experiments

Adhesion properties at the nanoscale were inferred from the measurement of force-distance curves using Bruker Dimension ICON AFM in peak force mode with a Si tip covered with its native oxides. Force-distance curves were collected and analyzed in real time using the software NanoScope Analysis Version 1.20 (Veeco) to produce adhesion maps that directly correlate to the topography. Data were collected from a scanning area of 0.5 μm × 0.5 μm as well as 2 μm × 2 μm. AFM adhesion mapping measurements have been performed for blends containing 20 vol% hydrogenous polystyrene and 80 vol% dLPS36k. Samples are prepared by spin-casting onto etched silicon wafers to make thin films. The hydrogenous polystyrenes studied here include hLPS36k (film thickness 850±5 nm), M24P28 (826±3 nm), Comb-OH (949±4 nm), Comb-C8F17 (1086±5 nm) and Comb-COOH (1144±6 nm).
E.2 Results and discussions

Results from AFM adhesion mapping measurements of various polystyrene blends are compared in Figure E.1. Both the average values and the widths of the distributions are potentially of interest. Averaged values of adhesion and their standard deviations over different scanning areas and spots for these blends are: 0.47±0.05 nN (hLPS36k), 0.49±0.06 nN (M24P28), 0.27±0.07 nN (Comb-OH), 0.30±0.05 nN (Comb-C₈F₁₇) and 0.33±0.05 nN (Comb-COOH). All polystyrene blends studied here show small adhesion values on the order of a few tenths of nN, which are expected since polystyrenes are nonpolar and there are only very small fractions of polar functional groups present in the blends. The distribution of adhesion values on the surface is narrower for the blend containing Comb-OH, Comb-C₈F₁₇ or Comb-COOH than for the blend containing unfunctionalized materials hLPS36k or M24P28.

Figure E.1 Distribution of values of adhesion measured by AFM adhesion mapping for various blends containing 20 vol% hydrogenous polystyrene and 80 vol% dLPS36k. Scanning area is 2 μm × 2 μm.
The blend containing the unfunctionalized comb M24P28 exhibits essentially the same surface adhesion properties as does the blend containing hLPS36k. AFM adhesion mapping measurements are able to detect the difference in adhesion values between blends with and without functionalized combs. However, the magnitude of the difference in adhesion values among blends containing various functionalized combs is of the order of the experimental uncertainty. The dependence of adhesion values on comb functionalities is complicated. For example, despite the attachment of high surface energy carboxyl groups at the branch ends of Comb-COOH, the adhesion value of the Comb-COOH/dLPS36k blend is lower than that of the M24P28/dLPS36k blend or hLPS36k/dLPS36k blend. There appears to be a correlation between the measured contact angles and adhesion values of these blends. The contact angle of a blend containing Comb-OH, Comb-C$_8$F$_{17}$ or Comb-COOH measured with DI water is higher than that of a blend containing M24P28 or hLPS36k as shown in Figure 6.12, and correspondingly its adhesion value is lower. However, the increasing order of contact angle is not consistent with the decreasing order of adhesion value.
APPENDIX F

COMPLETE CONCENTRATION DEPTH PROFILES OF BLENDS OF COMB AND LINEAR POLYSTYRENES

The complete concentration depth profiles of blends of comb PS and dLPS36k including the air/polymer surface and the polymer/substrate interface are presented in this appendix. A 2-layer model assuming only segregation of combs at the surface provides the best fit to NR curves of certain blends, while a 3-layer model assuming segregation of combs at both the surface and interface with the substrate provide the best fit to NR curves of the other blends.

NR curves of both the annealed and unannealed 20 vol% M24P28/dLPS36k blends are best fitted by 2-layer models. It is not necessary to envision segregation of M24P28 combs to the polymer/substrate interface in order to fit the NR data, as shown in Figure F.1. However, on the other hand, for the 12 vol% and 6 vol% M24P28/dLPS36k blends best fits are obtained by allowing for some very modest enrichment of combs at the polymer/substrate interface, as shown in Figure F.2, no matter whether the model assumes a “rough” or “smooth” air/polymer surface. If we take all three results together the primary conclusion is that the segregation at the polymer/substrate interface is quite
subtle compared to that at the air surface. The same is true for blends containing 22 vol% M24P14 and blends containing 6 vol% M15P105 or 10 vol% and 7 vol% M15P34. Data from the 22 vol% M24P14 and 6 vol% M15P105 blends do not seem to indicate any comb enrichment at the substrate interface, while data from the M15P34 blends show modest comb segregation at the polymer/substrate interface as shown in Figure F.3.

Figure F.1 Complete comb concentration depth profiles of annealed 12h at 180 °C (solid) and unannealed (dash) 20 vol% M24P28/dLPS36k blends.
Figure F.2 Complete comb concentration depth profiles of models with the best fits to NR data for 20 (red), 12 (blue) and 6 (black) vol% M24P28/dLPS36k blends. Solid lines represent for depth profiles of models with “rough” surfaces, and dotted lines represent for depth profiles of models with “smooth” surfaces.
The results for segregation of comb polymers at the polymer/substrate interface are puzzling. Some comb/linear blends studied here show no segregation of combs at the interface, which seems to be consistent with an enthalpy-driven surface segregation of comb polymers. However, combs do segregate to the polymer/substrate interface in the other comb/linear blends, although the interface excess is much smaller than the surface excess in these blends. We do not find a clear connection between the comb architecture and interfacial segregation of combs based on currently available NR data. In order to provide decisive conclusions about the segregation at the polymer/substrate interface, a
depth profiling technique directly sensitive to chemical composition variation with depth is needed ideally. Information obtained with such a technique can supplement current NR data to resolve concentration depth profiles of thin films of comb/linear blends.
APPENDIX G

RESULTS OF NEUTRON REFLECTIVITY MEASUREMENTS OF BLENDS OF FUNCTIONALIZED COMBS AND LINEAR POLYSTYRENES

NR results of functionalized comb/linear blends are discussed in this appendix. Each blend contains 20 vol% of one of the three functionalized combs (Comb-OH, Comb-C$_8$F$_{17}$ and Comb-COOH) and 80 vol% of dLPS36k. NR curves of the three blends are presented in Figure G.1. The three NR curves are significantly different from each other, indicating that the functionalities of the comb components greatly influence the blend film structures. By examining the beating behavior of each NR curve, one can see that the length scale of the segregation layer is different for each functionalized comb/linear blend. Fringes in the NR curves of the Comb-OH/dLPS36k and Comb-COOH/dLPS36k blends disappear at q below 0.15 Å$^{-1}$, while the fringes in NR curves of the Comb-C$_8$F$_{17}$/dLPS36k blend persist until 0.17 Å$^{-1}$. Rapidly decreasing amplitude of fringes in a NR curve may be caused by several reasons, including a rough surface or interface and lateral composition heterogeneity.
Figure G.1 Neutron reflectivity curves of blends of functionalized combs as marked in the legend and dLPS36k. Solid curves are the fits to the corresponding experimental data.

Obtaining a good fit to each of the NR curves of the three blends in Figure G.1 is challenging. The quality of fitting with a 3-layer model to the NR curve of Comb-C$_{8}$F$_{17}$/dLPS36k blend is barely acceptable, with $\chi^2 = 8.2$. However, the calculated curve does not fully capture the experimental curve. We were unable to obtain reasonable fits with 2-layer or 3-layer models to the NR curves of the Comb-OH/dLPS36k and Comb-COOH/dLPS36k blends.
The comb concentration depth file of 20 vol% Comb-\text{C}_8\text{F}_{17}/dLPS36k blend from the best fit to its NR curve is presented in Figure G.2. Details of the model parameters are shown in Table G.1. Strong surface segregation of Comb-\text{C}_8\text{F}_{17} is observed according to the depth profile, with surface comb concentration of 98 vol\%, which is in good agreement with the result of STOF-SIMS (0.99). There is also substantial segregation of combs at the polymer/substrate interface of the blend. This is consistent with the observation of Takahara et al.\textsuperscript{162}, who reported linear polystyrene chains functionalized with fluorinated ends segregating to both the air and substrate interfaces of a film of a
blend with deuterated linear PS with comparable molecular weight. In the present case the large molecular weight of the comb would tend to mitigate against enrichment of the comb at either interface. We could not obtain information about the location of functional branch chain ends at either the air/polymer surface or the polymer/substrate interface with the current NR measurements.

Table G.1 Model parameter values for 20 vol% Comb-C$_8$F$_{17}$/dLPS36k blend.

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<th>Fit parameter</th>
<th>Comb-C$<em>8$F$</em>{17}$</th>
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<td>$\varphi_H$</td>
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