SURFACE SEGREGATION OF BRANCHED POLYMERIC ADDITIVES IN POLYMER HOST

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Zhenyu Qian, Ph. D.

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This study makes major contributions to understand the surface segregation of branched polymeric additives in linear polymer host by both simulation and experiments. Firstly self-consistent field(SCF) lattice simulation was used to study the entropic effect of architecture of polymer additives on their surface segregation in polymer host. A lot of typical molecular architectures, such as star, comb and dendrimer, together with their symmetry, had been theoretically investigated and symmetric star architecture was proved to be entropically the best candidate for surface migration, given that other properties such as chemical composition, molecular weight are constant (Chapter 2). Secondly, two series of symmetric star polystyrenes with different molecular weights, which are 4-arm and 11-arm stars were then anionically synthesized to provide experimental evidences for architectural effect. Surface tensions of star polystyrene melts were measured as a function of temperature and as a function of molecular weight using a modified Wilhelmy plate technique. We find that architectural effect plays a significant role in determining the molecular weight dependence on melt surface tension. A variable density lattice model that considers effects of entropic attraction of polymer chain ends to surfaces, compressibility and density gradients in the region near the surface is used to determine the origin of this observation. This analysis is complemented with surface tension calculations using more classical thermodynamic models that consider only

bulk property changes with polymer architecture and molecular weight. These two models address different origins for such architecture effect but both provide a reasonably good quantitative estimation(Chapter 3). Finally these symmetric star polystyrenes were mixed as model additives with their linear counterparts, and the surface tension of the star/linear blend system were measured. We found that the star branched polymer tends to segregate at the surface, and the surface tension of the blends drops a lot from that of the linear component at low star weight concentration. Theoretical analysis and prediction of surface tension of pure component and blends were performed by both self-consistent lattice simulation and more classical bulk thermodynamic methods from Pressure-Volume-Temperature(PVT) information. We find that theory and simulation agree well with experimental results, at least qualitatively(Chapter 4).

BIOGRAPHICAL SKETCH

Zhenyu Qian was born in the city of Tianjin, China on January 22nd 1979. As he grew up, he developed his strong enthusiasm in science and technology. In his childhood, he continuously received scientific edification and education from his parents, both of whom are chemical engineers. Having an aptitude in Mathematics, Physics and Chemistry in his adolescent, he demonstrated his goal to become a scientist or engineer in the future. In 1997, his ambition reimbursed him the chance to pursue his bachelor's degree in Tsinghua University, which is the top 1 science and engineering university in China. He graduated with a bachelor's degree in 2001 and a master's degree in Chemical Engineering and Polymer Science in 2004. To my beloved fiancée, Rongrong Wang

This dissertation is dedicated to my parents Yonghong Qian and Hejuan Xu. When I grew up, they continuously encouraged and supported my interest in science and technology. As chemical engineers themselves, they spent a lot of their spare time teaching me Mathematics, Physics, Chemistry and most importantly, the goal of honesty, integrity and sincerity. They tried their best to provide me the best education and resources to be a good scientific researcher. Without their significantly beneficial influence, I wouldn't be in the position I'm right now. I also appreciated the help from my elder brother Tianlei Qian, because in my childhood he frequently took care of my study and life when my parents were busy in their work far away from home. From him I learned how to be independent and cooperative with others. All my teachers and advisors during my adolescence period brought me most fundamental knowledge I need to develop my interest. Their encouragement has always been an inner spiritual pillar of my academic achievement.

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CHAPTER 1

Introduction

1.1 Background

Polymer materials have been extensively used in many industrial applications, such as coating, adhesion, packaging and painting. Among these successful applications, physical and chemical control of polymer or polymer blend surfaces is very important. Polymer additives, which are added into the polymer host, are sometimes expected to migrate towards the surface or sometimes stay in bulk according to different requirements. In either case the fundamental study is very important. This study focuses its major interests in surface active additives, which are also commonly added into polymeric materials used in our daily life, compared with plasticizers. For example, high molecular weight silicone rubber with Polypropylene was used as an anti-scratch additive, and Polyether-co-Polyamide was used as an antistatic additive in electronics industry. Other examples where surface active additives are utilized are adhesion promoters, to improve paintablity, to impart biocompatibility to a surface or being used as anti-fogging coatings among a host of other applications. An additive-covered or additive-enriched thin layer is required to achieve the surface active functionality of these additives after processing steps. Thermodynamically, the surface enrichment of additives is determined by difference of surface energy and the bulk interaction between the additive and polymer host.

During past years, many studies have been focused on surface tension measurements of linear polymer melt at elevated temperatures or surface excess characterization of linear/linear polymer blends. Some of them will respectively be mentioned in detail in later corresponding chapters, however, here we would like to provide a main track of the development of experiments and measurement techniques.

Molecular weight dependence on surface tension is always a central issue concerned by the polymer surface scientists. As early as 40 years ago, people began to experimentally discover that for low molecular weight polymers and oligomers, their surface tension (γ) is proportional to the reciprocal of $M_n^{2/3}$, where M_n is the number-average molecular weight^{1,2}. These results don't seem to be consistent with the early evidence provided by Fox and Flory³ that most thermodynamic bulk properties, such as density, thermal expansivity and glass transition, show a M_n^{-1} dependence. The latter finding can be easily explained by a group contribution model, where the polymer main chain is composed of identical middle segments and end segments. The "concentration" of end segments, which also shows a M_n^{-1} dependence, determines the thermodynamic bulk properties. Experimental proofs were provided later⁴⁻⁶ that for relatively high molecular weight chains, the entropic contributions are negligible, which attributes to a $M_n^{-2/3}$ dependence on surface tension.

In their reviews, Wu⁷, Koberstein⁸, Dee and Sauer⁹ have tremendously discussed the surface and interface tension measurement techniques. Originally the most popular method, pendant drop technique, requires the shape analysis by a software program and an independent melt density measurement, is well applicable to small molecule liquids and oligomers. The demand of understanding surface properties for high molecular weight polymers requires more advanced techniques which could avoid the difficulty of high viscosity and the uncertainty of melt density input information. In the surface tension/interfacial tension measurements of a polymer species, as long as there exists a glass or metal probe, the size becomes a key issue because it determines the relaxation time the viscous polymer takes to reach equilibrium when interacting with the probe. Thus to shrink the size of the probe to a much smaller scale will help to achieve a quick surface property measurement at equilibrium state. However, this ambition should be balanced by the fact that sensitivity could be lost due to the scale down. The modified methods for measuring

interfacial tension between polymer melts "filament break-up method"^{10,11} or measuring surface tension of polymer melt "modified Wilhelmy method"¹² naturally take full advantage of these kinds of tiny probes to make major contributions to the surface measurements of high molecular weight polymers. In the latter case, freshly made clean glass fibers can be easily created therefore it solves a lot of practical problems due to surface contamination and incomplete wetting. Modified Wilhelmy method is the most important experimental tool for this study and will be introduced in details in chapter 3.

End segments, entropically or enthalpically, could make extra positive or negative contribution to the surface tension depending on their individual physical properties. Theoretically,¹³ Wu and Fredrickson,^{14,15} Theodorou,¹⁶ Hariharan,¹⁷ Mayes¹⁸, Minnikanti and Archer^{19,20} etc studied entropically driven end attraction. Experimentally there are several techniques to carry the surface characterization. Experimental investigations by neutron reflection(NR) by Zhao²¹ et al. and static secondary-ion mass spectrometry(s-SIMS) by Affrossman²² et al. have shown that isotopically chain-end-labelled polystyrene(PS) displays a small preference of end segment at the surface. However in this case the slight energetic advantage of deuteration is "large" enough to play a role. Neutron reflection and X-ray photoelectron spectroscopy(XPS), which can provide surface composition profiles normal to the surface plane with sensitivity as high as several nanometers, was utilized by Elman et al.²³ to capture an excess of short perfluoro end units or sec-butyl initiator end group along a polystyrene backbone and a depletion of carboxylic acid end group. However, the level of surface segregation of sec-butyl end group along a PS chain remains argumentative, and there are also other evidences available showing this effect is minor²⁴. Surface tension, as a measurement to the overall surface properties, and self-consistent field(SCF) lattice simulation may be used to indirectly analyze

such detailed contribution respectively from the end segments and the middle segments.

For the polymer blends, two typical systems were traditionally studied using the aforementioned techniques, one is hydrogenated polystyrene(H-PS)/deuterated polystyrene(D-PS) blend system, the other is polystyrene/poly(vinyl methyl ether) (PVME) blend system. In 1989, Jones and Kramer²⁵ used forward-recoil spectrometry(FRES) to study a linear/linear H-PS/D-PS blend system with molecular weights at the same order of magnitude and for the first time discovered the surface enrichment of the deuterated components. In 1993, Hariharan, Kumar and Russell²⁶ studied the same blend system using NR and found that it is not always the case that D-PS is preferred at the surface. Their experiments indicated that there exists a critical molecular weight of PS, beyond which DPS is still enriched at the surface, but below which it is depleted at the surface. We have done some similar preliminary studies for star PS/linear D-PS blend system by dynamic secondary-ion mass spectrometry(d-SIMS) and also found a critical molecular weight of star PS, which moves to high molecular weight regime due to the branched effect. In the former case only enthalpic factor takes action but in the latter one both enthalpic and entropic origins are compared simultaneously to determined which component should be enriched at the surface. Angel-dependent X-ray photoelectron spectroscopy(ADXPS) is applied to detect the segregation preference of ω -fluorosilane polystyrene to the surface as a result of the low surface energy fluorosilane end groups²⁷. In such systems, the surface-attractive end groups, not the isotopic effect, bring the whole chain towards the surface. For PS/PVME blend system, experimental investigations both by ADXPS by Forrey and Koberstein²⁸ and by blend surface tension measurement by Dee and Sauer²⁹ display a large amount of surface excess of PVME and the bulk interaction between PS and PVME turned out to be also very important to control the surface

tension versus composition profile. Due to the small difference of surface tension of blend components, before this study the only example of surface tension measurements of a chemically identical blend system is measured by modified Wilhemy method for a linear/linear polydimethylsiloxane(PDMS) blend system²⁹ with different molecular weights. The experimental data showed a strong surface excess of low molecular weight PDMS, which was also quantitatively modeled by density gradient theory.

Studies of the copolymer melt surface tension have also been reported to show a strong surface segregation of the low surface affinity block.³⁰⁻³³ Studies of polymer solution were also carried out, especially for the attractive case(PDMS in toluene) ³⁴ and the repulsive case(PS in toluene) ³⁴. Solid surface property is another branch of surface science studies. However, these subjects are not involved in this study so the interested readers are suggested to other references.

Throughout the total period of this study, we have also made other experimental efforts to characterize our self-made branched polymers using comprehensive techniques. For example, we were trying to compare the water contact angel on a solid surface of different polystyrenes but obtain no obvious distinction. Among all of them, we found modified Wilhelmy method provides the most direct and accurate experimental data for our system and for us it is the best way to distinguish the small surface tension difference of polystyrenes with different molecular weights or architectures. For a polystyrene blend system, XPS, NR, FRES and SIMS are always good candidate tools, depending on the resolution required, to directly or indirectly provide a surface concentration profile or surface excess as complementary proofs to surface tension measurement. Due to the local availability and essential equivalence to other tools, in this study we are experimentally more focused in the modified Wilhelmy method and also concentrated on the comparison of strength of different theoretical tools.

The surface energy of a polymeric material is influenced by many factors, which can be categorized into enthalpic and entropic origins. Enthalpically, different chemical compositions thus different physical properties simply determines the level of surface energy by characteristic average interchain distance³⁵; entropically, both end segment attraction^{14,15,19,20} and configurational entropy penalty³⁵ which corresponds to the chain molecular weight could influence the surface properties to some extent. One very interesting but practical question is that, given the aforementioned factors(chemical composition and molecular weight) fixed, how architecture or topological structure influences the surface properties or surface migration ability of polymeric additive. This study is mainly focused on studying the highly-branched effect of polymeric additives and their surface excess in polymer host.

Branched molecules, such as star, comb and dendrimer, are of two unique characteristics: one is the large number of ends; the second is branched architecture itself. First of all, for any segment along the polymer chain, it will lose some entropy to be at the surface^{14,15}, because the number of conformations it can adopt is reduced there. End segments will lose less entropy to be at the surface than middle segments because it has just one neighboring segment^{14,15,19,20}. So there is some advantage for end segments just due to its extra degree of freedom, which is so-called entropic driving force. Because of the higher number of ends, the entropic driving force for highly-branched polymers is predicted to be obviously higher than linear counterparts by the theories and simulations^{14,15,19,20}. Secondly, because of its highly branched architecture, it is difficult for the segments to pack together as well as linear chain. So the bulk density of highly branched materials is lower than that of linear chains. This effect will lower the surface tension, because thermodynamically cohesive energy

density(CED) is decreased by increasing the average interchain distance. This is so called enthalpic driving force. Therefore it is intuitive that, thermodynamically, both entropic and enthalpic driving force will favor the surface migration ability of branched molecules. (See Figure 1.1)

It is noteworthy that surface migration under quiescent state is emphasized in this study and there remains a topic for future study on influences of dynamic processing on surface migration. It is generally considered that the existence of shear will benefit or accelerate the surface migration of additives and shear time, shear rate and die geometry could influence a lot³⁶. However, the diffusion properties should be unavoidably taken into consideration so the branched effect may not benefit the surface migration from a dynamic perspective.

1.2 Factors that influence the surface migration of additives in a host

In polymer blend system, the surface concentration of additives is normally different from their bulk concentration so that a crest shape surface concentration profile is used to describe the situation. And also surface excess, which is the shaded area between the surface volume fraction profile and the bulk concentration baseline, is another key judgment of surface migration abilities as shown in Figure 1.2. There are a lot of factors that influence the surface migration of additives in host. Wu and Fredrickson^{14,15}, and Minnikanti and Archer^{19,20}, proposed a linear response theory that explains this effect in terms of a so-called entropic attraction of chain ends to surfaces and thermodynamic features of the blend near a surface and in bulk. In a binary polymer blend, the analysis leads to a simple closed-form expression for the surface excess, Z_1^* of the lower molecular weight and/or more branched blend species.



Figure 1.1 Schematic of comparison from entropic(chain end) and enthalpic(bulk density) origins between linear and branched species

$$Z_{1}^{*} = -(1/2) \left(\Delta U_{1}^{s} + \frac{n_{1}^{e} u_{1}^{e} + n_{1}^{j} u_{1}^{j}}{N_{1}} - \frac{n_{2}^{e} u_{2}^{e} + n_{2}^{j} u_{2}^{j}}{N_{2}} \right) / \left(\frac{1}{2 N_{1} \phi_{1}} + \frac{1}{2 N_{2} \phi_{2}} - \chi \right)$$
(1)

Here in a binary polymer blend system, Z_1^* is surface excess of species 1, ΔU_1^s is integrated strength of relative attraction of segments of species 1 towards the surface. u_k^e and u_k^j are the integrated attractions of the end and the joint segments towards the surface of species k; n_k^e and n_k^j are the number of end segments and joint segments; N_k and ϕ_k is the number of Kuhn segments and bulk volume fraction, respectively.

The first term in the numerator compares the enthalpic driving force between the additive and host, and the last two terms in the numerator are valid for any architecture and any species so they compares the entropic driving force. Thus the numerator compares both enthalpic and entropic factors to determine whether the additive will migrate towards the surface.

It is easily understood that in a compatible polymer blend system, if two components are chemically distinct, the one with the lower cohesive energy density(CED) will be enriched at the surface to lower the surface free energy of the blend system^{21,37-41}. Most commonly studied examples are polystyrene(PS)/ polyvinylmethylether(PVME) blend system²⁸. In this system PVME is always enriched at the surface because it shows a lower CED than PS. Another well studied blend system is polystyrene-deuterated polystyrene(DPS) system^{21,37-39}, where the isotopic effect provides a slight but large enough CED advantage for the deuterated component to be enriched at the surface^{40,41}. The degree of enrichment is determined by the difference of CED between two components. ΔU_1^s essentially contributes a large component to the difference of CED and other terms in the numerator make a relatively small contribution for linear chains.

It also turns out that these terms are directly relative to the molecular weight dependence on the surface tension⁴². If the surface tension of polymer species obeys linear relationship and it is plotted versus the reciprocal of molecular weight, the difference between intercepts is directly relative to ΔU_1^s , and the slope is relative to other terms. It will be more clearly seen in this schematic picture. So essentially the numerator is the surface tension difference between the additive and host. This is why surface tension comparison between additive and host can be used to determine the sign of surface excess of additives. Thus, to some extent, to study the surface tension is equivalent to study the surface excess. To study how these factors are influenced by the branched architecture is the goal of this study.

The sum of last two terms in the denominator is actually the spinodal critical interaction parameter(χ_s) of the blend system, and the other term χ is the real interaction parameter. The difference between these two parameters, which is also called compatibility, will influence the order of magnitude of the surface excess a lot.

Compared with linear structures, additives with a highly-branched architecture are therefore expected to manifest greater surface affinity both as a result of explicit features of their architecture^{19,20,43} (more chain ends increases the numerator) as well as from more subtle effects of architecture on the Flory interaction parameter⁴⁴.





1.3 Theories

We utilize linear response theory to introduce factors that influence the surface tension or surface segregation. However, there are a lot of other relative theoretical tools or simulation tools that are well studied. Cahn-Hilliard model⁵, discrete interface cell model⁹, SCF lattice simulation^{13,19,20,43} and linear response theory^{14,15,19} are mainly used in this study. Advantages and drawbacks are embedded in all current major theories or models, thus tests by experiments are highly desired. Even so, in terms of explanation of experimental data, still different models show their own argumentative points. We will provide a brief introduction here and will describe them in details if any is used in the later data analysis.

Traditionally, the classical Cahn-Hilliard square gradient approach is commonly used to determined the composition profile of components at surface. Physically, this principle states that the energetic driving force that brings the lower surface energy component to cover the surface region is balanced by the need to minimize large concentration gradient. This provides us a way to quantify the surface concentration profile of blend components. Based on a corresponding state principle⁴⁵, Cahn-Hilliard approach relies on the input information of sets of reduced parameters P*, V* and T* and these parameters are obtained by fitting experimentally measured PVT data to an appropriate Equation of State⁵. There are many Equations of State that have been tested, mostly fluid lattice type and cell type. Dee and Sauer⁵ used both to model the experimental data for PDMS liquid and concluded that Flory-Orwoll-Vrij(FOV) equation of state(cell model)⁴⁶ provides a better description than Sanchez-Lacombe(SL) equation of state(lattice model)^{47,48}. This approach works well for small liquid remains its shortcomings when dealing with polymer chain. Due to the characteristic of cell model, Cahn-Hilliard in conjunction with FOV model unavoidably ignores the entropic factors for polymer chain to stay at the surface. This

introduces a correction of predicted surface properties by 5~15% for linear chain⁹. For highly-branched polymer chain, this deviation still needs to be tested. A modified approach in corresponding-states principles has been utilized to make correction due to the configurational entropic penalty so that two universal curves, one for small molecular weight liquid, one for polymer molecules are used to quantify the deviation due to entropic effect³⁵. With similar spirits, discrete interface cell model^{9,35} considers both enthalpic and entropic contributions to the free energy but ignores the detailed microscopic information about the polymer character of the molecule. The advantage of this approach is its simplicity of application and mathematical computation.

Linear response theory proposed by Wu and Fredrickson^{14,15} predicts the surface enrichment of any arbitrary branched architecture when blended with simple linear host purely due to entropic reasons. This model localizes the entropic driving force to the end segment and branched segment of polymer chain and thus simplify the comparison of entropic attraction or repulsion between any branched architectures. Minnikanti and Archer^{19,20} developed a theory based on Random Phase Approximation^{49,50} that includes both energetic and entropic driving force, which finally bridges two types of theories together that take into account either only energetic factors(Schmidt-Binder Theory⁵¹) or only entropic factors(linear response theory ^{14,15,19,20}). This major progress made linear response theory a more general tool to analyze the experimental data of surface enrichment of any additive with any architecture in any polymer host, as long as the molecular weight dependence on surface tension of each single component is known. However, this information can be only obtained by experimental measurements, which in turn increases the difficulty of the application of this approach.

Other than different theoretical models mentioned above, self-consistent field(SCF) lattice simulations^{14,15,19,20} of polymer melts near surface can also be

performed to determined the surface properties of single/multiple component polymer or surface segregation of one of the component. Other techniques, such as Monte Carlo(MC) or molecular dynamics(MD) are indeed more accurate but much more computationally expensive compared with SCF lattice simulation, because the latter coarse grains the space by Kuhn length and assumes a mean field approximation. These assumptions make the sample space much larger, that is, computation of higher molecular weight samples becomes realistic. Although not perfectly accurate, SCF lattice simulation can still provide information as detailed as possible, especially in the case that polymer chain entropy and topology can be captured. However, it has been proved that incompressible lattice simulation that ignores density gradient and compressibility near the surface region could dramatically underestimate the order of magnitude of surface properties^{52,53}. On the other hand, variable density lattice simulation that allows this change to occur could only use fluid lattice model(such as SL equation of state) to predict the bulk density. This equation of state has also been proved to be poor when used to predict the bulk density of low molecular weight polymer chain⁵. Although the estimation could be reasonably good for high molecular weight polymer, the relatively accurate experimental data for surface tension of polymer melt could only be obtained for low and moderate molecular weight polymers. This makes the test of SCF lattice simulation even more difficult³⁴.

In summary, up till now no theoretical tool is perfect enough to predict accurate surface tension of polymer or surface segregation of polymer blend. The weak points could either be the acquisition of accurate input information or the strictness of various assumptions. Sometimes complementary analysis from different theories or models may provide a more comprehensive understanding.

1.4 Outlines

There are various architectures for branched or hyper-branched molecules, and which architecture is of the highest surface affinity still remains unclear. Dendrimers and combs may seem to be superior to the others due to their apparently highly branched architectures. To experimentally test these structures very tricky and tedious synthesis steps are required. In order to point out the clear direction, in chapter 2 entropy-driven segregation of linear, star, dendrimer and comb shape polymeric additives in chemically similar linear polymer hosts is studied using self-consistent (SCF) mean-field lattice simulations⁴³. Provided the number of arms and molecular weight of the branched additives are maintained constant, we find that the simplest branched architecture, the symmetric star, exhibits the strongest preference for the surface of binary polymer blends.

In chapter 3, in order to experimentally evaluate the effect of polymer architecture on surface tension, we synthesized a series of four-arm and eleven-arm symmetric star polystyrenes through anionic polymerization²⁴. Surface tension was measured as a function of molecular weight of the stars and temperature in the melt using a modified Wilhelmy plate technique. Finally we prove that architectural effects do play a significant role in determining the molecular weight dependence of polymer melt surface tension. Both classical thermodynamic model and variable density lattice simulation were utilized to model the experimental data. Although they address different origins, the theoretical prediction from both models were found to be reasonably good.

In chapter 4, we added these symmetric star polystyrenes as additives into their linear counterparts to study its surface migration behavior⁵⁴. The basic tool here is again to measure the surface tension, but this time the surface tension was plotted versus the weight fraction of the additives to get a profile. Experimentally, we found a

convex surface tension profile for both linear/linear polystyrene blends and star/linear blends The latter blend shows a much more non-linear profile, indicating stronger surface segregation of the branched additives relative to linear chains. Consistent with the experimental data, Cahn-Hilliard theory predicts a larger surface excess of star molecules in linear hosts over a wide composition range. Significantly, this result is obtained assuming a nearly neutral interaction parameter between the linear and star components, indicating that the surface enrichment of the stars is not a consequence of complex phase behavior in the bulk star-linear blends.

Theoretically, other related experiments could be performed by making star polystyrene/linear deuterated polystyrene blend films and use surface characterization techniques to determine the surface enrichment. From the linear PS/linear DPS results, one realized that in such a blend system DPS is not always preferred at the surface. There exists a crossover molecular weight of PS, below which the DPS is depleted at the surface. For star/linear blend system, this crossover molecular weight of PS should move to higher molecular weight regime if other conditions are constant. However these are complementary experiments that are somehow equivalent to surface tension measurement we've done in Chapter 4.

Up till now experimentally people mostly focused their vision on surface tension of linear polymers or surface enrichment of linear/linear polymer blend system. Examples will be provided in later chapters in details. Some experiments studied the bulk interaction between chemically similar but topologically distinct species, such as star/linear blends. Through experiments, simulation and theoretical analysis, this dissertation makes its major contribution of a systematic study of the origin of surface migration advantage of branched molecules, surface tension of star polymers and surface segregation of star-like surface active additives.

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CHAPTER 2

Surface Segregation of Highly Branched Polymer Additives in Linear Hosts

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Qian, Z.; Minnikanti, V. S.; Archer, L. A.

2.1 Summary

Entropy-driven segregation of various branched and hyperbranched polymeric additives in chemically similar linear polymer hosts is studied using self-consistent (SCF) mean-field lattice model. The simulations account for the effect of molecular architecture on local configurational entropy in the blends, but ignores the effect of architecture on local density and blend compressibility. Star, dendrimer, and comblike additives are all found to be enriched at the surface of chemically identical linear host polymers. The magnitude of their surface excess increases with increased number of chain ends and decreases with increased segmental crowding near the branch point. Provided the number of arms and molecular weight of the branched additives are maintained constant, we find that the simplest branched architecture, the symmetric star, exhibits the strongest preference for the surface of binary polymer blends. We show that a single variable, here termed the "entropic driving force density," controls the relative surface affinities of branched additives possessing a wide range of architectures.

2.2 Introduction

Spontaneous surface segregation of miscible additives in a polymer host is important for both practical and scientific reasons. Spontaneous migration of functional additives, for example, provides a simple, physical means of functionalizing polymer surfaces to enhance their paintability, wetability, and adhesion characteristics, without the need for post-processing (e.g. plasma or chemical treatment). Migration of small-molecule, low-surface-energy additives in polymeric hosts is commonplace, and the mechanism is readily understood in terms of the enthalpic contribution the additive makes to the surface free energy. This understanding is widely used in engineering practice to rationalize, and even control, plasticizer, tackifier, lubricant, and colorant migration to the surface of engineering polymers. In contrast, surface segregation of polymeric additives in chemically similar polymer hosts is poorly understood because the conformational entropy of the chains introduces a spatially-varying contribution to the surface free energy that must be taken into account.

In a bulk polymer melt, ideal chain statistics apply and the chain configurations are three-dimensional random walks. The existence of an impenetrable surface reduces the number of conformations the polymer chain can adopt, which lowers its entropy.^{1,2} The smaller number of neighboring segments near chain ends implies that the end segments of a polymer chain are preferred at a surface because the entropy loss is lower, compared with the middle segments^{2,3}. This is the physical origin of the enhanced surface affinity of end segments of a chain. It is also the reason why lower molecular weight polymeric components in a polydisperse melt are entropically attracted to the surface of the melt, which can increase its tackiness. These effects are, however, easily reversed by small changes in the surface energy of the low molar mass species.^{4,5}

If the migrating species is a highly branched molecule, however, whose many ends are attracted to the surface, the entropic factors may not be as easily defeated by enthalpic ones. This effect has been nicely demonstrated in our recent surface tension measurements using branched polystyrenes.⁸ These measurements show that the surface tension of an 11 arm star polystyrene can approach those found in copolymer additives commonly used in commercial practice as surface tension control agents in polymers. Using self-consistent field (SCF) simulations on a variable density lattice, the exceptionally low surface tension of these highly branched star polystyrenes has been shown to originate primarily from an enhanced attraction of the chain ends to the surface.⁸ The star-shaped molecules are therefore, to our knowledge, the first example of a polymer system of any kind in which entropic effects can produce changes in surface affinity comparable to what can be achieved by changes in the chain end chemistry.

The success of star-shaped molecules in lowering the surface tension in the melt, suggests that other, more complex architectures, such as combs, dendrimers, and hyperbranched molecules can be potent candidates for polymer surface functionalization. In their pioneering study, Walton and Mayes⁹ simulated surface enrichment of comb-like polymer additives in comb/linear blends. These authors reported a much larger degree of surface segregation than for linear/linear polymer blend systems. Extrapolation of their predictions to more complex hyperbranched additives requires caution because the end attraction in complex branched polymers is balanced by repulsion of the multiply-connected branch points, which favors migration away from the surface.^{2,3,5-7} Nevertheless, from the perspective of the rapidly growing capabilities for molecular design in polymer chemistry laboratories, it is important to determine which of the growing list of molecular architectures, star, dendrimer, comb, or something else, would be the most effective candidate for designing polymer additives with high degrees of surface affinity.

In this work, we use SCF lattice simulations of an incompressible model to answer these questions. This choice of simulation approach is attractive because it introduces a minimal number of parameters, which facilitates clear comparisons between polymers encompassing a wide range of molecular architectures. We also ignore inevitable chemical differences between chain segments near the ends, midsections, and branch point of the polymer. These choices produce limitations and

drawbacks that must be kept in mind as the inevitable comparisons with actual systems are made. First, the mean field approximation will break down when chain lengths are too small to justify random walk statistics. The mean field assumption is further weakened when a polymer with finite total molecular weight, but possessing a multiply branched architecture is considered. Second, the incompressible lattice model assumes a constant total segment fraction near the surface layer, which is not necessarily true for real polymers that possess finite compressibility. Local density gradients near the surface^{10,11} of a compressible polymer can significantly alter the end-group surface affinity. We have previously studied this effect in detail and have shown that, for sufficiently high molecular weight additives, it enhances surface segregation and can be described quantitatively in terms of an enhanced chain-end surface attraction using a Linear Response Theory^{2,5-8}. Finally, even in the most carefully synthesized star/linear blend systems, chemical differences between the chain ends, midsections and branch point are possible. These effects introduce additional energetic contributions to the surface free energy of the blend, which have been reported to enhance the surface concentration of chain ends.¹²⁻¹⁸ Jalbert, et. al.¹³, for example, preformed incompressible lattice simulations for polymer chains with heterogeneous end segments and found that surface composition of the end groups increases as the energy difference (χ_s) between the end and middle segments is increased.

2.3 Simulation approach

The SCF mean-field lattice model based on the method proposed by Fleer et al. has been discussed extensively in the literature.^{5-7,19} Briefly, we assume a lattice matrix comprised of several lattice layers which encompass polymer layers that span the distance from the surface to bulk. Each Kuhn segment of a polymer chain, linear or branched, occupies one lattice. A consequence of the mean-field approximation is that all the variables in this space only change in the direction perpendicular to the surface plane. Given the position of the end segment of a linear chain on the lattice, a propagator $G_{i}[i, j]$ defines the relative weight of finding a tail segment of a size-i chain of polymer species k in lattice layer j. $G_k[1, j] = \exp(-u_k[j]/k_BT)$, where $u_k[j]$ is the surface potential field species k experiences at the surface layer j, k_B is the Boltzmann constant, T is the thermodynamic temperature of the system. $G_k[1, j]$ is the Boltzmann factor for finding a free unconnected segment of species k in layer j. Once it is known, the propagator for the tail segment of any linear chain with arbitrary size can be calculated for any species using a first-order Markov Process and known combination rules.¹⁹ If the component possesses a branched architecture, the calculation of the propagator of the joint segment utilizes "chain walking" and combination rules. Algorithms for modeling a wide range of polymer chain architectures are described in detail elsewhere^{5-7,19}. The surface volume fraction of any segment of a chosen architecture is determined by the composition law¹⁹, the surface volume fraction of the entire chain is just its architecture-dependent sum. The detailed calculations of propagator matrices and volume fraction profiles for linear, star, symmetric dendrimer, and symmetric comb architectures used in this study are provided in the Appendix. Figure 2.1 is a schematic for these typical hyper-branched structures.

All simulation results reported in this paper assume an athermal blend system comprised of 5 vol% additive polymer and 95 vol% of its chemically identical linear polymer host. While this choice has no effect on the conclusions reported, it preserves

the implicit asymmetry in composition of additive and host found in actual systems. In the absence of bulk interactions, both components experience a common hard-core potential of entropic origin. For such a blend system, the surface field potential is,^{5-7,19}

$$u_1[j]/k_B T = u_2[j]/k_B T = \phi_1^b/r_1 + \phi_2^b/r_2 + \alpha[j]$$
(2.1)

where ϕ_k^b is the bulk volume fraction for species k, r_k is the total number of Kuhn segments for species k, $\alpha[j]$ is the Lagrangian parameter needed to ensure incompressibility, $\phi_1[j] + \phi_2[j] = 1$ for any surface layer $j \cdot \alpha[j] = \zeta(\phi_1[j] + \phi_2[j] - 1)$, where ζ is a large parameter whose value is basically set by the ease of convergence of the program simulation and criteria for incompressibility.

An initial guess is made for the surface potential profile, and the propagator matrix and volume fraction profile of both species calculated. This allows a new surface potential profile to be calculated using Eqn(2.1), which can in turn be used to calculate a new propagator and volume fraction profile using the same algorithm. This iterative procedure continues until the difference between the new and previous potential is less than 10^{-4} to establish self-consistency. The only input information required in this calculation is the degree of polymerization and architecture of the blend components.

Figure 2.1 Schematic illustrating how stars, dendrimers, and comb-like architectures are assembled in the SCF simulations. The total segments 1 is the only adjustable variable in simulations of linear molecules L(l). In a symmetric star labeled S(f;1) both the number of arms f and the number of segments 1 in each arm can be independently adjusted. For an asymmetric star labeled Sf $(l_1, l_2, l_3, \ldots, l_f)$, the number of arms f and the number of segments in each arm, $(l_1, l_2, l_3, \ldots, l_f)$, can be adjusted. Likewise for dendrimer chains designated Df $(l_1, l_2, l_3, \ldots, l_f)$, the number of generations n, the arm functionality within each generation f, and the number of segments for each arm (from outside to inside), $(l_1, l_2, l_3, \ldots, l_n)$, can be adjusted. Finally, for combs designated Cf (l_1, l_2, l_3) , the number of arms f, the number of segments in each arm l_1 , between adjacent arms l_2 and between the last arm and the chain end, l_3 can be adjusted. N_1 and N_2 are, respectively, the total number of segments belonging to the additive and its linear host polymer, which can be easily calculated for any architecture and substructure once the information is input.



By systematically adjusting each of these variables and characterizing their effect on the surface composition profile, SCF simulations allow us to study how the overall branched structures and substructures of branched polymer chains influence surface segregation. Throughout, we will use the variables N_1 and N_2 to define the total number of segments in the branched additives and linear host, respectively. The surface excess Z_1^* of the additive species is defined as $Z_1^* = \sum_{j} (\phi_1[j] - \phi_1^b)$, where j is surface lattice layer number, $\phi_1[j]$ is the volume fraction of the additive at layer j, and ϕ_1^b is the bulk volume fraction, which as pointed out earlier is maintained fixed at 0.05 in this work. For simplicity, the degree of polymerization of the additive (component 1) is fixed for different architectures and substructures. Our specific goals are to explore the effect of number of chain ends on surface excess of branched molecules, and to determine the effect of molecular substructure on surface excess.

2.4 Results and discussion

Typical surface volume fraction profiles for linear L(946), 3-arm star S(3*315), 12-arm comb C12(45,45,45) and a 12-ends dendrimer D3(45,45,45) additives with the same overall degree of polymerization (946) and at a fixed bulk volume fraction of 5% in a linear host polymer L(1000) are provided in Figure 2.2. In all cases studied, a surface excess of the additive species is observed and the volume fraction profile manifests a characteristic "crested" shape, which grows as the additive's architecture is made progressively more complex. Specifically, the surface excess created by the comb and dendrimer architectures are decidedly larger than those of the linear and symmetric star additives with the same degree of polymerization. This finding is consistent with expectations based on the notion that chain ends are on average more entropically favored at surfaces than midsection

segments, or branch points. It follows that because the dendrimer and comb possess more ends per molecule they are attracted more and manifest a larger surface excess.

There are nonetheless subtle differences between the volume fraction profiles for dendrimer and comb additives, even with the same number of chain ends. These differences can be related to the surface layer thickness, which is itself related to the radius of gyration Rg of the additive. This analysis suggests that for the same number of chain ends, the more compact molecular structure (dendrimer) is preferred at the surface because it produces the narrower surface layer thickness. This effect presumably arises from the greater ease of accommodating compact molecular structures in the surface region without incurring significant entropic penalty. Fredrickson² has suggested that the variable R_g^2/V , where V is the chain molecular volume, is related to the conformational entropy of chains near a surface. Figure 2.3 explores the effect of the additive molecular size on the surface excess for various symmetric star and linear additive species blended with a linear host polymer with a dimensionless (scaled by the Kuhn step size) R_g of 5. It is apparent from the figure that there is a unique value of R_g for each star additive beyond which it is depleted at the surface. This critical R_g value is respectively, 5.0, 4.62, 4.32, 4.24, and 4.16 for linear, 3-arm, 4-arm ,5 arm and 6-arm symmetric star. Furthermore, it is apparent from the figure that even at fixed R_g the surface excess of the stars is a strong function of molecular architecture. We therefore conclude that despite its physical appeal, the gyration radius of the additive is insufficient to characterize its relative surface excess.



Figure 2.2 Surface volume fraction profiles for star, dendrimer, and comb-like additives in a linear polymer host, L(1000). The bulk concentration of the additive is fixed at 5 vol% and N_1 maintained at 946 for all additives.



Figure 2.3 Surface excess of symmetric star additives in linear hosts as a function of the radius of gyration R_g of the stars. N_1 and the number of star arms are varied to adjust R_g . N_2 is maintained at 150, giving a dimensionless $R_g = 5$ for the linear host polymer

To explore these effects in greater detail, we simulated symmetric blends $(N_1 = N_2)$ of dendrimers and combs for which the number of segments within each branch is maintained fixed at 10, but (I) the number of generations of the dendrimer, (II) the arm functionality within each generation, and (III) the number of arms for the comb-shaped molecules are respectively varied. This allows us to investigate three different ways of increasing the number of chain ends within a given architecture. The volume fraction profiles obtained for Cases (I) and (III) are illustrated in Figs. 4(a) and 4(b), respectively. The profile for case II are similar to case I and are therefore not shown. Figure 2.4(a) shows that for dendrimer additives with fixed arm functionality and branch molecular weight, the surface excess increases with generation number. By generation four, the dendritic additive manifests a surface excess more than one order of magnitude larger than the three arm star. This result confirms the important role of chain end attraction to the surface enrichment of the additive. Figure 2.4(b) is the analogous result for comb-branched additives. Again the combs with the greater number of arms are selectively enriched.

Figure 2.4(c) summarizes the effect of architecture and number of chain ends on the surface excess. For low numbers of chain ends, architecture is unimportant. At larger numbers of ends, the surface excess of combs grows linearly with increased number of branches, but that of dendrimers, particularly the Df type, is quite nonlinear. Thus, even though a D3(l, l, l, l) dendrimer and a C24(l, l, l) comb are of nearly identical architecture, they possess the same number of arms, branch points, and even connector geometry, their surface excess is noticeably different. The differences are even larger when Df, Cf, and D3 type polymers with the same number of chain ends are compared. Thus, contrary to expectation from linear response theory, the number of arms, chain ends or branch points, is not the critical determinant of surface excess. This result implies that something else controls the surface excess of the branched additive, and whatever it is, it must be a function of the detailed "substructure" of the polymer.

To investigate the effect of molecular substructure, Figures 2.5a and 2.5b compare the volume fraction profiles for dendrimer and comb additives in which the number of arms is fixed at 24 and the number of dendrimer generations fixed at 4. For the isomers of dendrimer, $l_1 \sim l_4$ are tuned to resemble two extreme cases, 3-arm star and 24-arm star; for the isomers of combs, $l_1 \sim l_3$ are also tuned to resemble two extreme cases, linear and 24-arm star. It is readily appreciated from both figures that the different additive substructures yield significant differences in the surface excess. The figures also show that more compact architectures yield higher levels of surface enrichment. Dendrimer and comb-like additive architectures therefore seem to be the most promising of the popular polymer architectures to functionalize polymer surfaces. However, the dendritic structure that yields the highest surface excess is the one in which the segments are equally distributed in each branch, that is $l_i=l_j$, where i $\neq j$. This structure is therefore qualitatively the same as a symmetric star polymer, with the same number of arms.

Figure 2.4

(a) Surface volume fraction profiles for a series of dendrimers in symmetric blends ($N_1 = N_2$) with linear hosts. The number of segments within each branch is maintained at 10 and the arm functionality within each generation is fixed at 3.

(b) Surface volume fraction profiles for a series of combs in symmetric blends ($N_1 = N_2$) as a function of the number of branches f. The number of segments within each branch is maintained at 10.

(c) Surface excess of combs and dendrimers in symmetric blends ($N_1 = N_2$) with linear host polymers. The number of chain ends are allowed to increase in different ways. Triangles are for the case where the number of branches f of the comb is increased; rectangles are for the case where f is fixed at 3, but the number of generations of a dendritic additive increases; circles correspond to dendrimers where the number of generations is fixed at 3 but the functionality f in each generation is varied.





Figure 2.4(b) (continued)



Figure2.4(c) (continued)





Figure 2.5(a) Surface volume fraction of dendrimer additives, generation number 4 and functionality within each generation as 3, in the symmetric blend ($N_1 = N_2 =$ 946). The dendrimer substructure is manipulated by varying l_1 , l_2 , l_3 , and l_4 .



Figure 2.5(b) (continued) Surface volume fraction of 24-arm comb additives in symmetric ($N_1 = N_2 = 946$) comb/linear blends. Substructures are again manipulated by varying l_1 , l_2 , and l_3 .

The results above indicate that a balance between the number of chain ends and degree of segmental crowding within the branched core determines the degree of surface enrichment of architecturally complex polymer additives in linear hosts. The primary segment fraction, f_s, 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, provides one way to parameterize this balance. Figure 2.6 plots the surface excess for a wide range of polymer architectures as a function of their primary segment fraction; the linear ($f_s = 0$) and symmetric star ($f_s = 1$) architectures are the two limits for this curve because linear chains lack a branch point and all segments of a symmetric star connect a branch point to a chain end. The figure shows that plotted in this way, surface excess data for combs, dendrimers, linear chains, and symmetric stars all collapse, approximately, to a single universal curve. This finding confirms that the primary segment fraction is indeed a good variable for characterizing the relative ease with which symmetric polymer architectures segregate to interfaces in branched/linear blends. While it is possible to define a unique primary segment fraction for symmetrically branched architectures, f_s is insufficient to parameterize the combined effect of chain-end attraction and branch-point repulsion for asymmetrically branched molecules. Figure 2.7 considers two cases where the number of arms, total number segments, and primary segment fraction are the same, but the architectures possess different levels of asymmetry. The figure shows that structures sharing the same primary segment fraction but with higher level of molecular symmetry provides higher surface excesses than the asymmetric structures. The symmetric star architecture maximizes both the symmetry and primary segment fraction requirements for surface enrichment.



Figure 2.6 Surface excess of dendrimer and comb additives in the symmetric blend system defined in Figure 5. Results are plotted versus the primary segment fraction defined in the text. In each case the substructure of the additives are allowed to change by varving the number of segments in each arm.



Figure 2.7 Surface excess of two types of asymmetric stars in symmetric blends ($N_1 = N_2 = 937$). Results are presented as a function of the short arm length. The number of segments is varied to create asymmetric stars with different substructures.

A simple generalization of the two effects can be obtained by analogy to the response theory for polymer surface segregation.^{2,3,5-7} Specifically, this theory assumes that all branches are of infinite length and the entropic attraction of chain ends to the surface and entropic repulsion of the branch points are localized at the end and branch point, respectively. In a real polymer additive the molecular weight is finite, which means that the end-attraction and branch-point repulsion are felt over some number of chain segments near the actual end and branch points. As a first approximation, segments within a few correlation lengths from a chain end can be thought to experience an entropic attraction to the surface that decays exponentially in strength with position from the end. Likewise, each segment near the branch point can be thought to experience a net entropic repulsion from the surface that decays with distance of the segment from the branch point. Physically, this situation is analogous to a chain of connected balloons, each filled with gas of density slightly above, equal to, or slightly lower than that of the surrounding linear host. In this picture, the density is lowest near the end-point and highest near the branch-point and falls off (or rises) exponentially with distance from the branch point (or end). The influence of the surface is then experienced as a gravity-like field on each segment.



Figure 2.8 Schematic for qualitative comparison of entropic surface segregation ability within families of branched structures deduced from the entropic driving force density considerations outlined in the text. The greater than symbol is used here to indicate that the molecule with the structure to the left has a greater surface affinity under the conditions specified.

A segment with a lower ranking index from the end/tail is thus more likely to be at the surface. Thus, for a finite molecular weight additive any architecture change that leads to a net increase of segments with low ranking index from the end will lead to an increase in the surface excess. It is then apparent why the symmetric star architecture leads to the greatest surface excess. Any other architecture or substructure can be created by continuously moving segments from more attractive positions in a symmetric star polymer to less attractive positions. Using this simple rule, the relative surface affinities, or "entropic driving force densities" (keeping the analogy to segments of graded densities in a gravity-like field), of branched polymers in different families have been compared, and the results summarized in Figure 2.8.

As pointed out in the introduction, other factors not captured in the incompressible lattice model are expected to influence the surface excess of branched polymeric additives in linear hosts. One of the most important is the enthalpic contributions that arise from unavoidable chemical differences between the additive and host material, and between the chain ends and midsection segments of branched molecules. We have shown previously how these effects can be taken into account in computing the surface excess in branched linear blends.^{6,7} Another important contribution is expected to originate from the bulk compressibility of the additive and host material. Our recent PVT studies using symmetric stars, show that even the bulk compressibility is influenced significantly by the number of chain ends.⁸ The effect of compressibility on surface excess can in principle be calculated in a compressible lattice model, but requires a suitable lattice equation of state that can account for the effect of molecular architecture on density. The Sanchez and Lacombe (SL) equation of state²⁰ does not provide for an architecture influence on the density. Developing a lattice based EOS for architecturally complex polymers is a significant undertaking

and is outside the scope of the present study. Based on results for lattice simulations of linear/linear polymer blends in the compressible model,⁷ we nonetheless expect that compressibility will enhance the effective attraction polymer chain ends and magnify the architectural effects described in this study.

2.5 Conclusions

Using SCF lattice model in an incompressible model we have analyzed surface segregation for star, dendrimer and comb-branched additives in linear polymer hosts. These simulations are attractive because they allow us to evaluate the influence of purely entropic effects due to molecular architecture and substructure on surface affinity of polymers. We find that introduction of multiple symmetrically placed branches in an additive dramatically change the surface volume fraction profile and the surface excess. We further show that a new parameter, defined as the primary segment fraction collapses surface excess data for all symmetrically branched polymer architectures into a single universal curve. At one end of the spectrum are linear chains which have the lowest affinity for the interface. At the other extreme are symmetric stars for which the entropic attraction of the ends to the surface most dominates the repulsion of the branch point, producing the strongest surface affinity. For asymmetrically branched structures of finite molecular weight, we show that an analogy to the linear response theory can be formulated that captures the balance of end-attraction and branch-point repulsion on surface affinity. Specifically, this analysis is used to define a "ranking-index" rule, which is in turn employed to correctly predict the relative surface affinity of polymers with a range of architectures.

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APPENDIX: CALDULATION OF PROPAGATORS AND VOLUME FRACTION PROFILES FOR LINEAR, STAR, DENDRIMER AND COMB POLYMER ADDITIVES

 $G_k[i, j]$ describes the relative weight of an end/tail segment of a linear polymer chain(species k) with i segments to be in surface layer j. It is determined by a first-order Markov process. Thus, the propagator of a tail segment with chain size i in surface layer j is the linear combination of that of the tail segment with chain size i-1 in adjacent surface layer j-1, j, j+1.

$$G_k[i,j] = G_k[1,j](\lambda_1 G_k[i-1,j-1] + \lambda_0 G_k[i-1,j] + \lambda_1 G_k[i-1,j+1])$$
(A2.1)

where $G_k[1, j] = \exp(-u_k[j])$ is the Boltzmann factor for finding a free unconnected segment of species k in lattice layer j, $u_k[j]$ is....., $\lambda_1 = 1/6$, $\lambda_2 = 4/6$ is lattice parameter for cubic lattice.

Now let's consider a generic substructure that includes a branch point. Fig. 9 is a schematic representation for such a substructure, with different arm lengths n_1 , n_2 , n_3 and a corresponding set of propagators G_k^a , G_k^b and G_k^c , determined from the precursor chains. Because any branched architecture can be divided into such units, the approach can be used to describe any branched polymer. We assume the propagator of the initial segments for different arms are determined as $G_k^a[1, j], G_k^b[1, j], G_k^c[1, j]$, (for simplicity we choose index 1 in this example), and calculate the segmental volume fraction profile of the filled segment (Figure 2.9).



Figure 2.9 Schematic for the branched substructure employed to formulate propagator relations for any arbitrary branched linear polymer blend system.

Using Eqn.(A2.1), we can obtain:

$$G_{k}^{t}[i+1,j] = G_{k}[1,j](\lambda_{1}G_{k}^{t}[i,j-1] + \lambda_{0}G_{k}^{t}[i,j] + \lambda_{1}G_{k}^{t}[i,j+1]), t = a, b, c...$$
(A2.2)

The propagator of the joint segment is then computed as, $G_k^a[n_1+1, j], G_k^b[n_2+1, j]$. If we consider the joint segment as the initial unconnected free segment of the third arm and the middle segment as the connector for the first two arms, then we can calculate:

$$G_k^d[1,j] = G_k^a[n_1+1,j]G_k^b[n_2+1,j]/G_k[1,j]$$
(A2.3)

$$G_k^d[i+1,j] = G_k[1,j](\lambda_1 G_k^d[i,j-1] + \lambda_0 G_k^d[i,j] + \lambda_1 G_k^d[i,j+1])$$
(A2.4)

The volume fraction of the filled segment in lattice layer j, $\phi_2[s, j]$, is given by,

$$\phi_k[s,j] = \phi_k[s,\infty] G_k^c[n_3 - s,j] G_k^d[s+1,j] / G_k[1,j]$$
(A2.5)

where $\phi_k[s,\infty]$ is the volume fraction of segment with ranking index s in the bulk, ϕ_k^b/r_k . Here, r_k is the total number of segment of species k. This prefactor arises because the surface potential is chosen with reference to the bulk. The volume fraction for the joint segment is:

$$\phi_k[s',j] = \phi_k[s',\infty] \frac{G_k^a[n_1+1,j]G_k^b[n_2+1,j]G_k^c[n_3+1,j]}{(G_k[1,j])^2}$$
(A2.6)

where s' is an arbitrarily chosen number that depends on the ranking index order.

The total volume fraction of polymer chains in any lattice layer is simply a summation of contributions from all segments,

$$\phi_k[j] = \sum_{i=1}^{r_k} \phi_k[i, j]$$
(A2.7)

where r_k is degree of polymerization of species k.

Note that if the branched architecture is a p-arm structure ($p \ge 3$), the volume fraction of one segment in the p th arm can be obtained by generalizing Eqns. A2.3 and A2.6 to yield:

$$G_k^{p+1}[1,j] = \frac{\prod_{t=1}^{p-1} G_k^t[n_t+1,j]}{(G_k[1,j])^{p-2}}$$
(A2.8)

$$\phi_{k}[s',j] = \phi_{k}[s',\infty] \frac{\prod_{t=1}^{p} G_{k}^{t}[n_{t}+1,j]}{(G_{k}[1,j])^{P-1}}$$
(A2.9)

The denominator in Eqn. A2.8 accounts for the joint segment being over multiplied by a factor of p-2 when calculating the propagator of the joint segment of a p-1 arm branch structure. Likewise, Eqn. A2.9 accounts for the over multiplication by p-1 times when calculating the volume fraction of joint segments of a p arm branch structure.

With this generalization, calculation of the propagator matrix and volume fraction profiles for myriad branched architectures are readily achievable.^{5-7,19} The final task is to arrange the ranking index of the propagators and segments to produce the most efficient algorithm for simulating complicated architectures. In the following, we outline our approach for calculations involving stars (generalized to asymmetric), symmetric dendrimers and symmetric combs.

Simulating Stars

We assume a p arm star structure such as Fig.1(a), with variable number of arm segments $r_1, r_2, r_3, \dots, r_p$. The total number of segments in the star is $r = \sum_{f=1}^{p} r_f + 1$. In order to calculate the volume fraction of any segment of this structure, p+1 types of propagators are needed. We designate the "free" tail propagator as G[i, j], and other "branched head" propagators as G'[i, j, f], where $f = 1, 2, \dots, p$. The calculation of G[i, j] follows exactly the form of Eqn. A2.1. The calculation of G'[i, j, f] is straightforward,

$$G'[1, j, f] = \frac{\prod_{k=1}^{p} G[r_k + 1, j]}{G[r_f + 1, j](G[1, j])^{p-2}}$$
(A2.10)

$$G'[i+1, j, f] = G[1, j](\lambda_1 G'[i, j-1, f] + \lambda_0 G'[i, j, f] + \lambda_1 G'[i, j+1, f])$$
(A2.11)

We use $\phi[i, j, f]$ to represent the volume fraction of the *i* th segment of arm *f* in lattice layer j, and use $\phi[j]$ to represent the volume fraction of the whole chain at lattice layer j,

$$\phi[i, j, f] = \frac{\phi^b}{r} \frac{G[i, j]G'[r_f + 2 - i, j, f]}{G[1, j]}$$
(A2.12)

$$\phi[j] = \phi[r_1 + 1, j, 1] + \sum_{f=1}^{p} \sum_{i=1}^{r_f} \phi[i, j, f]$$
(A2.13)

where ϕ^{b} is bulk volume fraction of this species and the first term in right-hand side is the volume fraction for the joint point.

Simulating Symmetric Dendrimer Chains

We assume a symmetric dendrimer structure as in Fig. 1(b) comprised of n generations and branch functionality p. From outside to inside, we designate arms/branches generation by generation as arms 1, arms 2,.....arms n, respectively with corresponding number of segments for each arm as r_1, r_2, \ldots, r_n , thus the total number of segments is $r = \sum_{k=1}^{n} p(p-1)^{k-1} r_{n+1-k}$. In order to calculate the volume fraction of any segment of this structure, 2n kinds of propagators are needed. We designate the propagators as G[i, j, f], $f = 1, 2, \ldots, 2n$. Except for the free tail type propagator G[i, j, 1], we basically walk along one path of the dendrimer from one end to the other(end-to-end path). Every time when a new joint point is met, from which we can start to create a new propagator series(total number of propagator series is 2n-1) using known propagator series(see Fig.1(b) as an example when n=3). The symmetry of the dendrimer structure ensures that any segment can divide the whole molecule into several parts whose propagators are just several of those already known propagators. The calculation of G[i, j, 1] follows exactly the form of Eqn. A2.1. The calculation of other propagators is:

$$G[1, j, f] = \frac{(G[r_{f-1} + 1, j, f-1])^{p-1}}{(G[1, j, 1])^{p-2}} \quad \text{if } 2 \le f \le n+1$$
(A2.14)

$$G[i+1, j, f] = G[1, j, 1](\lambda_1 G[i, j-1, f] + \lambda_0 G[i, j-1, f] + \lambda_1 G[i, j+1, f])$$
(A2.15)

$$G[1, j, f] = \frac{G[r_{2n+2-f} + 1, j, f-1](G[r_{2n+1-f} + 1, j, 2n+1-f])^{p-2}}{(G[1, j, 1])^{p-2}} \quad \text{if } n+2 \le f \le 2n$$

(A2.16)

$$G[i+1, j, f] = G[1, j, 1](\lambda_1 G[i, j-1, f] + \lambda_0 G[i, j-1, f] + \lambda_1 G[i, j+1, f])$$
(A2.17)

We use $\phi[i, j]$ to represent the volume fraction of the *i* th segment along the half end-to-end path in lattice layer *j* (from the tail segment to center segment, in this case $1 \le i \le 1 + \sum_{f=1}^{n} r_f$), and use $\phi[j]$ to represent the volume fraction of the whole chain at lattice layer j, then:

$$\phi[i,j] = \frac{\phi^b}{r} G[r_1 + 1, j, 2n] \qquad \text{if } i = 1, \qquad (A2.18)$$

$$\phi[i,j] = \frac{\phi^b}{r} \frac{G[i,j,k]G[r_k - i + 2, j, 2n + 1 - k]}{G[1,j,1]} \quad \text{if} \quad 2 + \sum_{f=1}^{k-1} r_f \le i \le r_k + \sum_{f=1}^{k-1} r_f \text{ (A2.19)}$$

$$\phi[i,j] = \frac{\phi^b}{r} \frac{G[r_{k+1}+1,j,2n-k](G[r_k+1,j,k])^{p-1}}{(G[1,j,1])^{p-1}} \quad \text{if} \quad i = 1 + r_k + \sum_{f=1}^{n-1} r_f , \qquad (A.20)$$

where $k \subseteq [1, n]$ is a positive integer determined in the inequality condition in Eqn. A2.19 and A2.20 then plugged into the previous equations. For simplicity and universalism of the equation, we define $\sum_{f=1}^{0} r_f = 0$.

$$\phi[j] = \phi[1 + \sum_{f=1}^{n} r_f, j] + \sum_{f=1}^{n} \left\{ \sum_{i=r_{f-1}+1}^{r_{f-1}+r_f} (p-1)^{n-f} \phi[i, j] \right\}$$
(A2.21)

where the first term in right-hand side is the volume fraction for the center point.
Simulating Symmetric Combs

We assume a p arm comb structure like Fig.1(c), with different number of segments for different types of part(2 type a tails, p-2 type b teeth and p-3 type c branches with the number of segment as r_a , r_b and r_c), thus the total number of segments is $r = (p-2)r_a + (p-3)r_b + 2r_c + 1$. For simplicity we only consider this comb structure with an even number of type b teeth. In order to calculate the volume fraction of any segment of this structure, 3p/2-2 kinds of propagators are needed. We designate the propagators as G[i, j, f], $f = 1, 2, \dots, 3p/2 - 2$. Except for the free tail type propagator G[i, j, 1], we basically travel to any branch, and every time when a new joint point is met, from which we can start to create a new propagator series(total number of propagator series is 3p/2-2) using known propagator series(see Fig.1(c) as an example). The symmetry of the dendrimer structure ensures that any segment can divide the whole molecule into two parts, propagators for which are already known. The calculation of G[i, j, 1] follows exactly the form of Eqn. A2.1. For the calculation of other propagators, we ignore the Markov process (Eqn. A2.2, A2.11, A2.15, A2.17) and only show the algorithm for the joints. Note that the calculation of the propagator of a "late" visited joint requires a calculation of the propagator for an "early" visited joint.

$$G[1, j, f] = \frac{G[r_c + 1, j, 1]G[r_c + 1, j, 1]}{G[1, j, 1]} \qquad \text{if } f = 2 \qquad (A2.22)$$

$$G[1, j, f] = \frac{G[r_b + 1, j, f - 1]G[r_a + 1, j, 1]}{G[1, j, 1]} \qquad \text{if } 3 \le f \le p - 2 \qquad (A2.23)$$

$$G[1, j, f] = \frac{G[r_b + 1, j, p - 2]G[r_a + 1, j, 1]}{G[1, j, 1]} \qquad \text{if } f = p - 1 \qquad (A2.24)$$

$$G[1, j, f] = \frac{G[r_b + 1, j, p - 2]G[r_c + 1, j, 1]}{G[1, j, 1]} \qquad \text{if } f = p \qquad (A2.25)$$

$$G[1, j, f] = \frac{G[r_b + 1, j, f + 1 - p]G[r_b + 1, j, 2p - 2 - f]}{G[1, j, 1]} \quad \text{if } p + 1 \le f \le 3p/2 - 2$$

(A2.26)

We use $\phi[i, j]$ to represent the volume fraction of the *i*th segment along the "half comb" in lattice layer *j*, here we count the segments from one side of comb by sequencing type c tail, joint point, type a "teeth", type b branch, joint point, type a teeth, type b branch and so on until we reach the joint point belonging to the middle branch on the other side. $\phi[j]$ represents the volume fraction of the chains at lattice j.

$$\phi[i,j] = \frac{\phi^b}{r} \frac{G[i,j,1]G[r_c + 2 - i,j,p-1]}{G[1,j,1]} \quad \text{if } 1 \le i \le r_c$$
(A2.27)

$$\phi[i,j] = \frac{\phi^b}{r} \frac{G[i,j,1]G[r_a+1,j,1]G[r_b+1,j,p-2]}{(G[1,j,1])^2} \quad \text{if } i = r_c + 1$$
(A2.28)

$$\phi[i,j] = \frac{\phi^b}{r} \frac{G[i-r_c,j,p]G[r_a+r_c+2-i,j,1]}{G[1,j,1]} \quad \text{if } r_c+2 \le i \le r_a+r_c+1 \quad (A2.29)$$

$$k = 2, 3, \dots, \frac{p}{2} - 1$$

$$\phi[i,j] = \frac{\phi^b}{r} \frac{G[i - (k-1)r_a - (k-2)r_b - r_c, j, k]G[(k-1)r_a + (k-1)r_b + r_c + 2 - i, j, p-k]}{G[1, j, 1]}$$

if
$$(k-1)r_a + (k-2)r_b + r_c + 2 \le i \le (k-1)r_a + (k-1)r_b + r_c$$
 (A2.30)

$$\phi[i,j] = \frac{\phi^b}{r} \frac{G[r_a+1,j,1]G[r_b+1,j,k+1]G[r_b+1,j,k]}{(G[1,j,1])^2}$$
 if $i = (k-1)r_a + (k-1)r_b + r_c + 1$

$$\phi[i,j] = \frac{\phi^b}{r} \frac{G[i - (k-1)r_a - (k-1)r_b - r_c, j, k+p-1]G[(kr_a + (k-1)r_b + r_c + 2 - i, j, 1]}{G[1, j, 1]}$$

if
$$(k-1)r_a + (k-1)r_b + r_c + 2 \le i \le kr_a + (k-1)r_b + r_c + 1 = t_1$$
 (A2.32)

$$\phi[i,j] = \frac{\phi^b}{r} \frac{G[i - (\frac{p}{2} - 1)r_a - (\frac{p}{2} - 2)r_b - r_c, j, \frac{p}{2}]G[(\frac{p}{2} - 1)r_a + (\frac{p}{2} - 1)r_b + r_c + 2 - i, j, \frac{p}{2}]}{G[1, j, 1]}$$

if
$$t_2 = (\frac{p}{2} - 1)r_a + (\frac{p}{2} - 2)r_b + r_c + 2 \le i \le (\frac{p}{2} - 1)r_a + (\frac{p}{2} - 1)r_b + r_c = t_3$$
 (A2.33)

Thus
$$\phi[j] = 2\sum_{i=1}^{t_1} \phi[i, j] + \sum_{i=t_2}^{t_3} \phi[i, j]$$
 (A2.34)

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CHAPTER 3

Surface Tension of Symmetric Star Polymer Melts

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3.1 Summary

To evaluate the effect of polymer architecture on surface tension, glass transition, and other thermodynamic properties, we synthesized a series of four-arm and eleven-arm symmetric star polystyrenes. Surface tension was measured as a function of molecular weight of the stars and temperature in the melt using a modified Wilhelmy plate technique. We find that architectural effects play a significant role in determining the molecular weight dependence of polymer melt surface tension. A variable density lattice model that considers effects of entropic attraction of polymer chain ends to surfaces, compressibility and density gradients in the region near the surface is used to determine the origin of this observation. This analysis is complemented with surface tension calculations using more classical thermodynamic models that consider only bulk property changes with polymer architecture and molecular weight. Bulk thermodynamic properties for selected stars were derived from pressure-volume-temperature (PVT) measurements. These data are used to calculate the cohesive energy density (CED). This was then used to determine surface tension of the stars using a recently developed theory. Possible effects of the chemical differences of the sec-butyl terminal groups versus the backbone segments are also discussed in terms of bulk property modification and surface segregation of end groups.

3.2 Introduction

The surface tension of a molecular fluid is its excess free energy per unit area of surface.¹ For small-molecule liquids, the excess energy results from missing neighbors at the surface, and the surface tension is completely specified by the energetic interactions between molecules in the bulk.¹ The surface tension of a polymer is generally higher than that of a liquid of its unconnected constituent

monomers both because the number of accessible molecular conformations is lower at the surface,² and the bulk density of the polymer molecule is higher.^{3,4} There are two principle approaches to the theory of polymer melt surface tension. The first focuses on the limit of high molecular weight (M_n) and uses lattice models to predict the entropic and enthalpic contributions in the limit of large M_n . For a linear polymer in the limit of high M_n , this "entropic" contribution to the excess surface energy varies as $B - CM_n^{-\alpha}$, where α is a positive number of order unity,^{2,5-11} B is the "infinite molecular weight" contribution to the surface tension, and the parameter C quantifies the decrease in the infinite molecular weight conformational entropy contribution for finite polymer molecular weights. At large M_n , the generally larger "local" enthalpic contribution to the surface tension is also expected to be of the form, $D - EM_n^{-1}$. This form simply assumes that the local enthalpic contribution follows a reciprocal dependence on M_n analogous to other bulk thermodynamic properties (the end group effect).⁴ Equation of state models can be used to both describe this molecular weight dependence,⁴ and to estimate the coefficients D and E.

In the high molecular-weight limit, it was proven experimentally several years ago that the surface tension varies as M_n^{-1} ,¹² while it has been known for a much longer time that for very low M_n the dependence is weaker, $\gamma : M_n^{-2/3}$.^{12,13} As almost all other bulk properties vary as M_n^{-1} , ^{4,14} this latter observation has sparked much interest.¹³

There are many possible contributions of polymer chain ends to the molecular weight dependence of surface tension. First, chemical heterogeneity of end segments, compared with the middle segments, can produce enthalpic attraction of chains to the surface. It can also modify the bulk thermodynamic properties, including density, of the entire material, which influences the surface tension. Second, chain ends have extra degrees of freedom inaccessible to other segments of a polymer chain.⁴ For large

molecules, this leads to configurational entropy differences within the chain, wherein the whole polymer chain experiences a greater penalty than the ends for residence at a surface. ² In this work, we perform variable density SCF lattice simulations and apply classical thermodynamic models to understand the roles played by both effects on the surface tension of symmetric star and linear polystyrenes. A straightforward comparison between experimental data and ideal theoretical calculations allows the relative importance of these effects to be evaluated.

The literature of how surface/bulk properties of branched macromolecules affects their surface activity is sparse.¹⁵⁻²³ Detailed experiments by Elman, et al.¹⁵ and Jalbert, et al.^{16,17} have explored surface and interface segregation of polymers containing end groups that are neutral, attractive and repulsive to surfaces. Elman, et al.¹⁵ reported experimental evidence for surface enrichment/depletion of the corresponding end groups from neutron reflection studies of end functionalized polystyrenes. End-group effects on surface tension have proven very difficult to confirm experimentally. Surface excess profiles of deuterated and hydrogenated PS blends have shown that the surface tension may not be substantially modified by the presence or absence of a sec-butyl chain end.¹⁸

Lee and Foster^{19,20} anionically synthesized regularly branched molecules (polybutadiene and polystyrene), and studied thermodynamic properties, such as glass transition temperature, thermodynamic bulk interaction parameters, and phase diagrams of these branched molecules blended with their linear counterparts. Walton, Irvine, Mayes et al.²¹⁻²³ performed self-consistent mean-field lattice simulation blends of branched and linear polymers, and also experimentally studied the surface functionalization of a polylactide bioscaffold by utilization of a comb-like additives. Both simulation and experimental results indicate surface segregation of branched architectures.

3.3 Theoretical background

Compressible lattice theories that consider the effects of polymer chain entropy, finite compressibility, and density gradients on surface properties (e.g. surface tension and surface excess composition of a more surface active species in a blend), have recently been developed for polymer systems of widely varying architectures.^{11,23} Similar analyses based on incompressible lattice models underpredict these properties, indicating that the melt compressibility is an important determinant of the surface behavior. Linear response theory in the limit of high M_n has been shown to provide a good method for approximating surface properties obtained either using incompressible or compressible lattice models.^{11,24} This theory is advantageous for analyzing surface tension data because it yields a simple, analytical formula for the surface tension $\gamma|_M$ of an arbitrarily branched polymer with a functional form similar to those described above.⁹⁻¹¹

$$\gamma|_{M} \cong \gamma|_{\infty} + \frac{\rho_{b}RT\left(n_{e}U^{e} + n_{j}U_{ne}^{j}\right)}{M_{n}}$$
(3.1)

Here, $\gamma|_{\infty}$ is the surface tension of a theoretical infinite M_n polymer, which includes a contribution from the conformational constraints experienced by polymers in the limit of infinite molecular weight, and n_e and n_j are, respectively, the number of ends and branch points. U^e and $U_{ne}{}^j$ can be interpreted, respectively, as the "effective" attraction and repulsion of the ends and branch points to the surface. Considering chain ends to be chemically identical to the midsections, this model predicts that polymer chain ends are attracted towards the surface and the branch point is repelled away from it ^{9,10} making U^e is negative and $U_{ne}{}^j$ positive. Thus, even for the simplest branched polymer structure (the symmetric star), for which $n_j = 1$, this

equation predicts that the surface tension can be manipulated by changing the number of star arms. Furthermore, because U^e can also be a function of polymer chain-end chemistry, the effect can be amplified by these additional energetic components, as already illustrated for linear^{16,25} and hyperbranched polymers ²⁶ by suitable end functionalization of chain ends. In extreme cases of end-group modified linear polymers, Jalbert et. al.¹⁶ and McLain, et al.,²⁵ have in fact shown that such energetic contributions can provide a substantial driving force for a surface excess of chain ends.

It is well known that the larger degree of freedom associated with chain ends can also have a dramatic effect on the way bulk properties, such as density, glass transition, and cohesive energy density (CED), vary with polymer molecular weight.¹⁴ Dee and Sauer have shown that PVT data for many polymers and oligomers can be used to calculate their surface tension.^{4,27-29} This methodology ignores all aspects of chain architecture, or even chain connectivity, but is found to account very well for bulk thermodynamic property differences from changes in chemical structure and especially changes in Mn. These models²⁷⁻²⁹ can also partially account for the configurational entropy penalty of having high M_n chains at sharp interfaces.²

An equation of state (EOS) provides a simple means of capturing the thermodynamic information contained in measured PVT data.^{4,30} The Flory, Orwoll, and Vrij (FOV) equation has been extensively used to represent thermodynamic data for polymer melts.³¹ It can be adapted to provide an analytical expression for the surface tension of a liquid,³²

$$\widetilde{\gamma} = \gamma / \gamma^* = \left\{ -\frac{m}{\widetilde{V}} - T \ln \left[\frac{b \widetilde{V}^{1/3}}{\widetilde{V}^{1/3} - 1} \right] \right\} / \widetilde{V}^{2/3}$$
(3.2)

Here $\gamma^* = (0.11kP^{*2}T^*)^{1/3}$; k is Boltzmann's constant; where $\tilde{V} = v_{sp} / v_{sp}^*$ is the reduced specific volume, and P^* , V^* and v_{sp}^* are the critical pressure, temperature, and specific volume. These parameters are obtained by fitting the FOV EOS to thermodynamic data. Eqn.3.2 evidently has both an enthalpic and an entropic component. The relative magnitude of the two can be captured empirically by the values of the parameters m and b.^{27,28,32} For many polymers, this methodology yields estimates for the surface tension that are in good agreement with experimentally determined values.^{27,29}

3.4 Experimental

Benzene (Aldrich, >99%) and styrene were respectively purified using nbutyllithium and dibutylmagnesium. Living polystyrene chains with a range of molecular weights were synthesized using standard anionic techniques and secbutyllithium initiator. The polymerization reaction was initiated on a vacuum line and transferred to a MBraun glove box, where the polymerization was allowed to proceed for 24 hours under protection of nitrogen gas "boil off" from a liquid nitrogen source. To produce symmetric star polymers, the living poly(styryl)lithium chains were mixed in purified benzene with two multifunctional chlorosilane linking agents, bis(methyldichlorosilyl)butane (Gelest, >95%), to produce 4-arm stars, and 1,2,3,4,5,6-hexakis [(2-methyldichlorosilyl) ethyl] benzene, to produce 11-arm stars. A large excess of poly(styryl)lithium living chains ([Si-Cl/PS-Li]) was added to the selected linking agent to ensure high linking efficiency. The reactants were continuously stirred for several days to ensure that the linking reaction goes to completion. Excess living chains were terminated by degassed isopropanol. Salts created in the termination and linking steps were removed in a water wash performed in a separating funnel. Highly purified star polymers were obtained by fractionation in

a good solvent (toluene) – poor solvent (methanol) mixture.

Molecular weights of the resultant star polystyrenes and their linear precursors were characterized using matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry (MacroMass). Dithranol and Silver trifluoroacetate were used as the matrix and cationizing agent, respectively. MALDI-TOF measurements were complemented by size exclusion chromatography (SEC), performed using a Viscotek SEC comprised of four mixed bed columns and equipped with a laser light scattering detector (TDA302). Because of their small size, MALDI-TOF provides a more accurate means of characterizing the precursor molecular weight. Table 3.1 shows that for the 4-arm star polystyrene series, the experimentally determined molecular functionality is very close to the theoretical value, 4, for the linker used, irrespective of the arm molecular weight. In the case of the "11-arm" series, MALDI-TOF indicates functionalities close to 11, which is slightly lower than the theoretical maximum of 12 for the specific linker used. These differences are expected for high arm functionalities such as those attempted here, and can arise from multiple including imperfection of the 1,2,3,4,5,6-hexakis sources, [(2methyldichlorosilyl) ethyl]benzene linker itself, and the steric hindrance around the branch point. Molecular weights of the linear precursors of the 4-arm and 11-arm stars, the actual star functionalities, polydispersities, and glass transition temperatures are given in Table 3.1.

number	PS	Mn of	Mn of star	PDI of	Functionality ^c	T _g (°C)
of arms	sample	arm ^a	PS^{a}	star PS ^b		-
4	R25	470	2000	1.03	4	45
	R26	1150	4800	1.03	4.1	69
	R27	1500	6300	1.02	4.1	79
	R28	1750	7400	1.03	4.2	84
	R29	3200	12600	1.01	3.9	90.5
	R30	4000	16.8	1.03	4	93.8
11	R33	510	5900	1.03	10.6	64
	R34	660	7500	1.03	10.6	69
	R35	760	8800	1.03	10.9	73.5
	R36	1400	15800	1.04	10.9	81.5
	R37	2680	29000	1.04	10.6	92
	R38	5400	59000 ^b	1.03	10.8	100.5

Table 3.1: Polymer characterization

 ameasured by MALDI-TOF; bmeasured by SEC; cestimated from (M_{n,star}-M_{n,core})/M_{n,arm,}

The "micro"-Wilhelmy wetting method¹² was used for molten polymer surface tension measurements. In this method the standard Wilhelmy plate¹³ is replaced by a small-diameter clean glass fiber. A large increase of the viscous relaxation rate of the wetting meniscus due to the small wetting probe size provides substantially increased accuracy.^{4,12,33} Only about 0.1 gram of sample is required for the measurements. For relatively non-polar high surface energy polymers like high-M_w PS, wetting can become marginal at temperatures below 200 °C.³⁴ This finite contact angle can affect the liquid or melt surface tension measured by Wilhelmy plate or fiber techniques, even with a "clean" glass surface.³⁵ The surface tension values for many of the PS stars studied and lower M_w linear chains are sufficiently low that incomplete wetting or non-zero contact angles above 160°C only have a negligible effect on the measurements. This effect arises from the fact that the polymer surface tension decreases as temperature rises, while the glass surface free energy remains approximately constant due to its low thermal expansion coefficient.³⁵ Reliable surface tension measurements for non-polar polymers such as PS, also require that adsorbed water on the glass surface is minimized.³⁵

A Gnomix dilatometer was used for the PVT measurements of linear PS controls as described previously ³⁰. Because of the large sample volume required for these measurements, they were limited to a single representative 4-arm and one 11-arm star. Differential Scanning Calorimetry (DSC) (TA Instruments 2920, NewCastle, DE USA) was used to determine the mid-point glass transition temperature (T_g) of all materials used in the study.



Figure 3.1 Temperature dependent surface tension for representative linear, 4arm star and 11-arm star PS with different molecular weights

3.5 Results and Discussion

The surface tension for all polymers studied was measured as a function of temperature. Figure 3.1 provides temperature dependent surface tension data for representative linear and star PS molecules with molecular weights, M_n , in the range 1.8k to 20k. It is apparent from the figure that the slopes for all polymers are quite similar. This observation implies that changes in thermal expansion and other related bulk properties are unaffected by polymer molecular weight and architecture in the range studied. Comparison of the surface tension data at fixed temperature, however, reveals large changes with molecular weight and architecture over this same range.

Figure 3.2, for example, illustrates both the effect of polymer molecular weight and architecture on γ at a temperature of 160^oC. The values of γ for linear, 4-arm, and 11-arm symmetric star polystyrenes all manifest approximately linear dependences on $1/M_n$, with architecture-dependent slopes. The results in the figure indicate that polystyrenes with unusually low surface tension can be accessed at modest molecular weights simply by increasing the number of arms in the stars. This effect has never been seen before in such a series, especially at the higher branch numbers.

A straight-line fit of the experimental surface-tension values in Figure 3.2 yields an architecture-independent intercept $\gamma|_{\infty}$, and a slope of $\rho_b RT \left(n_e U^e + U_{ne}^j \right)$. These fits yield $\gamma|_{\infty} \sim 30.8$ mN/m, consistent with that extracted from published data for the linear controls.⁴ Table 3.2 summarizes the slopes, and the theoretical predictions will be discussed below.



Figure 3.2 Surface tension $\gamma|_{M}$ of linear and star polymers as function of inverse molecular weight M_{n}^{-1} at 160 ⁰C. Circles are linear PS, squares 4-arm star PS, and diamonds 11-arm star PS. The filled symbols are the predictions based on the PVT analysis, discussed later, for the respective systems.

Polymer architecture	$\rho_b RT(n_e U^e +$	$\rho_b RT(n_e U^e + U_{ne}^j) \left(\frac{mJ \cdot Kg}{m^2 \cdot mole}\right)$				
	Model value	Experimental value				
Linear	-4.6	-3				
4 arm star	-7.1	-10				
11 arm star	-20.2	-28				
With values of $U^e = -0.651nm$, $U_4^j = 0.607nm$ and						
$U^{j} = 1.502 \mu m$ estimated through entropic consideration using						

Table 3.2: Initial slope of surface tension vs inverse molecular weight

 $U_{11}^{j} = 1.503 nm$, estimated through entropic consideration using self consistent field theory of a polymer on a variable density lattice model.¹¹

The major factor governing γ is evidently the presence of chain ends. This is seen qualitatively in Figure 3.3 where the data are observed to converge to an approximate universal curve when normalized to account in some way for the ends. More specifically, the M_n of the arms appears to empirically scale the data but only if the linear molecule is assumed to have one end; i.e., the M_n for the "arm" is the M_n of the entire chain.



Figure 3.3 Surface tension $\gamma|_{M}$ of linear and star polymers at 160 0C as function of corrected inverse molecular weight. The term M_{arm}^{-1} is used to correct for the number of chain ends. Open circles are linear PS assumed to have 1 arm, open squares are 4-arm star PS, and open diamonds represent 11-arm star PS.

It is possible to estimate the contribution of the attraction of ends and repulsion of branch points to the surface tension of symmetric star polymers from self consistent field theory (SCF) simulations of a polymer on a lattice in the framework of Scheutjens and Fleer.³⁶ The technique to estimate these entropic potentials is described elsewhere.^{9,10} If a lattice polymer is considered to be completely incompressible, the value of the entropic attraction of the ends U^e is found to be -0.0975 in lattice spacing units.¹⁰ On a lattice, a polymer is typically considered to make a random walk on a length scale of a Kuhn length.³⁶ Hence taking a lattice spacing as one Kuhn unit which for polystyrene is 1.8nm,³⁷ one obtains a value for U^e to be -0.1755 nm. As is the case here, Kumar and Jones ^{38,39} have shown that considering a polymer to be incompressible significantly underestimates the derivative of surface tension with inverse molecular weight $d\gamma/d(1/M)|_{M\to\infty}$. Wu and Fredrickson considered the effect of finite compressibility on the linear response theory, but nonetheless compute the surface tension only in the incompressible limit.⁸ Walton and Mayes²³ also performed self-consistent mean-field calculations to study the effect of chain architecture on surface segregation. These authors found that the finite compressibility of polymer chains influence γ through its effect on density gradients at the surface. Minnikanti and Archer ^{10,11} showed that compressibility effects significantly increase the effective chain end attraction to a surface. Using a variable density lattice model that considers the effects of finite compressibility and density gradients, ¹⁰ U^e for a polystyrene like lattice polymer at 160°C was estimated to be -0.651nm which is substantially larger than the value -0.1755 nm, deduced for the incompressible model. In a similar fashion the entropic repulsion of the joint point of a branched molecule with n_e branches can be estimated.¹⁰ These values can be used to estimate the variable $\rho_b RT(n_e U^e + n_j U_{n_e}^j)$ for the linear and symmetric star polymers, the results are compared with their experimentally determined counterparts in Table 3.2. Here ρ_b is

taken to be the mass density of an infinite molecular weight polystyrene at 160° C and is determined using experimental data fit to the Sanchez and Lacombe (SL) equation of state ⁴⁰ to be 989 kg/m³, and U^e is computed in the variable density lattice model. It is evident from the table that the theoretical and experimentally determined slopes are in reasonably good agreement for the linear, four-arm, and eleven-arm stars. Considering the lack of precision of the experimental data, and the qualitative nature of the variable density contributions effectively extracted from the SL equation of state and used in the prediction of U^e and U_{ne}^{j10} , the theoretical prediction could be considered as quite good.

Chemical difference between the chain ends, linker, and backbone styrene segments can make contributions to U^{e} and U^{j}_{ne} . Additionally, (Eqn.3.1) is strictly only correct in the limit when the radius of gyration of the polymer is large compared to the Kuhn step length, which is not true for some of the polymers studied. For some of our samples, each arm is only about one Kuhn segment, so some deviation of the model prediction at low molecular weight is expected. However, for each architecture studied there are several samples of high-enough molar mass that lattice simulations can be regarded as predictive. Finally, the variable density lattice SCF calculations themselves introduce several well-documented errors.³⁶ Considering all of these potential sources of error, the good agreement between the calculated and experimental slopes seen in Table 3.2 imply that the variable density lattice calculations capture many of the important physics governing the surface tension of star molecules. Specifically, the comparisons show that the effect of polymer "architecture" on variable density lattice analysis of surface tension can by itself account for much of molecular weight on the surface tension of symmetric star polystyrenes.

One could go a step further in this analysis to obtain a rough estimate of the

specific contribution made by chain end chemical heterogeneity to the surface tension. Specifically, the end attraction per arm, U^e, can be separated into an "architecture" U^e_a contribution and a chemical U^e_c contribution (U^e = U^e_a+ U^e_c). The latter contribution reflects chemical differences between chain ends and midsections. If all other sources of discrepancy between the variable density lattice SCF calculated slopes and the measured ones (Table 3.2) are ignored, U^e_c can be readily computed for the four-arm and eleven-arm stars. This calculation yields U^e_c \approx -0.852 nm for the eleven arm stars and U^e_c \approx -0.854 nm for the four-arm stars. The similarity of the two values is consistent with what one would expect for stars, such as the ones used in the study, where the chain end chemistry is the same (i.e. sec butyl). The values of U^e_c also show that the end-group chemistry has a significant effect on the surface tension of the stars (its contribution to U^e is comparable to that provided by the purely entropic attraction of chain ends). Its overall effect on the experimentally deduced values of $d\gamma/d(1/M)|_{M\to\infty}$ is nonetheless modest, at most 35% for the four-arm and eleven-arm stars.



Figure 3.4 Differential Scanning Calorimetry (DSC) curves showing the glass transition temperature region for 11-arm star PS samples of different molecular weights and for 2 linear PS control samples. \dot{Q} is the heat flow rate.

Figure 3.4 provides DSC data for a wide range of 11-arm stars, and two linear controls. The glass transition for the stars are generally slightly broader than for the linear controls. R37 is one of the the highest molecular weight polymers ($M_n = 29,000$ kg/mol), but is comprised of low molecular weight arms ($M_n = 2,680$ kg/mol). The arms on all the others stars are substantially shorter, and may contribute to the breadth of T_g because the centers of the molecules are rigid.

Glass transition temperatures for the linear and star polymers deduced from the DSC data are presented in Figure 3.5 as a function of polymer molecular weight. It is apparent from the figure that T_g becomes progressively lower with increasing number of branches at a given total polymer M_n . These results are roughly consistent with changes anticipated from the larger degrees of freedom associated with chain ends.^{14,41} It is also possible that the sec-butyl end group has some contribution. The extrapolated T_g in the limit of infinite M_n is also seen to be approximately the same for the stars and linear materials, also in agreement with previous studies.^{42,43} Normalization of the data to the length of the longest chain segment (i.e., number of arms/[2M_n]), over-corrects the T_g data for the 11-arm (i.e., 5.5/M_n) (see Figure 3.6). This observation indicates that the effect of the increased number of chain ends on the glass transition is partially counteracted by the rigid branch points.⁴² Figure 3.6 in fact shows that a much weaker scaling, 2.75/M_n, correctly reduces the T_g data for the 11-arm star samples, underscoring the strong influence of the branch point in counteracting changes in the bulk T_g produced by chain architecture.



Figure 3.5 Glass transition temperature (T_g) of linear and star polymers as function of inverse molecular weight M_n^{-1} . Squares are linear PS, triangles 4-arm star PS, and circles 11-arm star PS.



Figure 3.6 Glass transition temperature (T_g) of linear and star polymer as function of inverse molecular weight of the longest chain segment. Squares are linear PS, diamonds 4-arm star PS, and triangles 11-arm star PS.

To evaluate how changes in bulk properties influence surface tension for some of these star polymers, PVT data were obtained for two 4-arm, and one 11-arm star PS, and representative linear PS molecules. Figure 3.7(a) - (c) provide a summary of the raw data for the stars. Gross comparison of these figures indicate that PS architecture only has a small effect on the shape of the V-T profiles at any given pressure. A more detailed analysis can be performed by first fitting the measured PVT data to the FOV Equation-of-state.⁴ These fits can be used to compute the CED for the respective polymers, and from it, to calculate the surface tension.^{27,28} The measured and calculated (from PVT) surface tensions for linear and star-PS samples are provided in Figure 3.8. Refinements that have been included in the PVT/CED analysis consider the slight offset in the scaling curves due to conformational entropy of chains confined at narrow interfaces, particularly for high molar mass, large radii of gyration chains.^{27,28} Specifically in this analysis, the 7.5k 11-arm star and the 0.7k linear PS samples were considered to be in this low M_n limit because of their very small R_g , which decreases the predictions by about $6\%^{28}$. Because of the much larger radii of gyration, the 4.8k and 6.3k 4-arm stars, and the 21.4 k linear molecules, these materials were considered to be in the large chain limit.



Figure 3.7(a) Pressure-Volume-Temperature data for linear polystyrene, $M_n = 21400$



Figure 3.7(b) (Continued) Pressure-Volume-Temperature data for 4-arm star polystyrene, $M_n = 6300$



Figure 3.7(c) (continued) Pressure-Volume-Temperature data for 11-arm star polystyrene $M_n = 7500$.

With the traditional definition of Gibbs dividing surface, the experimental versus temperature for selected polymers in Figure 3.8 show that the surface entropy $-\partial \gamma/\partial T$ is similar for many of the polymers in the range of molecular weight studied. This effect has never been measured before for a highly branched star. It is nonetheless consistent with the fact that the thermal expansion coefficient for these polymers and oligomers are similar. Only for very low molecular weight species $-\partial \gamma/\partial T$ and the thermal expansion coefficient vary from the polymer/oligomer values, and because of the high thermal expansion coefficient, $-\partial \gamma/\partial T$ is larger for solvents^{3,4,13}. This is seen to a small degree in the PVT generated curve in Figure 3.8 where the curve is slightly steeper for the 0.7 k linear PS.

It is apparent from Figure 3.8 that the calculated surface tensions agree well with experiment for the two linear polymers, over the entire range of temperature studied. For all three stars, the method correctly captures the temperature-dependence of the surface-tension, but underpredicts the surface tension values. These effects are also seen for the surface tension data at 160° C plotted in Figure 3.2. This figure indicates that, especially with the 4-arm stars, there is a trend toward theoretical values lower than those observed from experiment. If there was a surface activity of segments related to the sec-butyl containing termination, or surface excess of a low M_w fraction due to the slight polydispersity, we would expect the PVT-based predictions to be higher than the experimentally measured surface tension values. Here, the opposite effect is observed, indicating the lack of a substantial excess of sec-butyl ends. Evidentially, some elements of the physics responsible for the surface tension of the stars are not captured by the PVT-based analysis. Measurements using a wider range of star molecular weights are planned to explore these effects in more details.



Figure 3.8 Comparison of PVT-based predictions with experimental surface tension data

Previous studies have shown that the surface tension of polystyrene may not be substantially modified by the presence or absence of a sec-butyl chain end¹⁸. Further evidence of the relative importance of end group segregation to the surface tension can be deduced from the PVT predicted surface tension. Our results show that the surface tension predicted from PVT measurements on the stars are generally lower than the experimentally measured values (Figure 3.2 and 3.8). This finding suggests that the end-group surface enrichment of sec butyl groups reported by Elman et al.¹⁵ does not have as significant an effect on the surface tension as do bulk thermodynamic property changes due to the star architecture and end groups, at least for our system. In closing we also note that Jalbert, et. al. ¹⁶ also performed incompressible lattice simulations for polymer chains with heterogeneous end segments and compared their simulation results with experimentally measured surface tension of end-functionalized PDMS. These authors found that greater surface segregation of end groups with more surface energy difference(χ_s) between the end and middle segments. However, if χ_s is not too large, the effect on the molecular weight dependence on surface tension is also small.

3.6 Conclusions

We present the measurements of surface tension for symmetric star polymer melts with variable number of arms and molecular weights. We find that molecular architecture plays a very important role in determining the surface tension of polymers. Specifically, for 11-arm symmetric star polystyrenes the melt surface tension is about 15% lower than linear chains at molecular weights around 7 Kg/mol. Using results from a variable density lattice model that considers the effects of finite compressibility and density gradients,^{10,11} a simple response theory is used to explain the influence of entropic and enthalpic contributions of chain ends on the surface tension of stars. This analysis indicates that both contributions are responsible for the lower surface tensions observed in PS stars. It also suggests that even without chain end functionalization, substantial reductions in a polymer's surface tension can be achieved through changes in its architecture.

We also use PVT measurements to characterize the effect of polymer architecture on bulk thermodynamic properties. This latter approach, while applicable to all values of M_n , appends an entropic contribution due to conformational constraints that is only applicable in the limit of large M_n .⁵ A solution to this problem is to set this contribution to zero for small radius of gyration chains. ^{27]} These measurements also show that polymer architecture can affect surface tension through its influence on the bulk thermodynamic properties, mainly due to the reduced melt density and CED with increasing numbers of chains ends. A comparison of the measured and calculated (from the CED) surface tension values suggests that chemical heterogeneity due to the sec-butyl terminal groups has a negligible effect on melt surface tension of the polymers used in this study.

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CHAPTER 4

Surface Tension of Polystyrene Blends: Theory and Experiments

Submitted to J Polym Sci Part B Polym Phys 2008 Qian, Z.; Minnikanti, V. S.; Sauer, B. B.; Dee, G. T.; Archer, L. A.

4.1 Summary

Surface tension of linear-linear and star/linear polystyrene blends were measured using a modified Wilhelmy method. Our results show that for both polystyrene blend systems, the surface tension - composition profile is convex, indicating a strong surface excess of the component with lower surface energy. Star/linear blends display a more convex surface tension profile than their linear-linear counterparts, indicating stronger surface segregation of the branched component relative to linear chains. Self-consistent field (SCF) lattice simulations (both incompressible and compressible models) and Cahn-Hilliard theory were used to predict surface tension-composition profiles for blends. Lattice simulations reproduce a small surface tension differences at high molecular weights but are inappropriate at the low molecular weights where the largest surface tension differences are observed experimentally. To implement the Cahn-Hilliard density gradient theory, pressurevolume-temperature (PVT) data for each of the pure components in the blends were first measured and the data used as input for the theory. Consistent with the experimental data, Cahn-Hilliard theory predicts a larger surface excess of star molecules in linear hosts over a wide composition range. Significantly, this result is obtained assuming a nearly neutral interaction parameter between the linear and star components, indicating that the surface enrichment of the stars is not a consequence of complex phase behavior in the bulk star-linear blends.

4.2 Introduction

Polymer materials have been extensively used in many industrial applications, such as coating, adhesion, packaging and painting, where physical and chemical control of polymer or polymer blend surfaces is important. Fundamental questions related to wetting, foaming, and compatibilization of polymer mixtures require understanding of the surface tension (γ) of mixtures. In most applications, polymer materials include additives of one type or another that are expected to modify bulk and/or surface properties. Surface tension modifiers, for example, are required at the polymer surface and strategies for promoting surface migration are desired. It is generally understood that accurate measurements of surface tension of binary polymer blends provides a good starting point for studying surface segregation. The small differences in γ of the pure components, and the difficulty in making accurate polymer melt surface tension measurements have, until recently, limited such studies.¹ The study reported in Ref 1 used a modified Wilhelmy method to characterize surface tension of linear-linear PDMS and PS-PVME blends as a function of polymer molecular weight and concentration. Results from this study were shown to agree quantitatively with polymer blend surface tension predictions based on the Cahn-Hilliard theory.¹

Polymer additives with highly-branched architectures have recently attracted interest in both scientific and industrial fields. For example, polystyrene containing poly(benzyl ether) dendrimer additives² has been shown to manifest enhanced wettability, compared to the polystyrene host. Likewise, ultrafiltration membranes comprised of polyacrylonitrile(PAN) matrix with polyacrylonitrile-graft-poly (ethylene oxide) comb copolymer additives³ have been found to possess anti-fouling ability, not present in the PAN material alone. Finally blends of linear polyesters with hyperbranched polyester additives⁴ have been reported to considerably lower the surface tension of typical linear polymer matrix with weight fraction of 1%. While it can be concluded from these sort of studies that highly branched additives are typically more surface active than their linear hosts, until recently,⁵ very little attention has been devoted to determining which of the many branched molecular topologies provides the greatest surface activity. Specifically, using SCF simulations on an incompressible

lattice, we recently reported⁵ that the symmetric star should manifest greater surface affinity than other, more commonly used, hyperbranched additives architectures such as dendrimers or combs of comparable molecular weights and degrees of polymerization.

Previously, we presented measurements⁶ of surface tension for symmetric star polystyrene melts with variable number of arms and molecular weights. These studies confirmed that the surface tension of star polymers can be dramatically lower than those of their linear counterparts of comparable molecular weight. It follows that highly-branched star polymer additives in a chemically similar, compatible, linear host material should manifest lower surface energy than expected for the bulk blend. This follows both from the lower surface energy of the star component and a slightly unfavorable bulk interaction⁷ between two components in the blend. Wu and Fredrickson^{8,9}, and Minnikanti and Archer^{10,11}, proposed a linear response theory that explains this effect in terms of a so-called entropic attraction of chain ends to surfaces and thermodynamic features of the blend near a surface and in bulk. In a binary polymer blend, both analyses lead to a simple closed-form expression for the surface excess, Z_1^* of the lower molecular weight and/or more branched blend species,

$$Z_{1}^{*} = -(1/2) \left(\Delta U_{1}^{s} + \frac{n_{1}^{e} u_{1}^{e} + n_{1}^{j} u_{1}^{j}}{N_{1}} - \frac{n_{2}^{e} u_{2}^{e} + n_{2}^{j} u_{2}^{j}}{N_{2}} \right) / \left(\frac{1}{2 N_{1} \phi_{1}} + \frac{1}{2 N_{2} \phi_{2}} - \chi \right)$$
(4.1)

Here in a binary polymer blend system, Z_1^* is surface excess of species 1, ΔU_1^s is integrated strength of relative attraction of segments of species 1 towards the surface. u_k^e and u_k^j are the integrated attractions of the end and the joint segments towards the surface of species k; n_k^e and n_k^j are the number of end segments and joint segments; N_k and ϕ_k are the number of Kuhn segments and bulk volume fraction, respectively. The numerator of Eqn. 4.1 can be determined from the surface tension difference between the two blend species, while sum of first two terms in the denominator is recognized as the Flory interaction parameter at the spinodal, χ_s . χ is the bulk interaction parameter. Thus, in additional to the effect of chain architecture on the surface excess of species 1 (additive) is determined by the ratio of the surface energy difference between the additive and host polymer to the difference between χ_s and χ . Compared with linear structures, additives with a highly-branched architecture are therefore expected to manifest greater surface affinity both as a result of explicit features of their architecture (more chain ends increases the numerator) as well as from more subtle effects of architecture on the Flory interaction parameter. A detailed theoretical and experimental study of star/linear blend systems is needed to shed light on these effects.

4.3 Experimental

Materials. Benzene (Aldrich, >99%) and styrene were respectively purified in advance using n-butyllithium and dibutylmagnesium. Living polystyrene chains of specified molar mass were synthesized by mixing predetermined amounts of secbutyllithium initiator and purified styrene in benzene in glass reactors in a glove box filled with dry N_2 . To produce symmetric star polymers, the living poly(styryl)lithium chains were mixed in purified benzene with two multifunctional chlorosilane linking agents, bis(methyldichlorosilyl)butane (Gelest, >95%), to produce 4-arm stars, and 1,2,3,4,5,6-hexakis [(2-methyldichlorosilyl) ethyl] benzene, to produce 11-arm stars. Excess living chains were terminated by degassed isopropanol. Lithium salts created in the termination or linking step were washed by water in a separating funnel. Highly purified star polymers were obtained by fractionation in a good solvent – poor solvent (toluene - methanol) mixture.

Molecular weights of the resultant star polystyrenes and their linear precursors

were characterized using matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry (MacroMass) and size-exclusion chromatography (SEC). Dithranol and trifluoroacetate were used as matrix and cationizing agents, respectively, for polystyrene samples. MALDI-TOF provides a more accurate means of estimating the oligomeric precursor molecular weight than more commonly used methods such as size-exclusion chromatography, the latter is better suited for polymers in the medium and high MW range. Table 4.1 shows that for the 4-arm star polystyrene (R26), the experimentally determined molecular functionality is very close to the theoretical value, 4, for the linker used, irrespective of the arm molecular weight. In the case of the "11-arm" series (R33, R34), MALDI-TOF indicates functionalities closer to 11, which is slightly lower than the theoretical maximum of 12 for the specific linker used. These differences are expected for high arm functionalities such as those attempted here and can arise from multiple sources, including imperfection of the 1,2,3,4,5,6-hexakis [(2-methyldichlorosilyl) ethyl]benzene linker itself, and steric hindrance around the branch point.

number	PS	Mn of	Mn of star	PDI of		T (00)	
of arms	sample	arm ^a	PS ^a	star PS ^b	Functionality	$I_g(C)$	
linear	1.79k	1790	/	1.2	1	61	
linear	9k	9000	/	1.06	1	92	
linear	35k	35,000	/	1.06	1	105	
4	R26	1150	4800	1.03	4.1	69	
11	R33	510	5900	1.03	10.6	64	
11	R34	660	7500	1.03	10.6	69	

Table 4.1: Polymer characterization

^ameasured by MALDI-TOF; ^bby SEC; ^cestimated from (M_{n,star}-M_{n,core})/M_{n,arm}

Linear polystyrene samples were from Pressure Chem. Co. ($M_n=9k$ and $M_n=35k$) and Scientific Polymer Products Co. ($M_n=1.79k$). Molecular weights of the linear polystyrene samples, linear precursors of the 4-arm and 11-arm stars, the experimentally determined star functionalities, polydispersities, and glass transition temperatures⁶ are given in Table 4.1.

Differential Scanning Calorimetry (DSC) (TA Instruments 2920, NewCastle, DE USA) was used to determine the mid-point glass transition temperature (T_g) of the materials. It was also used to ensure the blended materials are in single-phase region. Specifically, all PS samples were solvent (toluene) blended, and the solvent evaporated at elevated temperature (around 200°C) under vacuum with a N₂ purge. Some of the blends are low-viscosity liquids in the melt, suggesting that melt blending in the thin (1mm thick) layers at the bottom of the 20 ml beakers used in the Wilhelmy measurement should be possible. However, DSC measurements revealed incomplete mixing even after annealing these melt blends for up to an hour at ca. 200°C. A systematic study of powder blending followed by better mixing in a thicker liquid layer showed sharp glass transitions identical to those achieved for the solvent aided blends. This DSC study also included higher MW linear samples in an effort to reduce the entropy of mixing and make miscibility less favorable. In the case of linear-35k toluene mixed with 11arm-5.9k, the glass transition was sharp and indicated complete miscibility. The Tg versus blend composition curve was also linear for a series of linear-35k 11arm-5.9k blends of different composition, as was the case for all blends studied here which is another indication of miscibility and close to neutral interaction parameter χ for all systems studied here.

The "micro"-Wilhelmy wetting method¹² was used for molten polymer surface tension measurements. In this approach the conventional Wilhelmy plate is replaced by a small-diameter clean glass fiber. This method is attractive for a variety of reasons.

A large increase of the viscous relaxation rate of the wetting meniscus due to the small wetting probe size provides substantially increased accuracy.^{12,13} Only about 0.1 gram of sample is required for a measurement, which is important for these studies where some polymers are of limited quantity. For relatively non-polar, high surface energy polymers like high MW PS, wetting can become marginal at temperatures below 200°C. The resultant finite contact angle can affect the liquid or melt surface tensions measured by Wilhelmy plate or fiber techniques even with a "clean" glass surface. Because many of the PS stars or lower MW linear polymers studied here have lower values of γ , this source of experimental error is removed and accurate surface tension measurements are possible above 160°C¹³. A set of four blend systems were chosen for surface tension and other measurements; lin-1.79k /lin-9k, 4arm-4.8k/linear 9k, 11arm- 5.9k/lin-9k, and 11arm- 7.5k/lin-9k. Later we discuss the importance of bulk thermodynamic data for understanding the surface tension of blends. To facilitate such analysis, a Gnomix dilatometer was used to characterize PVT properties of linear polystyrenes and star polystyrenes. The data for the stars is the first of its kind and were published recently.⁶ A detailed description of the PVT measurement procedure and data analysis can be found in the literature.¹⁴ For solid polymers at room temperature the densities were measured using an autopycnometer (Micrometrics).

4.4 Results and Discussion

To study the surface tension of linear/linear and star/linear homopolymer blends, three symmetric star polystyrenes were solvent blended with linear polystyrene sample with MW of 9k (4arm-4.8k/linear 9k, 11arm- 5.9k/lin-9k, 11arm- 7.5k/lin-9k). A linear sample with a molecular weight of 1.79k was also blended with linear 9k sample as a control. The surface tension of these blends was measured as a function of temperature and composition using the modified Wilhelmy method described above.



Figure 4.1 Experimentally measured surface tensions of an 11-arm star 5.9k/linear 9k blend plotted versus temperature at different weight fractions of the star.

Figure 4.1 provides temperature and composition dependent surface tension data for 11arm star 5.9k/linear 9k polystyrene blends. The surface tension of the pure star and pure 9k linear were also measured. The total surface tension difference is around 5 mN/m in the experimental temperature range, and it is even smaller for other blend systems, especially for linear 1.79k/linear 9k blend control. The experimental accuracy at elevated temperatures is ca. $\pm 0.2mN/m$, which allows us to distinguish the composition dependence of blend surface tension. The slopes for all curves in Figure 4.1 are readily seen to be quite similar. This is likely a result of the fact that the thermal expansion and temperature dependence of other bulk polymer properties that set this slope do not vary substantially over the range of blend compositions.⁶ To our knowledge, this is the first report of composition dependent surface tension data of star/linear polymer blends.

Figure 4.2(a) illustrates the composition dependence on γ of this star/linear blend at a fixed temperature of 180^oC. The data were obtained by interpolation of the fitted straight line for surface tension versus temperature at fixed star weight fraction. A highly non-linear relationship between the blend surface tension and weight fraction of the stars is clearly evident from the data. The surface tension is in fact seen to drop substantially with addition of small amounts of the star component and at around 30w% of the star PS, it reaches a limiting value close to that of the pure star component. This finding is important because it indicates an extreme enrichment of the star component at the surface. It also nicely demonstrates the utility of highlybranched architecture species as surface active additives in polymer hosts.



Figure 4.2(a) Surface tension of 11arm star 5.9k/linear 9k blend plotted as function of weight fraction of component 1 at 180° C

Experimental surface tension data for other star/linear or linear/linear blend systems are summarized in Figures 4.2(b), (c) and (d), which, respectively, report the surface tension of 11arm star 7.5k/linear 9k, 4arm star 4.8k/linear 9k and linear 1.79k/linear 9k polystyrene blends at 180^oC. Similar trends for the surface tension versus composition are observed for star/linear and linear/linear blend systems, but the latter yields a somewhat less convex curve (see Figure 4.2d, for example). The curvature of the surface tension versus composition plot for the linear/linear polystyrene blend is qualitatively similar to that reported earlier for linear/linear PDMS blends,¹ although the latter were based on blends of polydisperse polymers/oligomers.

In order to more systematically compare the shape of the surface tension for linear/linear and star/linear blend systems versus composition, we define a normalized surface tension, $\gamma_n = (\gamma - \gamma_1)/(\gamma_2 - \gamma_1)$, which ranges from 1 to 0 in a binary blend with increasing weight fraction w of the lower surface tension component (1). γ_k is the surface tension of component *k*. Figure 4.3 is a plot of the normalized surface tension for all materials studied, as a function of star/linear polymer volume fraction. It is apparent from the figure that the surface tension of the star/linear blends collapse onto a single curve, that is distinct from what is observed for the linear-linear blends. It should be noted that the magnitude of total surface tension change for the 4-arm star/linear and linear-linear blend systems are small, and although we attempted to make extremely accurate measurements of surface tension with many reproducibility tests, the accuracy is lower. A slight error for the measurement of either pure component may stretch the profile, so the ability to compare subtle distinctions between star/linear blends with different number of arms for the star component is limited.



Figure 4.2(b) (Continued) Surface tension of 11arm star 7.5k/linear 9k blend plotted as function of weight fraction of component 1 at 180° C.



Figure 4.2(c) (Continued) Surface tension of 4arm star 4.8k/linear 9k blends plotted as function of weight fraction of component 1 at 180° C.



Figure 4.2(d) (continued) Surface tension of linear 1.79k/linear 9k blends plotted as function of weight fraction of component 1 at $180^{\circ}C$.



Figure 4.3 Normalized surface tension at 180° C plotted versus weight fraction of linear 1.79k for those blend systems described in Figure 4.2.

4.5 Simulations and theory

Insight into the physics responsible for the qualitative differences between surface tension of star/linear and linear/linear homopolymer blends, and the general nonlinear relationship between γ_n and w can be can be obtained from computer simulations and theories for the surface free energy and composition profile in such blends. For example, the simplest theories indicate that a linear surface tension dependence with blend composition indicates a surface composition essentially identical to bulk composition, and a convex profile indicates that there the component with lower surface energy segregates to the interface. A few decades ago, Prigogine and Marechal¹⁵, Defay and Prigogine¹⁶ and Gaines¹⁷ proposed theories with the assumption that the system is homogeneous up to its surface layer, but the surface composition is different compared to the bulk. Enthalpy is determined by a specific microscopic model and entropy determined by the Flory-Huggins model. These are then used to calculate the chemical potential. One then equates the chemical potential of the bulk and surface to obtain expressions for surface tension. Gaines' model is known to provide a good description for polymer solution surface tensions as well as for the surface tension of small molecule liquid mixtures.

The Cahn-Hilliard(CH)¹³ theory uses bulk thermodynamic properties which are obtained by fitting experimentally measured pressure, volume and temperature (PVT) data to an equation of state. Using the Flory, Orwoll and Vrij(FOV) equation of state¹⁸, Dee and Sauer¹ reported good agreement between experimentally measured surface tensions for a linear32k/linear0.77k poly(dimethylsiloxane) (PDMS) blend system and predictions by Cahn-Hilliard model. This model provides a good description of the curvature of surface tension versus composition profile of the blends, and the ultimate accuracy is partly based on the PVT measurement and how well the PVT data can predict surface tension of both pure components. The configurational entropy of

polymer chains at surfaces cannot be incorporated into this theory, so these features cannot be captured.

The SCF mean-field lattice simulation based on the method presented by Fleer et al ^{10, 11, 19, 20} captures the detailed information of entropic attraction or repulsion of any segment for any specific architecture through the Markov chain-like calculation of propagator matrix. Based on the simulation results, the entropic driving force, that is the combinative attraction for all the segments along the chain, provides a better description of the existence of entropic contribution than R_g^{5} . This approach is therefore very helpful for evaluating the effect of polymer architecture upon the surface tension of single component or blends. Qian, et al.⁶ previously showed by both lattice simulations and experiments that linear and star architectures with 4 and 11 arms all produced slopes in terms of the molecular weight dependence of melt surface tension and the star architectures produced sharper slopes than linear. For polymer blend systems, both incompressible lattice and compressible lattice models can be applied to evaluate how these changes influence the curvature of surface tension versus composition plots for blends. Computations on an incompressible lattice are known to offer only a qualitative description of the blend interactions and surface behavior, but requires less computational time and fewer input parameters, which often yields clearer physical insights. Computations on a compressible lattice are more accurate because compressibility and density gradients near the surface can be taken into account. SCF simulations on a compressible lattice generally works well for high molecular weight polymers, but the surface tension measurement of interest in the present study are for polymer blends of low or medium molecular weights where several of the assumptions (e.g. Gaussian coils, and weak gradients on the length scale of lattice elements) that underpin these simulations begin to break down.²¹ This dilemma obviously restricts comparison of blend surface tension data with predictions

deduced from lattice simulations.

It is also important to note that even in the most carefully synthesized star/linear blend systems, chemical differences between the chain ends, midsections and branch point are possible. These effects introduce additional energetic contributions to the surface free energy, which can enhance the surface concentration of chain ends.²²⁻²⁷ We have nonetheless shown in a previous study⁶ that for polystyrene chains with sec-butyl ends, the pure effect of branching on surface tension (ie. without consideration of end group chemical differences) is large and distinct. We therefore focus on lattice simulation which ignore the extra energetic effect of the sec-butyl groups and on a Cahn-Hilliard model that lumps the end-group effect into bulk thermodynamic properties accessible from PVT measurements.

Self-Consistent Field Lattice Simulation

The SCF mean-field lattice model based on the method presented by Fleer et al. has been discussed extensively in the literature.^{5, 6, 8-11, 19, 20} Briefly, we assume a lattice matrix comprised of several lattice layers which cover the depth from surface to bulk. Each Kuhn segment of a polymer chain, linear or branched, occupies one lattice. A consequence of the mean-field approximation is that all the variables in this space only change in the direction perpendicular to the surface plane. Given the position of the tail segment of a linear chain on the lattice, a propagator $G_k[i, j]$ defines the relative weight of finding a tail segment of a size-*i* chain of polymer species *k* in lattice layer *j*.

$$G_{k}[1, j] = \exp(-u_{k}[j]/k_{B}T)$$
(4.2)

where $u_k[j]$ is the surface potential field species k experiences at the surface layer j, k_B is the Boltzmann constant, T is the thermodynamic temperature of the system.

 $G_k[1, j]$ is the Boltzmann factor for finding a free unconnected segment of species k in layer j. Once it is known, the propagator for the tail segment of any linear chain with arbitrary size can be calculated for any species using a first-order Markov Process and known combination rules.²⁰

$$G_k[i,j] = G_k[1,j](\lambda_1 G_k[i-1,j-1] + \lambda_0 G_k[i-1,j] + \lambda_1 G_k[i-1,j+1])$$
(4.3)

where $\lambda_1 = 1/6$, $\lambda_2 = 4/6$ is lattice parameter for cubic lattice.

If the component possesses a branched architecture, the calculation of the propagator of the joint segment utilizes "chain walking" and combination rules. Algorithms for modeling a wide range of polymer chain architectures are described in detail elsewhere^{5, 6, 8-11, 19, 20}. The surface volume fraction of a segment *s* of species *k* with a chosen architecture, $\phi_k[s, j]$, is determined by the composition law²⁰, and the surface volume fraction of the entire chain of species *k*, $\phi_k[j]$, is just its architecture-dependent sum. The interested readers are referred to ref 5, 10, 11, 19 and 20 for the detailed calculations of propagator matrices and volume fraction profiles for linear, star and other branched architectures.

The difference between incompressible and compressible models is the specific functional form of $u_k[i](\phi_1[i], \phi_2[i])$, Thermodynamic density extrapolated by Sanchez-Lacombe Equation of State and density gradient at surface are taken into consideration by a compressible model. A detailed description is summarized in Appendix.

An initial guess is made for the surface potential profile, and the propagator matrix and volume fraction profile of both species calculated. This allows a new surface potential profile to be calculated using Eqn.(A4.1), which can in turn be used

to calculate a new propagator and volume fraction profile using the same algorithm. This iterative procedure continues until the difference between the new and previous potential is less than 10^{-4} to establish self-consistency. The only input information required in this calculation is the degree of polymerization and architecture of the blend components.

Cahn-Hilliard Theory

The extension of Cahn-Hilliard theory to multi-component systems²⁸ is also used in this work. In the following we just concisely introduce the formalism of this model, and refer the interested reader to the detailed description in the literature¹. The interfacial tension, γ , for a planar interface is

$$\gamma = (A - A_e) / S_0 \tag{4.4}$$

where A and A_e is respectively the Helmholtz free energy of the inhomogeneous system with the interface and that of the homogeneous system without interface but with the same density and composition as the inhomogeneous system. S_0 is the surface area of the interface.

A specific equation of state can be used to evaluate the Helmholtz free energy of homogeneous system at a given density, as follows:

$$A_{e} = V(\rho_{1}\mu_{1}^{e} + \rho_{2}\mu_{2}^{e}) - P_{e}V$$
(4.5)

where ρ_i is the number density of the mers of the respective components to the system, μ_i^e is the equilibrium chemical potential of the respective component of a homogeneous mixture at a pressure P_e and V is the system volume. μ_i^e can be calculated once specific microscopic model and equation of state are selected. The FOV equation of state provided a better fit than the lattice equation of state¹³, so it was used here

$$\widetilde{P}\widetilde{\nu}/\widetilde{T} = \widetilde{\nu}^{1/3}(\widetilde{\nu}^{1/3} - 1) - 1/\widetilde{T}\widetilde{\nu}$$
(4.6)

Where $\tilde{P} = P/P^*$, $\tilde{T} = T/T^*$ and $\tilde{v} = v_{sp}/v_{sp}^*$ are reduced pressure, temperature and specific volume. These fitted parameters P^* , T^* and v_{sp}^* are directly related to the microscopic parameters in the cell model and equation of state and they can be determined by fitting Eqn.(4.6) to experimentally measured PVT data.

A detailed discussion of the assumptions underlying this microscopic model and of the description of mixtures in the FOV equation of state formalism can be found in the appendix of reference 1. To calculate *A*, contributions from local density and composition gradient must be considered. The first can be again calculated from equation of state, and the second from statistical mechanics by only remaining the square gradient term and ignoring entropic contributions.

$$A = S_0 \int dx \left\{ a_0(x) + \frac{1}{2} \left[\kappa_{11} \left(\partial \rho_1 / \partial x \right)^2 + \kappa_{12} \left(\partial \rho_1 / \partial x \right) \left(\partial \rho_2 / \partial x \right) + \kappa_{22} \left(\partial \rho_2 / \partial x \right)^2 \right] \right\} (4.7)$$

where $a_0(x)$ is the local Helmholtz free energy density, κ_{ij} are the coefficients of the square gradient terms which quantify the enthalpic contributions to the free energy from the presence of density gradients. Previously we found that one specific κ is enough to optimize the match between theory and experiment for one polymer species(for polystyrene the reduced κ is around 0.47)¹³, and in the blend systems, a geometric type average is used to obtain κ_{12} .

$$\kappa_{12} = \sqrt{\kappa_{11}\kappa_{22}} \tag{4.8}$$

Using Eqn.(4.5), Eqn.(4.7) in Eqn.(4.4), the interfacial tension is

$$\gamma = \int dx \left\{ \Delta a(x) + \frac{1}{2} \left[\kappa_{11} \left(\partial \rho_1 / \partial x \right)^2 + \kappa_{12} \left(\partial \rho_1 / \partial x \right) \left(\partial \rho_2 / \partial x \right) + \kappa_{22} \left(\partial \rho_2 / \partial x \right)^2 \right] \right\}$$
(4.9)

where $\Delta a(x) = a_0(x) - (\rho_1 \mu_1^e + \rho_2 \mu_2^e) + P_e$

If final solutions $[\rho_1(x), \rho_2(x)]$ can minimize the surface excess energy in Eqn.(4.9), it yields the Euler-Lagrange equations

$$\kappa_{11} (\partial \rho_1 / \partial x)^2 + \kappa_{12} (\partial \rho_2 / \partial x)^2 - \partial \Delta a / \partial \rho_1 = 0$$

$$\kappa_{12} (\partial \rho_1 / \partial x)^2 + \kappa_{22} (\partial \rho_2 / \partial x)^2 - \partial \Delta a / \partial \rho_2 = 0$$
(4.10)

Eqn.(4.10) simplifies Eqn.(4.9) for the interfacial tension as

$$\gamma = \int dx \left[\kappa_{11} (\partial \rho_1 / \partial x)^2 + \kappa_{12} (\partial \rho_1 / \partial x) (\partial \rho_2 / \partial x) + \kappa_{22} (\partial \rho_2 / \partial x)^2 \right]$$
(4.11)

We solve Eqn.(4.10) using a relaxation method, and provide the density gradient profiles $[\rho_1(x), \rho_2(x)]$, which are then used to calculate γ .

Blend Lattice Simulations

We next apply SCF lattice simulations to model the surface tension of polymer blend systems. The Cahn-Hilliard theory will be used to describe the composition profiles in later sections. Figure 4.4 shows the incompressible lattice simulation results for the surface volume fraction profile of the lower surface energy component (1) in various linear/linear and star/linear homopolymer blends in which $\phi_1 = 0.2$. Unless stated otherwise, all subsequent SCF calculations assume $N_1 = 221$, $N_2 = 300$ for convenience, where N_k is the total number of Kuhn segments in species k. For simplicity we also assume segments in both components are chemically identical. Z_1^* , defined as $Z_1^* = \sum_i (\phi_1[i] - \phi_1^b)$ is the surface excess of component 1 in the blends. We will initially focus on an athermal blend system, where the interaction effect is switched off and the space filling potential term dominates Eqn.(A4.2).



Figure 4.4 Incompressible lattice simulation for surface volume fraction profile of linear/linear(circles), 4arm-star/linear(rectangles), 11arm star/linear(diamonds) blends, the total number of segments of component 1 is 221, the total number of segments of component 2 is 300. Both components are chemically identical and the same simulation conditions are also applied to Figure 4.5 and Figure 4.7. $\chi = 0$ is for all the blend systems

It is apparent from Figure 4.4 that the whereas the linear structure remains well dispersed throughout the blend, molecules with star-branched architectures are enriched at the surface, with the polymer with the larger number of arms providing the largest surface excess. This surface excess, as the first summation term in Eqn.(A4.3), should have a significant impact on the surface tension of the star/linear blend systems. Figure 4.5 compares the dimensionless surface tension of the respective blends as a function of volume fraction of component 1. Physically this means that in an incompressible lattice, a more negative space filling potential must be applied to more branched architectures to ensure their occupancy at the surface. This lowers the surface tension of the polymer blend. Significantly, Figure 4.5 also shows that while the surface tension for all blend systems is approximately linear over the range of compositions simulated, a detectable convex shape can be seen for the 11-arm star/linear blend system, but even then the curvature is substantially lower than observed experimentally.



Figure 4.5 Dimensionless surface tension of blends plotted versus volume fraction of component 1.

Figure 4.6 illustrates the effect, upon surface tension, of switching on energetic interactions in the SCF simulations of an 11-arm star/linear blend. In these simulations interactions are tuned by varying χ over an arbitrary range. It is apparent from the figure that at large enough values of χ , the surface tension profiles deduced from the simulations take on the decidedly non-linear shapes observed in our experiments. Furthermore, for $\chi = 0.004$, a strong flattening of the profile is observed at relatively low star volume fractions, even though the blends are strictly miscible. While it is not intuitive why such a strong unfavorable bulk interaction parameter should exist between two chemically identical polymer blend components, architectural effects to χ are anticipated both from the small mismatch in chemistry near the branch point²⁵ and from the large curvature observed in the surface-tension versus composition plots for the stars originates from the lower miscibility of these species in the linear host material.

Kumar and Jones³² showed that incompressible lattice simulation underestimates the dependence of molecular weight on surface tension $d\gamma/d(1/M)|_{M\to\infty}$ by ignoring the existence of the density gradient or voids at the surface. Therefore a polymer melt with finite compressibility has significant contributions to γ . Minnikanti and Archer^{10,33} compared entropic and enthalpic contributions to surface tension of single components between incompressible and compressible lattice model, and found that the compressibility and density gradient do have a profound effect. We now study how this effect influences the surface tension for the polymer blend systems. We also consider how higher order factors, such as the bulk interaction parameter and deviations from random mixing, influence surface tension in star/linear and linear/linear blends.



Figure 4.6 Dimensionless surface tension of 11arm star/linear blend plotted versus bulk volume fraction of component 1. Interaction parameter is allowed to be tuned as 0, 0.001, 0.002, 0.003 and 0.004 from top to bottom.

Figure 4.7 summarizes results from SCF simulations of a polystyrene-like material on a compressible lattice, at a temperature of 453 *K* and nearly zero pressure. Polystyrene is here taken to have a characteristic temperature $T^* = 735K$ and pressure of $P^* = 358MPa^{10, 33, 34}$. We recall Eqn. (A4.6):

$$\chi_{13} = T_1^* / T; \chi_{23} = T_2^* / T; \chi = (\sqrt{\chi_{13}} - \sqrt{\chi_{23}})^2 + 2(1 - \eta)\sqrt{\chi_{13}\chi_{23}}, \qquad (11)$$

If we assume both components share a common characteristic temperature and they are randomly mixed by dispersion forces (i.e., $\eta=1$), the athermal blending condition is recovered. It is apparent from Figure 4.7 that while the normalized surface tension of the blends is again a stronger function of composition for the star with the greatest degree of branching, the curvature of the plots are inconsistent with what is seen experimentally. This means that the compressibility of the blends is not the source of the discrepancies between simulations and experiment identified in Figure 4.5. On physical grounds alone, one might reason that if one component in the blend is highly branched deviations from random mixing might be expected near its crowded core. This will obviously influence η , and through equation (11) might manifest as an enlarged interaction parameter; choosing $\eta<1$ therefore allows us to mimic interactions less favorable than needed for random mixing, while for $\eta>1$ interactions between the blend components are more favorable than required for random mixing.



Figure 4.7 Compressible lattice simulation of blend surface tension versus volume fraction profile for 3 blend systems at a temperature of 453K and pressure of 0MPa. $\chi = 0$ is for all the blend systems. All conditions are same as Figure 4.4, and in this compressible lattice, characteristic properties for both components are: $T_1^* = T_2^* = 735K$, $V_1^* = V_2^* = 1.71 \times 10^{-5} m^3 / mole$.

Figure 4.8 summarizes how this effect influences the surface tension of star/linear binary blends. Again we assume $T_1^* = T_2^* = 735K$, η is systematically varied, from 1, 0.999, 0.9985 and 0.998, from the top to the bottom of the plot. These values are chosen to ensure that the phase stability criterion, is satisfied for the blends³⁵. It is important to point out that in these simulations when $T_1^* = T_2^*$, the entropic difference between the two blend components is the only source of a surface tension difference; the bulk density is sensitive to enthalpic effects, which can enlarge the surface tension difference. The surface tension versus composition profiles in Figure 4.8 can be made systematically more nonlinear by decreasing η , however for η values in the range required for phase stability, the profiles are still qualitatively quite different from their experimental counterparts. Thus, we can conclude that without introduction of strong repulsive interactions between blend components in the bulk, SCF simulations are unable to explain the shape of the surface tension versus composition profiles in the surface tension star/linear homopolymer blends.

A generally accepted method for evaluating bulk phase stability in polymer blends is to compare the sharpness of the glass transition of the pure components with that of the blend. Differential scanning calorimetry (DSC) is the experimental technique of choice for such measurements. DSC data for representative star/linear polystyrene blends are provided in Figure 4.9. The figure also includes results for the corresponding pure polymers (linear and star). While it is clear that the glass transition for the linear and star polymers are quite different, the glass transition in all of the blends are as sharp as those seen in the pure components, providing clear proof that the star/linear blends are in fact miscible in the bulk. Because of the relatively low molecular weights of the blend components, however, the entropy of mixing is large. This means that the miscibility of the star/linear blends in of itself cannot rule out a large positive χ parameter. We revisit this point later in the paper.



Figure 4.8 Compressible lattice simulation of a blend system composed of 11arm star/linear blend system($N_1=221$, $N_2=300$) where $T_1^* = T_2^* = 735K$. From the top to the bottom, a parameter η controls the deviation from random mixing approximation, changing from 1 to 0.999,0.9985, and 0.998



Figure 4.9 Differential Scanning Calorimetry (DSC) curves showing the glass transition temperature region for representative linear 9k/11 arm star 7.5k polystyrene blends with different star weight fractions as 0%, 7%, 15%, 30%, 100%. \dot{Q} is the heat flow rate.

Cahn-Hilliard Analysis of Surface Tension

The Cahn-Hilliard density gradient theory can be used to derive the surface excess profiles in homopolymer blends. It also allows one to indirectly probe the nature of the interaction parameter for polymer blends including our low molecular weight polymers by comparing predictions with experimental blend surface tension data.¹ To apply this theory, PVT data for each pure component were first experimentally measured. Fitting this data by the FOV equation of state¹⁸ over a fairly narrow temperature region provides a convenient way to deduce analytical expressions for thermodynamic variables, including the surface tension.^{1, 13}. The reduced parameters obtained by fitting small sections of our PVT data centered around 180^oC are given in Table 4.2. The reduced parameters were used to calculate Δa in Eqn.(4.9) and thus the density profile $\rho_i(x)$ and surface tension γ . Errors in the PVT measurements will lead to errors in calculating the surface tension by the Cahn-Hilliard model, and errors in surface tension measurement for polystyrene around 180^oC by the modified Wilhelmy method are ca. $\pm 0.2mN/m$.

PS sample	Mn of star PS ^a	$P^{*}(MPa)$	V^* (ml/g)	$T^{*}(\mathbf{K})$	
1.79k	1.79k	525.9	0.8464	8052.5	
9k	9k	496.9	0.8459	8439.2	
R26	4800	444.4	0.8400	8212	
R34	7500	430.1	0.8472	8312.4	
	PS sample 1.79k 9k R26 R34	PS sample Mn of star PS* 1.79k 1.79k 9k 9k R26 4800 R34 7500	PS sample Mn of star PS ^a P [*] (MPa) 1.79k 1.79k 525.9 9k 9k 496.9 R26 4800 444.4 R34 7500 430.1	PS sample Mn of star PS ^a P* (MPa) V* (ml/g) 1.79k 1.79k 525.9 0.8464 9k 9k 496.9 0.8459 R26 4800 444.4 0.8400 R34 7500 430.1 0.8472	PS sample Mn of star PS ^a P* (MPa) V* (ml/g) T* (K) 1.79k 1.79k 525.9 0.8464 8052.5 9k 9k 496.9 0.8459 8439.2 R26 4800 444.4 0.8400 8212 R34 7500 430.1 0.8472 8312.4

Table 4.2 Reduced parameters at 180° C of PVT data to the FOV equation of state.

The interaction parameter in Cahn-Hilliard model, X_{12} , is defined as:

$$X_{12} = P_1^* + P_2^* - 2d_{12}\sqrt{P_1^*P_2^*}$$
(4.12)
The X_{12} values are directly related to the χ parameter discussed above³⁶, except the magnitudes are different.

For star-linear and especially linear-linear blend systems, we expect polystyrene segments to interact with each other through simple dispersion forces. So d_{12} is set equal to a critical value in the case of random mixing to give a neutral interaction parameter ($X_{12} = 0$). Setting d_{12} greater or less than that critical value mimics attractive or repulsive bulk interaction parameters ($X_{12} > 0$ or $X_{12} < 0$), respectively. Note that for different blend systems this critical d_{12} where $X_{12} = 0$ varies because the PVT parameters (P^*) are different for each polymer in Eqn.(4.12).

PVT properties were only measured for the pure materials, and blend values of surface tension are calculated with a high degree of precision based on mixing rules only; i.e., no PVT properties were measured for blends. Thus, the main error in the predictions is from the pure component values Figure 4.10(a) shows the experimental results and theoretical predictions for the surface tension of linear9k-linear1.79k polystyrene blends. Recall that any negative deviation (convex curvature) from the linear dependence of γ versus blend weight fraction in a plot such as experiment and theory in Figure 4.10a or 4.10b indicates that there is surface segregation of the lower MW components. For the theoretical calculations, we intentionally chose based on Eqn.(4.12), three representative values of X_{12} including $X_{12} = 0.41$ J/ml(or MPa) for repulsive interaction parameter, $X_{12} = -4.7$ J/ml for attractive interaction, and one chosen to be zero that results in a neutral interaction. This last X_{12} is different for each blend pair because of the different P^* values that factor into Eqn.(4.12).

Generally for a blend of chemically similar homopolymers, the reduced square gradient parameters are assumed to be the same for each pure component ($\kappa_{11} = \kappa_{22} = 0.47$). For polydimethylsiloxane used in the earlier study¹, $\kappa_{11} = \kappa_{22} = 0.50$, gave relatively good agreement for γ as compared with experiments

for both pure components. Because of the poor agreement with experiment for the pure 1.79k linear PS in Figure 4.10a, one of the square gradient coefficients, κ_{22} , is also varied from 0.47 or 0.423 in order to shift the pure component value for this low surface energy 1.79k PS. This is shown to provide better general agreement with the data (Figure 4.10a), but Figure 4.10b shows that the level of convexness of the curves does not change substantially by assuming $\kappa_{11} \neq \kappa_{22}$, as is also shown in more detail for the 11-arm blend below. Adjusting κ_{22} is a somewhat empirical method to correct for improper accounting for possible configurational entropic contributions^{37,38,39} for the smaller molecules (such as 1.79K linear PS in Figure 4.10a, or the 11-arm stars below), that is ignored as soon as one assumes κ_{22} is equal to κ_{11} for a "high MW" chain such as 9k linear PS the mismatch between experiments and theories in Figure 4.10a possibly results from the error in the PVT measurement of this component and/or improper accounting for any configurational entropic contributions for this small molecule.^{37,38,39}

For linear 1.79k and linear 9k blend systems, there is some qualitative agreement between the experiment and theoretical predictions, especially in terms of the slightly convex shape of the data. Figure 4.10(b) shows this more clearly where experiment and theoretical predictions are plotted after normalization. For $\kappa_{11}/\kappa_{22} = 0.47/0.423$ parameter pair, a good match is obtained when $X_{12} = -4.7$ J/ml, i.e., a slightly attractive interaction case; or for $X_{12} = 0.41$ J/ml and 0.47/0.47 agreement seems to be just as good for this slightly repulsive case. Because of the various issues discussed above, it is clear the theory is somewhat qualitative for this blend pair. For these blends one would expect a close to neutral interaction parameter, but not an attractive one. Because of the small changes measured here, the comparison with experiment is too qualitative to determine the magnitude of the interaction parameter.



Figure 4.10(a) Surface tension of a blend of linear 9k and linear 1.79k polystyrenes at 180°C predicted by Cahn-Hilliard Model, plotted as a function of the weight fraction of the low molecular weight component. Different X_{12} and κ_{11}/κ_{22} parameter pairs are applied to the theoretical calculation, as indicated in the legend.



Figure 4.10(b) (Continued) Normalized experimental and Cahn-Hilliard predicted surface tensions plotted as a function of the weight fraction of linear 1.79k.

Figure 4.11(a) and (b) give various predictions for the 11-arm 7.5k/linear9k blend system. The very convex nature of the data in Figure 4.11(a) illustrates the large excess of 11-arm star molecules segregated at the surface relative to the linear/linear blends, and this is also predicted by theory depending on the choice of X_{12} . In Figure 4.11(a) we have plotted only the $X_{12} = 0$ case with two different values of κ_{22} that modify the end points as expected. Even with $X_{12} = 0$, the strong surface excess is seen, but these results prove that the excess is not substantially affected by the two different choices of κ_{22} . The convex nature of both theoretical curves seems to agree equally well with experiment, although both seem to have sharper decreases than experiment at low weight fractions (i.e., $< \sim 0.1$ wt. fraction) of 11-arm star. In the previous study of PS/poly(vinyl methyl ether) miscible blends where the pure components had a large difference in γ , a similar problem with theory was found at weight fractions of PVME below about 0.02. The tendency that theory always produces a more convex initial curvature at very low concentrations for star/linear blends could be related to the large difference of surface energy of star and linear components. There could also be a concentration dependent interaction parameter over and above the equation of state contributions taken into consideration by the theory. There is also the well known failure Flory-Huggins combinatorial mixing at low wt. fractions¹ and it is also likely that the assumption of non-random mixing at low volume fractions is inaccurate.¹



Figure 4.11(a) Cahn-Hilliard predictions and experiment for 11-arm star polystyrene (7.5k) / linear polystyrene (9k) blends at 180°C. Predictions were made using a neutral interaction parameter ($X_{12} = 0$), but allowing κ_{22} vary slightly from 0.47 to 0.423.



Figure 4.11(b) (Continued) Cahn-Hilliard predictions and experiment for 11-arm star polystyrene (7.5k) / linear polystyrene (9k) blends at 180°C. Predictions using different values of the interaction parameter at constant κ_{22} ($\kappa_{11}/\kappa_{22} = 0.47/0.423$).

Figure 4.11(b) gives theoretical curves for the 11-arm blends for three different interaction parameters at a fixed κ_{22} . It is obvious that a mildly repulsive interaction $(X_{12} = 2.41)$ leads to far too high of a surface excess, and that the curvature is qualitatively correct for the case of $X_{12} = 0$. For the mildly attractive interaction $(X_{12} = -3.14)$, the convex curvature in the range 0.1<weight fraction< 1.0 is a little too flat compared to experiment, while again all seem to fail to different degrees at wt. fraction<0.1. Note that at zero star weight fraction, the agreement with experiment is perfect because this was fixed by our choice of κ_{11} for 9k linear PS.

Figure 4.12 gives experiment and theory at different X_{12} values for 4-arm 4.8k/linear9k. Again, theory is able to reproduce the strong convex nature of the experiment. We only used one value of κ_{22} because varying this did not substantially affect the curvature at each X_{12} . The shape of the curves relative to experiment is fairly well represented by the $X_{12} = 0$ curve. As with the 11-arm, the curve obtained using a mildly repulsive interaction ($X_{12} = 1.46$) leads to a very high level of surface excess not seen by experiment.

Density gradient profiles from Cahn-Hilliard theory are used to calculate surface tensions of blends and pure materials. Figure 4.13 provides representative profiles at 180°C for linear/linear and 4-arm star/linear blends where the lower surface tension component was set to a weight fraction of 20% in each case. Note that these are the density profiles normal to the plane of the interface, and the sum of the concentrations of the two individual components in the bulk (left-hand side of the profiles) will give the bulk blend density in g/ml calculated by theory at 180° C. Surface tension governs the sharpness of the gradients, and for most materials with $15 < \gamma < 70$ mN/m, the interface widths are on the order of ca. 10Å. Theory does not consider conformational entropy penalties of constraining chains at interfaces, so it is possible that these predicted curves are slightly narrower than those in experiments.



Figure 4.12 Surface tension of a blend of 4arm star polystyrene(4.8k) and linear polystyrene(9k) at 180°C predicted by Cahn-Hilliard Model, plotted as a function of the weight fraction of the star component



Figure 4.13(a) Surface concentration profiles normal to the interface of both components at 180°C where the weight fraction of the low surface tension component is 20%. linear 9k/linear 1.79k blends with $X_{12} = -4.7$ (attractive), $\kappa_{11} / \kappa_{22} = 0.47 / 0.423$



Figure 4.13(b) (Continued) Surface concentration profiles normal to the interface of both components at 180°C where the weight fraction of the low surface tension component is 20%. linear 9k/linear 1.79k blend, with $X_{12} = 0.411$ (repulsive), $\kappa_{11} / \kappa_{22} = 0.47 / 0.423$



Figure 4.13(c) (Continued) Surface concentration profiles normal to the interface of both components at 180°C where the weight fraction of the low surface tension component is 20%. 4arm star 4.8k/linear 9k blend with $X_{12} = -3.23$ (attractive), $\kappa_{11}/\kappa_{22} = 0.47/0.47$,



Figure 4.13(d) (Continued) Surface concentration profiles normal to the interface of both components at 180°C where the weight fraction of the low surface tension component is 20%. 4arm star 4.8k/linear 9k blend, with $X_{12} = 1.46$ (repulsive), $\kappa_{11}/\kappa_{22} = 0.47/0.47$.

In each case the profiles were determined for the two cases discussed above with a slightly repulsive ($X_{12} < 0$) and slightly attractive ($X_{12} < 0$) interactions. The lower surface energy component, 1.79k linear polystyrene, shows a slight surface excess at the vapor-liquid interface at 20% weight fractions(Figure 4.13 (a) (b)), and the more attractive interaction in Figure 4.13(b) leads to a slightly lower surface excess of this lower MW component as expected.^{1,7} Other weight fractions of 1.79k were evaluated, and the density profiles show similar trends. It is also seen that the gradients in the blends drop bulk values to that of the vapor phase over a narrow surface region with gradient normal to the interface of about 10 Å.

Figure 4.13 (c) and (d) provide the comparable profiles for the 4arm star/linear blends. Here a much larger excess of the low γ component is seen relative to the linear/linear blends in Figure 4.13 (a) and (b), especially for the slightly attractive case in Figure 4.13(c). Again, the large excess also directly translates to the convex shape of γ versus composition in Figure 4.12 for the 4-arm star blends.

Compared with lattice simulations, there are some advantages of utilizing Cahn-Hilliard method to model the surface tension data. The main issue is that the polystyrene blends studied experimentally were lower MW than those accessible in the lattice simulations. The lattice simulation with its 3-D Kuhn segment random walk assumption requires a high molecular weight limit to be strictly precise. For most of our star polystyrene samples, each arm is not even longer than one Kuhn length. Secondly, there are also other reasons involved, including the uncertainty of the input parameter(T^*) for highly-branched samples and possibly the bulk interaction between low molecular weight linear and branched species. Thirdly, in lattice simulations a uniform interaction parameter up to the surface layer is simply assumed, which may not be the case in practice. Finally, the chemical heterogeneity of the end segments is ignored by lattice simulation in this work but the extra energetic effect of sec-butyl

end segment of our anionically synthesized polystyrenes always exist.(Recently Benzyl-ended linear polystyrenes have been synthesized⁴⁰ in order to quantify the influence of sec-butyl versus benzyl end groups.) In summary, lattice simulations reveal that the blend surface tension profiles (Figure 4.5 or Figure 4.7) appear to be almost linear as would be expected for fairly high MW blends if the segments of both components are randomly mixed. A strong unfavorable bulk interaction must be introduced in order to make the profile substantially convex. At these high molecular weights, lattice simulations could provide accurate estimation of the neutral interaction because lattice simulation and density estimation from Sanchez-Lacombe equation of state work much better in this regime and in reality the interaction between chemically identical species with high MW is indeed negligible.

Foster et. al. ³¹ studied bulk interaction parameter χ in deuterated 6-arm star polystyrene 157k/linear polystyrene 231k and they subtracted the influence due to deuterated effect and obtained an architecture-dependent bulk interaction on the order of magnitude of 10⁻⁵. This number could be slightly larger for our simulated systems, but still much smaller than the interaction parameters (O(10⁻³)) required to produce the results in Figure 4.6. Results from the Literature indicates that in the high molecular weight regime, a large repulsive interaction parameter in a blend system composed of chemically identical but topologically distinct components is unrealistic. However, for low molecular weights, it not known in the literature whether a strong unfavorable bulk interaction is needed to provide the curvature of the profile. As shown in our DSC study in Figure 4.9, a sharp glass transition is observed, which confirms the polymer blends possess good miscibility. Then why could SCF lattice simulation only capture the non-linear profile by assuming a strong interaction? One possible reason is that at low and medium MW range Sanchez-Lacombe equation of state^{41,42} does not predict the bulk density of the blend in lattice simulation accurately.

4.6 Conclusions

Surface tension of 11-arm star/linear, 4-arm star/linear and linear/linear miscible polystyrene blends were experimentally measured for the first time. The blend surface tension versus composition profiles for the star/linear blends are more convex than those for the linear/linear blend, indicating a much higher level of surface segregation of star components. Normalized blend surface tension versus composition profiles for 11-arm star/blends and 4-arms star/linear blends almost collapse to a single universal curve. We present a detailed self-consistent lattice field simulation for both incompressible and compressible models, to predict the surface tension of higher MW miscible blend Entropic (molecular weight, systems. architecture), enthalpic(P^*, V^*, T^*) and bulk interaction(χ, η) information is embedded in the compressible simulation. The compressible lattice simulation provided a more realistic magnitude of surface tension changes relative to the incompressible model because the former considers the effect of compressibility and density gradients in the surface layer. At these high MWs, it predicts a slightly convex curve which is inconsistent with our experimental observations. Increasing the repulsive bulk interaction parameter, yields surface tension versus composition profiles qualitatively similar to the experimental results, but no clear justification exists for such high levels of repulsion in a homopolymer blend. The Cahn-Hilliard model was also used to predict the surface tension of the linear/linear and star/linear blends. This theory was shown to semi-quantitatively reproduce the composition dependence of surface tension using a neutral bulk interaction parameter. The Cahn-Hilliard analysis shows that the strong surface excess of the branched additives in the blends with linear chains is the likely source of the strongly convex composition dependence of the surface tension for star/linear homopolymer blends.

APPENDIX: INCOMPRESSIBLE AND COMPRESSIBLE LATTICE SIMULATION TO CALCULATE THE SURFACE TENSION OF POLYMER BLEND SYSTEM

The interested readers are referred to ref 20 for details of this part.

For incompressible lattice model where the density is by definition constant in all lattice layers, space-filling potentials must be applied on polymer segments near the wall to maintain the incompressibility. Thus, the surface potential profile for species 1 is:

$$u_1[j]/k_BT = \chi(\langle \phi_2[j] \rangle - \phi_2^b) + (\phi_1^b/r_1 + \phi_2^b/r_2 + \chi \phi_1^b \phi_2^b) + \alpha[j]$$
(A4.1)

where k_B is the Boltzmann constant, T is the thermodynamic temperature of the system, χ is interaction parameter between Kuhn segments, ϕ_k^b is the bulk volume fraction for species k, r_k is the total number of segments for species k, $\alpha[j]$ is Lagrangian parameter needed to ensure incompressibility $\phi_1[j] + \phi_2[j] = 1$ for any surface layer $j \cdot \alpha[j] = \zeta(\phi_1[j] + \phi_2[j] - 1)$, where ζ is a large parameter whose value is basically set by the ease of convergence of the program simulation and criteria for incompressibility. The sum of last two terms at right hand side is actually dimensionless "hard-core" potential $u'[j]/k_BT$. The term $\langle \phi_2[j] \rangle$ signifies the mean volume fraction of species 2 around a lattice site in layer j.

$$<\phi_2[j]>=\lambda_1\phi_2[j-1]+\lambda_0\phi_2[j]+\lambda_1\phi_2[j+1]$$
 (A4.2)

where $\lambda_1 = 1/6$ and $\lambda_2 = 4/6$ according to the cubic lattice coordinate and the same mean rule applies to any term.

The dimensionless surface tension γ for this blend system is:

$$\frac{\gamma a_s}{k_B T} = -\sum_j (\phi_1[j] - \phi_1^b + \phi_2[j] - \phi_2^b)$$

$$-\sum_j u'[j] - \frac{1}{2} \chi \sum_j (\phi_1[j] < \phi_2[j] > +\phi_2[j] < \phi_1[j] > -2\phi_1^b \phi_2^b)$$
(A4.3)

where a_s is related to the area of each lattice site.

For compressible lattice model, where a special third species, void, is taken into consideration. Sanches-Lacombe(SL) equation of state is used to extrapolate the bulk density of the blend system at certain temperature and average degree of polymerization for the blend.

$$\widetilde{\rho}^2 + \widetilde{P} + \widetilde{T}[\ln(1 - \widetilde{\rho}) + (1 - \frac{1}{r})\widetilde{\rho}] = 0$$
(A4.4)

where \widetilde{T} , \widetilde{P} , $\widetilde{\rho}$ and \widetilde{V} are reduced temperature, pressure, density and volume defined $\widetilde{T} = T/T^*; \widetilde{P} = P/P^*; \widetilde{\rho} = 1/\widetilde{V} = V^*/V$ (A4.5)

where T^* , P^* and V^* are characteristic temperature, pressure and volume as input parameter for the compressible lattice simulation. Different components are of different characteristic properties, and Sanchez and Lacombe propose a mixing rule to estimate a unique set of characteristic properties for the blend system as follows:

$$P_{1}^{*} = RT_{1}^{*} / V_{mix}^{*}; P_{2}^{*} = RT_{2}^{*} / V_{mix}^{*}; \Delta P^{*} = P_{1}^{*} + P_{2}^{*} - 2\eta \sqrt{P_{1}^{*}P_{2}^{*}}$$

$$P_{mix}^{*} = \phi_{1,b}^{rel} P_{1}^{*} + (1 - \phi_{1,b}^{rel}) P_{2}^{*} - \phi_{1,b}^{rel} (1 - \phi_{1,b}^{rel}) \Delta P^{*}; T_{mix}^{*} = P_{mix}^{*} V_{mix}^{*} / R; r_{mix} = \frac{1}{\phi_{1,b}^{rel} / r_{1} + \phi_{1,b}^{rel} / r_{1}}$$

$$\chi_{13} = T_{1}^{*} / T; \chi_{23} = T_{2}^{*} / T; \chi = (\sqrt{\chi_{13}} - \sqrt{\chi_{23}})^{2} + 2(1 - \eta) \sqrt{\chi_{13}\chi_{23}}$$
(A4.6)

where *R* is ideal gas constant, P_k^*, V_k^*, T_k^* are characteristic properties for species *k*, r_k is number of segment for species k, $P_{mix}^*, V_{mix}^*, T_{mix}^*$ are mixed characteristic properties for blend system, $\phi_{k,b}^{rel}$ is relative volume fraction of species $k(\phi_{1,b}^{rel} + \phi_{2,b}^{rel} = 1)$, r_{mix} is averaged number of segments, η is random mixing parameter, χ_{k3} is interaction parameter between voids and species k, χ is interaction parameter between species 1 and species 2.

The surface potential profile is:

$$u_{1}[i]/k_{B}T = -2\frac{T_{mix}^{*}}{T}(\phi_{1}[i] - \phi_{1}^{b}) - 2\frac{T_{mix}^{*}}{T}(\phi_{2}[i] - \phi_{2}^{b}) - \ln(\frac{1 - \phi_{1}[i] - \phi_{2}[i]}{1 - \phi_{1}^{b} - \phi_{2}^{b}}) - \frac{T_{mix}^{*}}{3T}(\phi_{1}[i - 1] - 2\phi_{1}[i] + \phi_{1}[i + 1]) - \frac{T_{mix}^{*}}{3T}(\phi_{2}[i - 1] - 2\phi_{2}[i] + \phi_{2}[i + 1])$$
(A4.7)

The dimensionless surface tension is:

$$\frac{\gamma a_s}{k_B T} = \sum_i (1 - \frac{1}{r_1})(\phi_1[i] - \phi_1^b) + (1 - \frac{1}{r_2})(\phi_2[i] - \phi_2^b) + \sum_i \ln(\frac{1 - \phi_1[i] - \phi_2[i]}{1 - \phi_1^b - \phi_2^b}) + \sum_i \chi_{13}[\phi_1[i] < \phi_1[i] > -(\phi_1^b)^2] + \chi_{23}[\phi_2[i] < \phi_2[i] > -(\phi_2^b)^2] + \frac{1}{2}\sum_i (\chi_{13} + \chi_{23} - \chi)(\phi_1[i] < \phi_2[i] > +\phi_2[i] < \phi_1[i] > -2\phi_1^b\phi_2^b)$$
(A4.8)

In incompressible lattice model, the interaction parameter χ is a directly input parameter, while in compressible model, and it is tuned by random mixing parameter η and interaction between polymer components and voids. The absolute order of magnitude of surface tension for pure component is totally determined by the characteristic pressure, temperature and volume, but the composition dependence on surface tension of polymer blend is influenced by multiple factors such as η , χ_{13} and χ_{23} . One needs to be careful to tune χ or η so that a theoretical phase separation or "mathematical" unstable region is avoided.

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