SYNTHESIS AND SURFACE FLUCTUATIONS OF CYCLIC POLYSTYRENES
AND THEIR INTERFICIAL SEGREGATION IN BLENDS WITH LINEAR
POLYSTYRENES

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Thesis

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ABSTRACT

A well-defined cyclic polystyrene (CPS, $M_n = 6,000$ g/mol) was synthesized using a combination of anionic polymerization and metathesis ring closure. A new synthetic route was developed to produce CPS ($M_n = 4,600$ g/mol) with higher yield using anionic polymerization, linking chemistry and metathesis ring closure. The formation of cyclic polystyrenes was accurately characterized using Matrix Assisted Laser Desorption Ionization Time-of-Flight Mass Spectrometry (MALDI-ToF MS). The monoisotopic peaks at values of $m/z$ that were 28 units less than those of the corresponding precursor peaks are characteristic of cyclization. These peaks appear due to the elimination of an ethylene molecule during the cyclization reaction.

The interface segregation of binary blends of cyclic and linear polystyrenes with similar molecular weights was investigated using Neutron Reflectometry (NR) to determine the chain molecular weight at which the segregation behavior crosses over from a behavior characteristic of low molecular weight blends, for which the linear chain is preferred at the surface, to a behavior characteristic of high molecular weight blends, for which the macrocyclic chain is preferred at the surface. The enrichment of one component at both the air/polymer and polymer/substrate interfaces of these blend films was studied for chains of molecular weight 2k, 6k and 16k. The blends were composed of
80 wt% deuterated species and 20 wt% hydrogenous species. In the 2k blends, the isotopic effect is negligible, and surface segregation is dictated by the chain architecture. As the molecular weight increases, the enrichment of the air surface in linear chain becomes weaker, despite the fact that the isotopic effect that tends to drive the perdeuterated linear species to the surface becomes stronger as molecular weight increases. For the 16k blend no enrichment of the blend surface can be resolved with NR measurements, suggesting that at a molecular weight near that value the strength of the driving force for surface enrichment of linear chains due to isotopic labeling is about equal to the driving force for surface enrichment of cyclic chains due to effects of the molecular architecture on the chain packing.

Surface fluctuations of melt films of 6k CPS and linear analogs with different thicknesses were measured using X-ray photon correlation spectroscopy (XPCS). The surface fluctuations of the 6k linear melt films thicker than 17 nm and the 6k cyclic melt films thicker than 28 nm can be described by a hydrodynamic continuum theory (HCT). When the film of CPS is thinner than 24 nm, the behavior of the surface fluctuations is no longer captured by the HCT, and the relaxation times are much longer than predicted by the HCT. However, unlike the confinement effect reported for films of entangled linear chains, there is no evidence of an effective modulus in the very thin films of cyclic chains. In the context of the HCT, the behavior of the very thin films can be rationalized by supposing that the films have effective viscosities higher than the bulk value. One possible explanation for this behavior could be an increase in glass transition temperature \(T_g\) of a CPS film with decreasing thickness for thicknesses below 28 nm. Such a
change would be opposite to the change in $T_g$ with thickness seen for linear PS melt films and needs to be experimentally investigated.
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CHAPTER I

INTRODUCTION

Cyclic polymers have properties that differ strongly from those of the corresponding linear polymers. For example, macrocyclic polymers exhibit lower solution viscosities, higher size exclusion chromatography (SEC) elution volumes, higher melt densities,\(^1\) lower mean square radii of gyration and higher glass transition temperatures\(^2\)-\(^4\) than do their linear analogs, so great interest has been aroused to synthesize ring polymers. In this thesis synthesis of cyclic polystyrene using anionic polymerization and metathesis ring-closure as proposed by Quirk \textit{et al.}\(^5\) will be discussed and a new method using anionic polymerization, linking chemistry and metathesis ring closure will be investigated.

Polymer blends of chains with different architectures, but similar molecular weights, have been demonstrated as a useful route to control surface properties by controlling interfacial segregation.\(^6\) They have potential applications such as tuning cell responses to tissue engineering scaffolds and creating membranes for purifying water.\(^7\)-\(^9\)

So it is worthwhile investigating the surface segregation phenomena of polymers with different architectures to rationalize the mechanism of this surface segregation and thus in return, various kinds of devices are designed utilizing this phenomenon.
In this thesis, interfacial segregation of blends of polystyrenes with similar molecular weights and different structures (cyclic and linear) will be investigated using neutron reflectrometry and the variation in their tendency to segregation with molecular weight will be probed.

Surface height fluctuations on polymer melts have attracted interest due to the fact that they affect the wetting, adhesion and friction of such surfaces. Recent developments in X-ray photon correlation spectroscopy (XPCS) have made it possible to probe the length scales and time scales characteristic of the cooperative motion of thermally stimulated capillary waves controlled by the surface tension of polymer melts and shear viscosity. Wang et al. investigated the surface fluctuations of low molecular weight cyclic polystyrene melt films and found that their relaxation times are much longer than those of their linear analogs. A hydrodynamic continuum theory (HCT) predicts that the characteristic surface relaxation time, \( \tau \), of cyclic polystyrene melt film varies with film thickness, \( h \), and in-plane wave vector, \( q_{||} \), according to a universal scaling when the film is thick enough (i.e. > 40 nm). In this case, data from films of different \( h \) collapse onto a single universal curve when plotted as \( \tau/h \) vs. \( q_{||}h \). However, when the film becomes thinner, the data points no longer collapse onto the theoretical curve, which indicates that some confinement effect is present. In this thesis, the confinement will be investigated using XPCS measurements of films of 6k cyclic polystyrene of various thicknesses.
CHAPTER II

BACKGROUND

In this chapter, the major synthetic procedures for the synthesis of macrocyclic polymers will be reviewed. After this, surface segregation of polymer blend films containing chains with various architectures will be discussed. In the last part of this chapter, the measurement of surface fluctuations of melt polymer films using XPCS will be introduced.

2.1. Synthesis of Cyclic Polymers

Synthesis of cyclic polymers is a challenge. To date, known synthetic strategies for cyclic polymers can be generalized into two main categories: ring-expansion methods\(^{15}\) and ring-closure techniques.\(^{16}\)
2.1.1 Ring-closure Techniques

In the ring-closure methods, cyclic polymers are prepared by applying highly efficient coupling chemistry to end-functionalized linear telechelic polymers. These techniques provide us with elegant means to synthesize well-defined macrocylic polymers with narrowly distributed molecular weights. The first successful synthesis of well-defined cyclic polymers was based on the bimolecular process.

![Figure 2.1. The reaction scheme for the bimolecular process.](image)

In this method, linear chains with dilitho or disodio living ends were first synthesized using difunctional anionic initiators, and then they were terminated using coupling agents in highly dilute solutions to form the cyclic polymers. Using this method,
cyclic homopolymers such as polystyrenes, poly(2-vinylpyridine), poly(vinyl-naphthalene) and poly(9,9-dimethyl-2-vinylfluorene) can be prepared. Cyclic block copolymers can also be prepared via this route, as demonstrated by Hadjichristidis and coworkers and Hogen-Esch. Although the polydispersity of the polymers produced by this method is low, the yield of cyclization is low (10 ~70%), which is due to the fact that two components, living chains and coupling agents, exist in the system.

To overcome this drawback, Ishizu et al. and Oike et al. introduced the interfacial condensation cyclization technique and electrostatic self-assembly-covalent fixation to achieve high efficiency of cyclization. The interfacial condensation cyclization is illustrated in Figure 2.2 and electrostatic self-assembly and covalent fixation illustrated in Figure 2.3. The molecular weight range for the interfacial condensation cyclization is from 20,000 to 550,000 g/mol, while for the electrostatic self-assembly and covalent fixation, it ranges from 4,300 to 14,000 g/mol.

Figure 2.2. The reaction scheme for interfacial condensation cyclization of polystyrene.
Preparation of cyclic polymers using the bimolecular process must always contend with linear impurities, i.e. dimers, which are difficult to separate from the cyclic product to obtain pure cyclic polymers. This is because the reactivity of the living chains is so high that side reactions in the system cannot be avoided. The problem can be solved by introducing well-defined α, ω-telechelic polymers in place of living chains. Tezuka and coworkers\textsuperscript{27, 28} are pioneers in the synthesis of cyclic poly(tetrahydrofuran) and poly(methyl acrylate). They accomplished these syntheses by metathesis ring-closure using vinyl groups at both chain ends of the linear precursor using the 1\textsuperscript{st} generation Grubbs catalyst.\textsuperscript{15} Quirk and coworkers\textsuperscript{5} applied this approach to precursors synthesized using living anionic polymerization to develop an efficient synthesis procedure, which uses metathesis ring-closure methods, for synthesis of well-defined, macrocyclic polystyrenes over a broad molecular weight range. In their work, a series of well-defined, α,ω-divinyl polystyrene precursors were synthesized using 4-pentenyllithium-initiated polymerization of styrene followed by termination with 4-chloromethylstyrene, followed

Figure 2.3. The reaction scheme for electrostatic self-assembly and covalent fixation for cyclic poly(tetrahydrofuran)\textsuperscript{27}
by cyclization of these α,ω-divinylpolystyrene precursors using the 1st generation Grubbs catalyst as well. Baba et al.\textsuperscript{29} proposed a route through atom-transfer radical polymerization (ATRP),\textsuperscript{30} followed by ring-closing metathesis to synthesize cyclic polystyrene and cyclic polystyrene-\textit{b}-poly(ethylene oxide). In their work, the 1st generation and 2nd generation Grubbs catalysts were used to cyclize telechelic polystyrene and polystyrene-\textit{b}-poly(ethylene oxide), and both syntheses showed high efficiency of cyclization. The advantage of the metathesis ring-closure method is that the structures of the linear and macrocyclic polymers can be easily distinguished by MALDI-ToF Mass Spectrometry due to the elimination of one ethylene group (m/z = 28) per polymer chain.

Figure 2.4. The reaction scheme for synthesis of cyclic polystyrenes by metathesis ring closure of well-defined telechelic precursors synthesized by living anionic polymerization.\textsuperscript{5}
One of the exciting developments in the synthesis of cyclic polymers is the application of “click” reactions, which are simple reactions with high efficiency. Laurent and Grayson\textsuperscript{18} first demonstrated the accessibility of “click” to attain a high yield of cyclic polystyrene. An \(\alpha,\omega\)-telechelic polystyrene was prepared via ATRP, followed by end-group coupling using the copper-catalyzed azide/alkyne cycloaddition (CuAAC)\textsuperscript{31} “click” reaction under dilute conditions, as shown in Figure 2.4. Synthetic methods like ring-opening polymerization,\textsuperscript{32-34} reversible addition-fragmentation chain transfer polymerization (RAFT)\textsuperscript{35-37} and nitroxide-mediated radical polymerization (NMR)\textsuperscript{38} have been used to obtain \(\alpha,\omega\)-telechelic polymers as well. To avoid intermolecular reaction with this “click” chemistry, cyclization must be carried out in a high excess of end-groups of CuBr/Ligand condition. The fast reactions produced cyclic polymers in shorter time, thus higher feed rates and weight fractions of polymer can be obtained during the reaction. Lonsdale \textit{et al}.\textsuperscript{39} discovered that using N\textsubscript{3}-polystyrene-\text{C}≡\text{CH} as a precursor significantly increased efficiency in the cyclization. Efficiency can also be improved with the proper choice of solvent and ligand. A kinetic investigation showed that cyclic polymers can be obtained in less than nine min at 25 \({\degree}\text{C}\). Besides homopolymers, block polymers with ring structures can be synthesized using “click” reactions as well.\textsuperscript{40, 41} "Click" reactions can even be used as a probe to detect the self-assembly properties of cyclic polymers in solutions.\textsuperscript{41}
2.1.2 Ring-expansion Techniques

Ring-expansion techniques, which are based on the insertion of monomer units into an activated cyclic chain, face several challenges including limited types of suitable monomers, a time-consuming process for synthesizing the cyclic initiators, sensitivity to functional chemical groups and broad molecular weight distributions of the cyclic products. Kricheldorf et al.\textsuperscript{42-44} were the pioneers, carrying out ring-expansion reactions with different cyclic lactone and lactide monomers using Bu$_2$Sn as initiator, as shown in Figure 2.5. A further drawback of this route is that the cyclic polymers are degraded to their liner analogues when exposed to air, because the tin-oxygen bond is susceptible to hydrolysis.\textsuperscript{45}
Waymouth and coworkers\textsuperscript{46} developed a zwitterionic strategy to polymerize ring structure monomers to generate cyclic polymers. The initiator was heterocyclic carbene with a nitrogen-atom, which attacks the carbonyl group in a lactide to form a zwitterionic species in organic solvent, followed by a backbiting reaction of an alkoxide anion with the imidazole cation to form the ring. Based on their characterization of the product, the authors demonstrated that little linear analogue material was observed during or after the polymerization of lactide. The reaction was completed within minutes and the polydispersity index was low.
Ring expansion metathesis polymerization (REMP) was introduced by Grubbs and coworkers.\textsuperscript{15,47} The general mechanism is that monomers insert into a cyclic ruthenium complex to form a macrocycle. When the kinetics of polymerization is dominated by chain transfer reactions, the polydispersity index (PDI, $M_w/M_n$) of the cyclic polymers will approach 2. In recent work,\textsuperscript{48} they have demonstrated the ability to obtain cyclic brush polymers with narrower molecular weights distribution (PDI < 1.3) with ultrahigh molecular weight ($9.1 \times 10^6$ Da) using macromonomers.

Figure 2.8. The reaction scheme for the ring-expansion method using REMP to synthesize polyoctenamer.\textsuperscript{4}

Tew et al.\textsuperscript{49} proposed two unique molecular templates for generating polymeric material with cyclic molecular architectures based on ring-expansion metathesis polymerization and click chemistry. The first method used pentafluorophenol activated ester side groups while the other method used molecules containing alkyne clickable side groups. The cyclic polymers could be further functionalized on their reactive sites using click chemistry. Several polymers with cyclic topologies were developed based on the
click templates above, including functional cyclic polymers, microscopic cyclic polymer brushes, and macroscopic cyclic gels. According to its mechanism, these cyclic polymer templates could be expanded to incorporate other types of click chemistry, such as thiol-ene coupling\textsuperscript{50,51} and Diels-Alder click reactions, by incorporating the functional groups into the cyclic chains, as shown in Figure 2.7. Even more interesting is the fact that, because of the high selectivity of click chemistry and orthogonal reaction mechanisms, these templates could be combined. Using these methods, it is possible to create materials having an advanced hierarchy, such as new double-network materials containing two independent cyclic macromolecules to form the network.

![Figure 2.9. An example of the reaction scheme for thiol-ene coupling.\textsuperscript{31}](image)

2.2 Interface Segregation

The composition of a binary blend film at its interfaces generally deviates from that in the bulk so as to minimize the overall free energy of the film. In this case, the
component with lower interfacial energy enriches that interface. To quantify the strength of the enrichment, or segregation of one component at an interface, the interfacial excess, $Z^*$, has been introduced. As pictured in Figure 2.10, $Z^*$ is defined as the integral through the film of the difference between the actual composition depth profile and a hypothetical depth profile for the case of no interfacial segregation:

$$Z^* = \int_0^z [\Phi(z) - \Phi_{bulk}(z)] \, dz$$

where $\Phi(z)$ is the volume fraction of the one component at depth $z$ and $\Phi_{bulk}(z)$ is the volume fraction in the bulk of the same component. A component is distributed uniformly through the film when $Z^*$ for that component is zero. A positive value of $Z^*$ indicates that species is enriched at the interface; while a negative value indicates that the species prefers to be in the bulk to minimize the total free energy of the whole system. Many studies have investigated interfacial segregation phenomena in polymer blends to understand the parameters that drive the segregation to occur.
Figure 2.10. Schematic description of surface segregation in a binary blend (left) and the corresponding depth composition profile of the film (right) for the specific case in which the interfacial energy of one species is lower at both interfaces. This is not always the case. (From Wang, S. Ph.D. Dissertation, The University of Akron, 2011. With permission)

Neutron reflectometry (NR) is one of the most accurate and reliable techniques to study interfacial segregation. The dramatic difference between the scattering lengths of hydrogen ($-0.374 \times 10^{-12} \text{ cm}$) and deuterium ($0.667 \times 10^{-12} \text{ cm}$) provides NR with an excellent sensitivity in probing thin films with various depth profiles.\textsuperscript{54} The reflectivity, illustrated in Figure 2.11, is measured as a function of wave-vector transfer $Q$ ($Q=k-k_o$, $Q=|Q|=(4\pi \times \sin \theta)/\lambda$) in the specular condition, where $k_o$ and $k$ are the incoming and scattered beam wave vectors, $\theta$ is the half angle between incident and scattered directions and $\lambda$ is the wavelength of neutrons. Neutron reflectivity can probe spatial length scales down to the nanometer range with 10 Ångström resolution.\textsuperscript{55} Non specular reflectivity, on the other hand, is influenced by in-plane scattering length density (SLD) correlations.\textsuperscript{56} The depth profile is inferred indirectly from the specular reflectivity data by modeling.
when using reflectivity. Dynamic secondary ion mass spectroscopy, static secondary ion mass spectroscopy, and nuclear reaction analysis are three other techniques that can as well be used in characterization of interfacial segregation. The use of these techniques provides direct information on the depth profile and therefore complements NR.

Figure 2.11. Schematic of neutron reflection on a smooth planar surface.

The earliest study on surface segregation driven by the isotopic difference between linear polystyrenes was carried out by Jones et al. They discovered that in blends of hydrogenous polystyrene (hPS) and deuterated polystyrene (dPS) with similar molecular weight, dPS was enriched at the surface. This can be rationalized from the atomic mass difference between hydrogen and deuterium atoms, which causes the carbon-deuterium bond to be shorter than the carbon-hydrogen bond, leading to the deuterated species having a slightly lower polarizability and cohesive energy density. Therefore, the dPS enriches the surface in a dPS/hPS blend with components of similar molecular weight. Hariharan et al. and others investigated surface segregation in other miscible binary polymer blends of components having similar molecular weights. They found that the component with lower surface energy enriches the surface, which is consistent with a
lattice model prediction\textsuperscript{63} that even with a small difference in surface energies of the two components, the component with lower surface energy will segregate to the surface. They also predicted with a compressible mean field theory that in a binary blend of components with identical repeat units, but with different molecular weights, the component with lower molecular weight tends to segregate to the surface due merely to entropic effects. Their prediction was first demonstrated experimentally using neutron reflectometry\textsuperscript{61} and scanning force microscopy.\textsuperscript{62} Both the fact that shorter chains suffer a lower conformational entropic penalty when going to the surface and the fact that chain ends localize at the interface contribute to this phenomenon. Hong \textit{et al.}\textsuperscript{64} investigated the segregation of a blend of hPS and dPS using surface enhanced Raman spectroscopy. They argued that for isotopic blends of components having different molecular weights the molecular weight effect dominated the segregation of the blend, although the isotopic effect favored dPS enrichment at the interfaces. The total surface free energy was reduced by having the hPS with lower molecular weight at the surface. Hopkinson \textit{et al.}\textsuperscript{58} studied the isotopic effect in surface segregation using blends of hydrogenous poly(methyl methacrylate) (hPMMA) and deuterated poly(methyl methacrylate) (dPMMA) of identical molecular weight, and their results were inconsistent with the study of polystyrene blends, which they attributed to the fact that the difference in surface energy between hPMMA and dPMMA (0.00-0.04 mJ/m\textsuperscript{2}) is significantly lower than that between hPS and dPS (0.08 mJ/m\textsuperscript{2}).\textsuperscript{60} Thus the preference for one species to segregate to the surface to minimize the free energy of the whole system was difficult to see. Blends of partly deuterated and hydrogenous random poly(ethyl-\textit{r}-ethylene) were studied by Budkowski \textit{et al.}\textsuperscript{65,66} They found that in a system with little difference in surface energy
between components, the component present at lower concentration preferred to segregate to the surface, while in a blend in which the difference was large, the one with lower surface energy dominated the segregation. They also mentioned that the isotopic effect played a weak role in the behavior of surface segregation.

Another factor affecting surface segregation is the effect of the chain ends due to their chemical difference from the rest of the chain. Both entropic and enthalpic effects play a role in segregation induced by the chain end effect. Wu et al.\textsuperscript{67} theoretically calculated the chain end effects of a polymer melt near a surface using a self-consistent field theory (SCFT) with the result that there existed an attraction of chain ends to the surface without taking architecture and chemical differences between the backbone segments and chain ends into consideration. Jalbert et al.\textsuperscript{68} came to a conclusion, based on considerations with a Scheutjens-Fleer lattice self-consistent mean-field model, that as regards the effect of chain ends, surface segregation was significantly dominated by the difference in surface energy between the backbone segments and chain ends. Experimental investigations confirmed the theoretical prediction that the components having chain ends with lower surface energy are favored to enrich the surface in a binary blend film.

Molecular chain architecture plays a role in determining interfacial segregation in binary blend films. Fredrickson and coworkers\textsuperscript{69, 70} proposed a SCFT theory to predict segregation of long-branched chains that only considered the contribution of conformational entropy in blends with the flexible linear and long-branched chains at equilibrium. However, simulations carried out by Yethiraj et al.\textsuperscript{71} predicted a depletion of
short chain branched chains in an athermal system using a Monte Carlo simulation. Foster et al.\textsuperscript{72} studied short chain branched polyethylene propylene-\textit{block}-polyethylethylene (PEP-\textit{b}-PEE) diblock copolymers and found that the more compact polyethylethylene (PEE) block enriched the surface, which is consistent with the prediction of SCFT. Further investigations by Sikka \textit{et al.}\textsuperscript{73} supported the finding that the more compact short chain branched block was preferentially segregated to the interface due to the slightly lower entropic penalty for placing the more compact block at the interface. Surface segregation in a mixture of poly(methyl methacrylate) (PMMA) with a long chain branched random copolymer of methyl methacrylate and \(\alpha\)-methoxy poly(ethylene glycol)-\(\omega\)-monomethacrylate(P(PPA-\(\tau\)-MnG)) was studied by Walton \textit{et al.}\textsuperscript{74} and they found that although the branched copolymer chains had a higher surface energy, they tended to enrich at interfaces. Segregation in blends containing dPS and hyper-branched polystyrene (HBPS) with different end functionalities was investigated by Tanaka and coworkers.\textsuperscript{75} They discovered that in the blends in which HBPS had hydrophobic ends, the HBPS enriched at both interfaces while in the blends in which HBPS had hydrophilic ends, they were depleted from the air-surface. The results of blends with a long chain branched component can also be predicted by SFCT as well.\textsuperscript{79} Archer \textit{et al.} proposed a theory to describe the surface segregation of long branched polymers in blends with their linear analogues based on SFCT, taking into consideration the enthalpic contributions and compressibility near the surface,\textsuperscript{76, 77} in addition to the entropic effects considered earlier by Wu and Fredrickson.\textsuperscript{70} They also demonstrated experimentally that the long branched polymers had lower surface tension than their linear analogues.\textsuperscript{78}
A SCFT study by Wu and Fredrickson\textsuperscript{79} predicts that in a blend of a linear polymer and a cyclic polymer having the same repeat unit and molecular weight, the cyclic will be preferentially segregated to the surface and interface and in a manner that does not vary with molecular weight. Investigations of the segregation by Wang \textit{et al.}\textsuperscript{53} with NR showed that the degree of surface segregation of cyclic polystyrene (CPS) in such a blend is profoundly impacted by the molecular weight of the cyclic chain. They found experimentally that for 2k CPS blends with 2k linear dPS, the linear component enriched the surface. For a 37k CPS/dLPS blend the cyclic chain is preferred at the surface. While SCFT properly captures (nearly quantitatively without adjustable parameters) the segregation of the cyclic chain at the surface for the 37k blend, it does not work for the small chains. These work showed,\textsuperscript{6} however, that a Wall-PRISM (Polymer Reference Interaction Site Model)\textsuperscript{69} theory, which incorporates packing effects at the surface, works better than the SCFT to capture the thermodynamic behavior of the 2k cyclic/linear blend. An objective of the work presented here was to identify more closely the molecular weight at which the behavior crosses over from the linear chain being preferred at the surface to the behavior of the cyclic chain being preferred at the surface.

2.3 Dynamics of Macroyclic Polystyrene Melts

The study of surface fluctuations on polymer melts has been made possible by recent developments in XPCS.\textsuperscript{10-12} Using this technique, it is possible to probe the length scales and time scales characteristic of the cooperative motion of thermally stimulated capillary waves controlled by the surface tension of polymer melts and shear viscosity.\textsuperscript{10}
The pioneer works to investigate the surface fluctuations of polymer melts were based on the assumption that the scattering from the surface was due to capillary waves and used specular and off-specular X-ray reflectivity. Sinha and coworkers found that, when the film is thick enough, the surface relaxation times, \( \tau \), of linear polystyrene (LPS) melts, when scaled by film thickness, \( h \), varied with a dimensionless in-plane wave vector \( q || h \) such that data from films of different thicknesses collapsed onto a universal curve predicted by J. J. Kle using a hydrodynamic continuum theory (HCT) under a non-slip condition at the substrate,

\[
\frac{\tau}{h} = \frac{2\eta [\cosh^2(q || h) + q^2 || h^2]}{\gamma q || h [\sinh(q || h) \cosh(q || h) - q || h]^2}
\]

where \( \gamma \) is the surface tension and \( \eta \) is the zero shear viscosity of the bulk melt.

In recent work, Jiang et al. reported that LPS melt films supported on substrates evidenced a confinement effect when the thicknesses of the films were less than four times the radius of gyration (\( R_g \)) of the entangled polymer chains. They were able to fit the shape of the curves of relaxation time vs. \( q || \) when an elastic modulus accounted for in the original HCT for capillary waves was retained to account for viscoelasticity. Further investigation revealed that the surface fluctuations of melt LPS films with different thicknesses behaved differently in different temperature regimes using various incident angles (0.13-0.26°). Akgun et al. studied the surface fluctuations of polystyrene brushes with grafting densities in the range of 0.12-0.6 chains/nm², to discern the effect of end tethering on the melt surface fluctuations. Those studies revealed that no
fluctuations could be observed on the polymer brushes in the experimentally accessible $\tau$ (0.1~1000 s) and $q_{||}$ window. Their observation was consistent with predictions\textsuperscript{86, 87} from thermodynamic considerations in the sense that those theories anticipate fluctuations should be suppressed on the brush. Further, the observations were consistent with the suggestion of Obukhov and Rubinstein\textsuperscript{88} that chain relaxations in the brush could be very slow. Foster and coworkers\textsuperscript{12, 89, 90} also investigated the effect of architecture on surface fluctuations of melt polystyrene films using XPCS. They found that though the hydrodynamic continuum theory can describe the surface height fluctuations of melt films of macrocyclic polystyrenes and some unentangled comb polystyrenes, it could not fully capture the dynamics characteristic behavior of end-branched polystyrene melt thin films. The film viscosities of the melt macrocyclic polystyrene films derived from XPCS matched that from the bulk rheology for films of thickness 40 nm and higher, while the viscosities derived from XPCS data of some comb and all the end-branch polystyrene films, even as thick as 100 nm, tended to be higher than the viscosities from bulk rheology.

Green and coworkers\textsuperscript{91, 92} studied the dynamics of thin films of star polystyrenes with different numbers of arms and molecular weights using positron annihilation lifetime spectroscopy. They found that the variation in segmental movement in the arms with film thickness, as reflected by the value of $T_g$ of the films, depended on the number of arms in the stars and their molecular weights. For example, for the 8-arm star with arm molecular weight of 10k, the $T_g$ increased as the film thickness decreased when the films
were thinner than 60 nm, while for the star with either fewer arms or higher molecular weight the opposite behavior was observed. Confinement and temperature effects on surface capillary wave dynamics in bilayer polymer films near the glass transition were also studied by Torkelson and coworkers.$^{93}$ In their studies, thin polystyrene layers supported on polymeric substrates with varying moduli were characterized by XPCS. They found that an immiscible polymer domain may significantly influence the dynamics of a second, neighboring immiscible polymer at a temperature near the $T_g$ of the second polymer and over length scales that greatly exceed those of both cooperative segmental mobility near $T_g$ and the polymer radius of gyration. They also reported on the effect of confinement on surface wave relaxations in polymer films near $T_g$ and at low $q/h (< 1)$, with $\tau/h$ values increasing with decreasing PS layer thickness when measured on a given substrate at 110 °C. The behavior of the surface fluctuations deviated from the universal curve. However, when the measurements were taken far above bulk $T_g$ (i.e. $T_g, \text{bulk} +40 ^\circ\text{C}$), both substrate and confinement effects were negligible.
3.1 Handling of Air Sensitive Materials

To prevent the initiators or active centers from being deactivated, it is essential to exclude impurities such as oxygen, carbon dioxide and moisture from the reaction system. Here, high vacuum techniques and dry box manipulations were used to handle these air sensitive materials.\textsuperscript{95}

3.1.1 High Vacuum Technique

Anionic polymerizations were performed in all glass reactors on a high vacuum line system to exclude impurities such as water, oxygen and carbon dioxide. The layout of the high vacuum system is shown in Figure 3.1. High vacuum was produced by the connection of a mechanical pump (Edwards RV-8) and an oil diffusion pump (ChemGlass). Volatile materials were collected in a liquid nitrogen trap. The main line consisted of an upper manifold and a lower manifold connected by two glass tubes. Extending from the lower manifold were arms with either standard ground glass joints or grease taps. Each arm was separated from its manifold by a stopcock.\textsuperscript{95}
The degree of vacuum in the line was checked using a Tesla coil by bringing the tip near the glass on the high vacuum line. The absence of noise from the interaction of the Tesla coil with the vacuum system indicated that the pressure in the high vacuum system was less than $10^{-3}$ mm Hg. In order to maintain the efficiency of the two pumps, it was important to keep the proper oil level in each pump and to change the oil for the mechanical pump regularly.

3.1.2 Dry Box Manipulation

A Vacuum Atmospheres Model HE-43-2 glove box was used to transfer and weigh air-sensitive compounds and metals. The purification system in the glove box was a
column packed with molecular sieves and a copper catalyst. The column was regenerated by slowly purging with 5% hydrogen in nitrogen to reduce the catalyst and to remove the resident water vapor. Equipment and chemicals were brought into the box through an antechamber. The antechamber was pumped and refilled with argon gas at least three times before moving items from the antechamber into the dry box to remove the water vapor formed. The condition of the atmosphere within the dry box was checked using the Sekutowshi and Stucky method. When exposed to the dry box atmosphere, a solution of \((\text{Cp}_2\text{TiCl})_2\text{ZnCl}_2\) remains green if the dry box contains less than 5 ppm oxygen. If the indicator changes to an orange or red color, that means that the oxygen level is above 5 ppm, and it is necessary to regenerate the atmosphere in the dry box.

3.2 Purification of Reagents

In this section, the purification of solvents, monomers and terminating agents used for anionic polymerization will be discussed. The handling of the initiator and ring-closure agents will be addressed as well.

3.2.1 Solvents

In order to remove impurities such as oxygen, moisture and carbon dioxide, the solvents must be purified using stringent procedures, and stored in the proper way.
3.2.1.1 Benzene, Cyclohexane and Heptane

Benzene (ACS grade, EMD; 99%), cyclohexane (EMD, 99%) and heptane (EMD, 99%) were stirred with freshly crushed calcium hydride (Sigma-Aldrich, 95%) overnight under vacuum in a long-necked, round-bottom flask. The mixture was frozen and degassed three times using freeze-pump-thaw cycles in an isopropyl alcohol/dry ice bath (-78 °C), and then the solvent was transferred by vacuum distillation into an evacuated round-bottom flask containing sodium metal dispersion. The solvent was stirred with the sodium dispersion overnight. The purified solvent was then vacuum distilled into a storage round-bottom flask with a Rotoflo® stopcock, containing oligomeric poly(styryl)lithium. Persistence of the orange color indicated that the solvent was pure. Purified solvent was distilled from the flask into ampoules or a reactor when needed.

3.2.1.2 Tetrahydrofuran (THF) and Diethyl Ether

THF (ACS grade, Fisher scientific, >95%) or diethyl ether (EMD, 99%) was stirred with freshly crushed calcium hydride (reagent grade, Sigma-Aldrich, 95%) overnight under vacuum in a long-necked, round-bottom flask. The mixture was frozen and degassed three times using freeze-pump-thaw cycles in an isopropyl alcohol/dry ice bath (-78 °C), and then the ethereal solvent was transferred by vacuum distillation into an evacuated round-bottom flask containing sodium metal dispersion. The solvent was stirred with the sodium dispersion overnight, and then the mixture was frozen and degassed once more by a freeze-pump-thaw cycle. The purified solvent was vacuum distilled into a storage round-bottom flask fitted with a Rotoflo® stopcock, containing a
sodium mirror. Perseverance of the sodium mirror indicated the purity of the solvent. Purified solvent was stored in a dark place, and was distilled from the flask into ampoules or reactors when needed.

3.2.1.3 Dichloromethane

Dichloromethane (ACS grade, Fisher scientific, >95%) was stirred with freshly crushed calcium hydride (reagent grade, Sigma-Aldrich, 95%) overnight under vacuum in a long-necked, round-bottom flask. Then the mixture was degassed once using a freeze-pump-thaw cycle in a liquid nitrogen bath (−196 °C), and twice in an isopropyl alcohol/dry ice bath (-78 °C). Then the solvent was transferred by vacuum distillation into an evacuated round-bottom flask containing calcium hydride dispersion and stirred overnight. The purified dichloromethane was vacuum distilled into a storage round-bottom flask with a Rotoflo® stopcock. Purified solvent was distilled from the flask into ampoules or reactors when needed.

3.2.2 Monomer

In this project, the monomer used was styrene. The styrene can easily undergo self-polymerization, so the received product contains inhibitors to prevent it from reacting. In order to undergo anionic polymerization, both the inhibitors and impurities were eliminated before reaction.
3.2.2.1 Styrene

Styrene (Aldrich, 99%) was stirred with freshly crushed calcium hydride overnight under vacuum in a long-necked, round-bottom flask. Then the mixture was degassed three times using freeze-pump-thaw cycles in a liquid nitrogen bath (−196 °C). Then the monomer was transferred by vacuum distillation into an evacuated round-bottom flask containing calcium hydride dispersion and stirred overnight. The purified styrene was vacuum distilled into a storage round-bottom flask equipped with a Rotoflo® valve and containing dibutylmagnesium. Perseverance of the yellow color indicated the styrene was pure. Purified styrene was stored in the refrigerator and was distilled from the flask into ampoules or reactors when needed.

3.2.3 Terminating Agents

The terminating agents were used to quench the reactivity of the living chains. The purification procedures of these terminating agents will be discussed in this section.

3.2.3.1 Methanol

Methanol (Fisher Scientific, reagent ACS, 99.8%) was degassed three times using freeze-pump-thaw cycles in a liquid nitrogen bath (−196 °C) to remove air. The degassed methanol was transferred into ampoules with break-seals and each ampoule removed from the line by flame-sealing.
3.2.3.2 4-Vinylbenzyl Chloride (VBC)

4-Vinylbenzyl chloride (90%, Sigma-Aldrich) as received was stabilized with 500 ppm tert-butyl catechol and 500 ppm nitro paraffin. A reduced pressure distillation was performed to remove the inhibitors. Then the reagent was stirred with freshly crushed calcium hydride on the high vacuum line. The mixture was degassed three times using freeze-pump-thaw cycles in a liquid nitrogen bath before transferring into a round-bottom flask with a Rotoflo® valve by short path distillation. The flask was removed from the line by flame-sealing. Distribution of the 4-vinylbenzyl chloride (VBC) was effected in the dry box. The VBC was stored in a crimp-cap bottle and kept in the refrigerator. Before each use, the VBC was distributed into ampoules in the dry box and then degassed using the high vacuum system.

3.2.3.3 Dichlorodimethylsilane

Dichlorodimethylsilane (>99.5%, Aldrich) was distributed into a round-bottom flask with a Rotoflo® valve containing calcium hydride in the dry box, and stirred overnight. The flask was then connected to the high vacuum line. After three freeze-pump-thaw cycles in a liquid nitrogen bath (−196 °C) to remove air, the purified dichlorodimethylsilane was transferred into ampoules with break-seals. The coupling agent was then diluted by benzene and degassed. Each ampoule was removed from the line by flame-sealing.
3.2.3.4 Ethylene Oxide

Ethylene oxide (>99.5%, Aldrich) was transferred into a long-necked, round-bottom flask with ground calcium hydride in an isopropyl alcohol/dry ice bath (−78 °C) through the high vacuum line. After stirring overnight, the purified ethylene oxide was vacuum distilled into a round-bottom flask equipped with a Rotoflo® valve and containing dibutylmagnesium, and stirred for another 2 h in an isopropyl/dry ice bath. Then it was transferred into ampoules with break-seals and diluted with benzene. The ampoules were degassed three times using freeze-pump-thaw cycles in a liquid nitrogen bath, sealed off using flame-sealing and stored in the refrigerator.

3.2.4 Initiator Materials

5-Litho-1-pentene was the alkylolithium-initiator in this project. The route to synthesize the initiator will be discussed in 3.2.4.1. The materials used to prepare the initiator were lithium metal and 5-bromo-1-pentene. The procedures to deal with these chemicals will be addressed in this section.

3.2.4.1 5-Bromo-1-Pentene

5-Bromo-1-pentene (95%, Aldrich) was distilled under reduced pressure first, and then the reagent was stirred with freshly crushed calcium hydride on the high vacuum line. The mixture was degassed three times using freeze-pump-thaw cycles in a liquid nitrogen bath before transferring into a calibrated ampoule and flame sealed.
3.2.4.2 Lithium Powder

Lithium metal (stabilized, 1% Na, FMC) was stored in the dry box. Before each use, the powder was distributed into the dry box and then degassed in the high vacuum system.

3.2.5 Ring-closure Catalyst

The efficient end-to-end cyclization reaction with telechelic (α,ω-difunctional) precursors was achieved using the ring-closure catalyst. In this system, the Grubbs 1st generation catalyst was used as the ring-closure agent.

3.2.5.1 Grubbs Catalyst

The 1st generation Grubbs catalyst [(bis(tricyclohexylphosphine)benzylidene ruthenium(IV) dichloride, Aldrich, 97%)] was stored in the dry box. Before each use, the powder was dissolved in purified dichloromethane and then distributed into an ampoule in the dry box. The ampoule was degassed and flame-sealed on the high vacuum system.

3.2.6.1 Synthesis of 5-Litho-1-Pentene

The reactor used is shown in Figure 3.2. Ampoules of diethyl ether (20.30 mL, D), 5-bromo-1-pentene (4.10 mL, 0.0346 mol, A) and lithium metal (2.4032 g, 0.346 mol, B) were attached to a 250 mL, Morton-creased reactor with a medium sized filter (F). An empty ampoule was connected to the reactor as shown in Figure 3.2. Heptane
(approximately 50 mL) was transferred into the reactor through the vacuum line. The reactor was removed from the line by flame-sealing. The break-seals of the lithium metal and 5-bromo-1-pentene ampoules were smashed sequentially and the ampoules rinsed with heptane by cooling with the isopropyl alcohol/dry ice mixture. The mixture was stirred for three days at room temperature, and then the reactor was cooled to 0 °C in a water/ice bath. The break-seal of the diethyl ether ampoule was smashed before stirring the mixture for another 24 h at 0°C. The reactor was then again attached to the vacuum line through a break-seal (E). The break-seal was smashed and the solvent removed out of the reactor through the line. Another batch of heptane (approximately 50 mL) was transferred into the reactor by distillation and the mixture was passed through the medium sized filter (F) into the empty ampoule (G). The reactor was rinsed with heptane using the isopropyl alcohol/dry ice mixture so that most of the initiator was collected in the ampoule. The product was a yellow transparent solution. The ampoule was then flame-sealed from the reactor and transferred into the dry box. After that, the initiator was diluted with heptane (approximately 40 mL) and distributed into two crimp-cap bottles and sealed. The concentration of the initiator was determined by injecting 1.0 mL of the product by a syringe into each of two crimp-cap bottles, each containing 10 mL freshly distilled cyclohexane and sealing. The bottles were taken out of the dry box, and distilled water (10 mL) was used to deactivate the initiator solutions. The solutions were titrated with 0.1 M standard hydrochloric acid solution using phenolphthalein as the indicator. The average concentration of the 5-lithio-1-pentene initiator was 0.23 M.
3.2.6.2 Synthesis of 6 k α-4-Pentenyl-ω-(p-vinylbenzyl) Precursor

The glass reactor system used for synthesis of the precursor is shown in Figure 3.3. Ampoules of styrene (5.40 mL, 0.0472 mole, A), THF (1.70 mL, 20.9 mmol, B), as well as methanol (approximately 2 mL, E), were attached to the upper reactor. The lower reactor (H) was equipped with another ampoule (J) containing 4-vinylbenzyl chloride solution (2.60 mL, 18.47 mmol in 120 mL of THF) and connected to the upper reactor by a bent glass tube with a capillary as shown in Figure 3.3. The 5-lithio-1-pentene initiator (5.40 mL, 0.012 mmole) was injected into the upper reactor using a 10 mL gas-tight syringe under the protection of nitrogen gas, followed by flame-sealing of the glass tube.
during evacuation. Then benzene (approximately 80 mL) was distilled into the upper reactor and frozen before it was removed from the line by flame-sealing while under evacuation. When the reactor was warmed to room temperature, the break-seals of the styrene and THF ampoules were broken sequentially. Then the solution was put into a water bath at 30 °C. After 3 h, the reactor was reattached to the line through break-seal (D), and the solvent removed from the reaction via distillation. Then another batch of THF (approximately 100 mL) was distilled into the upper reactor to dissolve the product, and the solution turned red. The reactor was removed from the high vacuum line by flame-sealing.
Figure 3.3. Illustration of the apparatus used to synthesize the α-4-pentenyl-ω-(p-vinylbenzyl) precursor.

An isopropyl alcohol/dry ice mixture (−78 °C) was used to cool the whole apparatus. The break-seal of the 4-vinylbenzyl chloride/THF solution ampoule was smashed and the solution flowed into flask H. Then the solution was stirred while the α-4-pentenylpoly(styryl)lithium solution was slowly added into the reactor H dropwise via
the capillary, and the solution turned yellow. The small amount of solution left in the upper reactor was terminated by smashing the break-seal of the methanol ampoule. After the reaction, the solvent was removed using a rotary evaporator. The crude product was dissolved in benzene (15 mL), and precipitated into methanol (approximately 200 mL). The precursor was purified once more using the above mentioned dissolution-precipitation method, and then washed with an abundance of methanol. The powder was dried in a high vacuum oven overnight before it was characterized using $^1$H NMR, SEC, and MALDI-ToF mass spectrometry.

3.2.6.3 Synthesis of Macrocyclic Polystyrene

For the description of the synthesis of the macrocyclic polystyrene, refer to the schematic of the reactor in Figure 3.4. In the dry box, $\alpha$-4-pentenyl-$\omega$-($p$-vinylbenzyl)polystyrene (0.9355 g, 0.173 mmol; $M_n = 6,000$ g/mol) and bis(tricyclohexylphosphine)benzyliminoruthenium(IV) chloride (0.3635 g, 0.441 mmol) were distributed into ampoules A and B, respectively. Freshly distilled dichloromethane (approximately 20 mL) was injected into each of the ampoules and the ampoules were sealed. The ampoules were then taken out of the dry box and attached to the high vacuum line. Both solutions were degassed three times using freeze-pump-thaw cycles in a liquid nitrogen bath (−196 °C) before removing them off from the line by flame-sealing. The reactor was then connected to the high vacuum line and dichloromethane (approximately 1.2 L) was distilled into it through vacuum. When the reactor warmed to room temperature, the break-seals of the $\alpha$-4-pentenyl-$\omega$-($p$-vinylbenzyl)polystyrene and
Grubbs catalyst ampoules were smashed sequentially. The reaction was carried out in a water bath (40 °C) for 24 h. The solution turned from pink to orange when the reaction was completed. The solution was then exposed to the air before removing the residual catalyst by silica gel column chromatography using toluene as eluent. The product was precipitated into methanol and was dried in the high vacuum oven (-100 kPa) overnight before it was characterized using $^1$H NMR, SEC, and MALDI-ToF mass spectrometry. The crude product was fractionated several times using toluene and methanol to get rid of the high molecular weight impurities until the SEC spectrum only displayed a symmetrical, monomodal peak.
3.2.7 New Synthesis of Cyclic Polystyrenes

Although the synthetic route mentioned above is an efficient way to synthesize well-defined cyclic polystyrenes, it still encounters many problems. One of its drawbacks is the formation of a side-product resulting from lithium-halogen exchange between α-4-pentenylpoly(styryl)lithium and p-vinylbenzyl chloride to form α-4-pentenyl-ω-chloropolystyrene. Once the intermediate α-4-pentenyl-ω-chloropolystyrene is formed, it can further undergo Wurtz coupling\(^{102}\) with α-4-pentenpoly(styryl)lithium to form dimer as depicted in Figure 3.5. In order to overcome this problem, a new method to synthesize well-defined cyclic polystyrenes has been proposed.

The anionic initiator containing an olefinic vinyl group, 5-litho-1-pentene, was synthesized and titrated using the method described in Section 3.6.2.1. The glass reactor
system used for synthesis of the precursor is shown in Figure 3.6. Dichlorodimethysilane (0.05 mL, 0.44 mmol)/benzene (0.5 mL) (A) and 5-litho-1-pentene (7.4 mL, 1.11 mmol, 0.15 M) (B) and were distributed into ampoules in the dry box, and then flame-sealed using the high vacuum line. Styrene (2.8 mL, 22.5 mmol) (C), THF (1.8 mL, 22.2 mmol) (D), ethylene oxide (~1 mL)/benzene (~5 mL) (E) and methanol (~2 mL) (F) were distilled into their respective ampoules using the high vacuum line before they were sealed off using flame-sealing. These six ampules were connected to a 100 mL Morton-creased reactor, and the reactor was attached to the high vacuum line to evacuate the air from it. Benzene was distilled into the reactor and the reactor was sealed off from the line. Initiator, THF and styrene were added to the reactor by smashing the break-seals of the ampoules sequentially. The reaction was carried out at 0 °C for 2 h to achieve full conversion of the styrene. Then the break-seal of the dichlorodimethysilane solution ampoule was broken and the reactor was kept at 0 °C for another 2 h. Finally, ethylene oxide and methanol were added to the reactor via smashing break-seals sequentially to terminate the reactive centers of excess arms. The resulting hydroxyl-functionalized excess arms were removed using toluene as eluent and the α,ω-telechelic polymer was characterized using SEC, $^1$H NMR, $^{13}$C NMR and MALDI-ToF mass spectrometry. Then the cyclization and characterization were carried out under conditions similar to those discussed in Section 3.6.2.3.
Figure 3.6. Illustration of the apparatus used to synthesize the α,ω-telechelic precursor.

3.3 Molecular Characterization

3.3.1 NMR Spectroscopy

$^1$H NMR spectra were obtained using a Varian Mercury 300 instrument (300 MHz) with CDCl$_3$ (99.8% Cambridge Isotopes) as solvent. $^{13}$C NMR spectra were obtained using a Varian Mercury 500 instrument (500 MHz) with CDCl$_3$ (99.8% Cambridge Isotopes) as solvent. The relaxation time was set as 30 sec and the spectrum scanned 512 times for each sample.
3.3.2 Size Exclusion Chromatography

Size exclusion chromatography was performed on a Waters 150-C Plus instrument equipped with three HR-Styragel columns. The detectors were a laser light scattering detector (Wyatt Technology, DAWN EOS, λ = 670 nm), a differential refractometer (Waters 410), and a differential viscometer (Viscotek 100). The eluent was THF at the rate of 1.0 mL/min at 30 °C. Wyatt ASTRA (version 4.73.04, Viscotek Corp) and OmniSEC 82 (Version 4.3.1.246) software were used to analyze the data. From the analysis of the data, the number average molecular weight ($M_n$) of the $\alpha$-4-pentenyl-$\omega$-(p-vinylbenzyl)polystyrene was determined to be 6,000 g/mol with $M_w/M_n=1.01$. And for the $\alpha,\omega$-divinylpolystyrene, the number average molecular weight was 4,600 g/mol and its polydispersity index (PDI) was 1.09.

3.3.3 MALDI-ToF Mass Spectrometry

MALDI-ToF mass spectra were collected using a Bruker Ultraflex-III MALDI-ToF mass spectrometer (Bruker Daltonics, Bullerica, MA) with a Nd:YAG laser (355 nm). The following solutions were made in tetrahydrofuran (THF) (Aldrich, 99.9 %): 20 mg/mL of the matrix molecule \{2-[(2E)-3-(4-t-butylphenyl)-2-methylprop-2-enylidene]malononitrile\} (DCTB, Alfa Aesar, 99+%), 10 mg/ml of the cationizing salt, silver trifluoroacetate (Aldrich, 98%), and 10 mg/mL of the polymer. These three solutions were mixed together at a ratio of matrix:cationizing salt:polymer of 10:1:2. The mixture was then dropped onto the MALDI sample target and allowed to dry. The intensity of the laser beam was optimized. Analyses were run in the positive reflectron.
and linear modes, and the mass-to-charge ratio was calibrated using a polystyrene standard with a molecular weight close to that expected for the sample under consideration.

3.3.4 Differential Scanning Calorimetry

A TA Instruments Q10 DSC was used to measure the glass transition temperatures of the macrocyclic polystyrenes. The scans were carried out from 20 °C to 120 °C at the rate of 10 °C /min. Then the sample was cooled at the rate of -10 °C /min to 20 °C using liquid nitrogen to eliminate the thermal history, and a second scan was performed using the same conditions as for the first scan. The thermal data were collected from the second heating scan and analyzed using the Universal Analysis software developed by TA Instruments-Waters LLC.

3.4 Preparation of Polymer Films

Polymer films for the study of surface segregation in cyclic/linear blends and surface fluctuations on the tops of pure melt films were prepared by spin-casting the appropriate solution onto an etched silicon wafer. The procedures for these samples will be described in the following chapters separately.
3.4.1 Preparation of Cyclic/linear Polymer Blend Films

Polymer mixtures with 20 wt% hydrogenous polystyrene (hPS) and 80 wt% perdeuterated polystyrene (dPS) with similar molecular weights were dissolved in toluene (EMD, 99.5 %). The substrates used to cast the films were 3-inch, one-side polished silicon wafers (El-Cat). The optimum substrate thickness for reflectivity measurements was 1 mm, but substrates of thickness 0.35 nm were used (this made some measurements difficult). Each wafer was checked for planarity of the substrate using an x-ray rocking curve before being selected for sample preparation. A piranha solution (mixture of 30% hydrogen peroxide and 70% sulfuric acid by volume fraction)\(^{101}\) was prepared to remove the organic impurities from the surface of the silicon wafers. Wafers were cleaned by immersion in the piranha solution for 20 min. After this, the native oxide layer was removed from each wafer by dipping the wafer into a 1% aqueous solution of hydrofluoric acid for about 40 seconds, and then rinsing with ultra-purified water and drying with nitrogen gas. Each wafer was rinsed with 5 mL toluene, and then approximately 1 mL of a prepared solution was spun-cast onto the wafer at a rotation speed of 2000 rpm for 2 min. The concentration of the solution was varied from 1 to 3 wt% according to the target thickness of the film. Before spin-casting a film, a 0.45 μm filter (Whatman, PTFE) was used to filter both the pure solvent and solution five times. The prepared samples were annealed in a vacuum oven (1×10\(^{-7}\) Pa) at 120 °C to remove the residual solvent in the films and allow the blends to come to equilibrium states at that temperature. The samples were cooled to the glass transition temperature over about 0.5 h, further cooled to room temperature and then removed from the vacuum. Thus the state of
the sample when transported to the beamline was probably not the equilibrium state for
120 °C, but rather a state characteristic of some temperature below 120 °C, but above $T_g$.

3.4.2 Preparation of Polymer Films for XPCS

Pure melt films for study with XPCS were also made by spin coating. A solution in
toluene (EMD, 99.5%) was made for each polystyrene of whatever architecture (i.e.
linear cyclic) at a concentration appropriate to achieve a target film thickness. The
substrates used to cast the films were 2.0 cm × 1.5 cm one-side polished silicon wafers
(0.35 nm, preferred thickness of 0.7 mm) and were checked for surface roughness using
an x-ray reflection wafer check before the wafers were selected as the substrates for
sample preparation. A piranha solution was prepared to remove the organic impurities
from the surface of the silicon wafers. After this, the native oxide layers were removed
from the wafers by dipping the wafers into a 1 % aqueous solution of hydrofluoric acid
for about 40 seconds, and then rinsing with ultra-purified water and drying with nitrogen
gas. The wafers were rinsed with 5 mL toluene, and then approximately 0.5 mL of the
prepared solution was spun-cast onto each wafer at the rotation speed of 2000 rpm for 2
min. The concentrations of the solutions were varied from 1 to 3 wt% according to the
target thicknesses of the films. Before spin-casting a solution, a 0.45 μm filter (Whatman,
PTFE) was used to filter each solution five times. The prepared samples were annealed in
a high vacuum oven at 120 °C to remove the residual solvent in the films and ensure that
the blends were in a state close to the equilibrium at 120 °C before the XPCS
measurements. As for the blend films, the actual state of a film when pulled from the
over was probably not exactly that of equilibrium at 120 °C due to the time required to cool the sample before removing it from the oven.

3.5 Instruments for the Study of Surface Segregations and Surface Fluctuations

The surface segregation of cyclic/linear polystyrene blends was probed using neutron reflectometry at beamline NG7 at the National Center for Neutron Research (NCNR) at NIST to find out the crossover molecular weight at which no segregation occurs. The surface dynamics of melt films were investigated using XPCS at the Advanced Photon Source (APS) at Argonne National Laboratory. The instruments used for these two techniques are described in the following sections.

3.5.1 Neutron Reflectometry

NR experiments were performed at the NG7 horizontal neutron reflectometer at NCNR in Gaithersburg, MD. The features of the instrument are shown in Figure 3.7. A pyrolytic graphite monochromator was used to select the beam for the experiment from the polychromatic cold neutron beam using Bragg diffraction. The usage of graphite crystals provides a substantially narrowed energy spectrum, while maintaining the intensity of the beam high enough so that a variety of experiments are feasible. The incident neutron wavelength, \( \lambda \), is 4.75 Å with a resolution (\( \Delta \lambda/\lambda \)) of 2.5%. The maximum range of scattering vector, \( q_z \), available is 0.03 to 2.4 nm\(^{-1}\) with a relative resolution (\( \Delta q/q \)) from 0.02 to 0.15 depending on the slits used. The resolution when measuring the samples was as high as possible. The beam width was fixed at 35 nm and
the slit gaps were increased with $q_z$ so that the footprint size on a sample could be regarded as constant and the intensity at larger values of $q_z$ could be higher.

To account for the effect of the varying slit sizes a main bean scan, which measures only the change in incident intensity with slit size, was run. To correct for background due to all sources, including incoherent scattering, electronic noise, and cosmic radiation, background scans were run. Incoherent scattering from the hydrogenous species in the film was the largest contributor to the background scattering, and this was most pronounced at the highest values of $q_z$. The background signal directly beneath the specular peak has to be estimated, since it cannot be measured directly. This is done by running two scans, one with the incident angle offset below the specular value ($I_{\text{bgd} \theta - \delta}$) and one with the incident angle offset above the specular value ($I_{\text{bgd} \theta + \delta}$). The value of the offset is chosen in order to measure the background signal on that side of the specular peak and no part of the specular intensity. Therefore the offset grows with incident angle in a way well-established from earlier measurements by this group on polymer blend films. The background signal under the specular peak ($I_{\text{bgd under spec}}$) is estimated by a linear interpolation from the two measured background values:

$$I_{\text{bgd under spec}} = 0.5 \times (I_{\text{bgd} \theta - \delta} + I_{\text{bgd} \theta + \delta}).$$

After these two scans, the true reflectivity of the sample could be calculated by subtracting the scan of background intensity from the raw reflectivity scan. In general, it is necessary to measure a background scan for each sample. However, since the substrate thickness, sample environment and slit sizes used were similar for the whole batch of samples, only one measurement of background sufficed for the reduction of all data sets.
from one beam time. The reduced data were analyzed using the Reflpack software obtained from NIST. A reasonable model of film structure was set first, and was compared with the experimental data. The parameters of the model (i.e. layer thickness, interface roughness and scattering length density) were adjusted until the sum of squared errors between experimental and model points was achieved. The best fit curve was checked using a “mass balance” criterion. According to this criterion, the total scattering length per sample area calculated by integration of the SLD profile of the whole film should be close to the value of total scattering length per area calculated to have been put into the sample. If the two calculated values differed by 2% or more, this model was excluded and the model parameters varied to search for a "fit" meeting this criterion.

Figure 3.7. Schematic features for the horizontal neutron reflectometer at NG7 at NIST. (From NCNR website, NG7 Reflectometer Features.)
3.5.2 X-ray Photon Correlation Spectroscopy

Surface fluctuations of melt cyclic films were measured at beam line 8-IDI at the Advanced Photon Source at the Argonne National Laboratory with a partially coherent monochromatic x-ray beam (E=7.5 keV). The schematic geometry of the instrument is illustrated in Figure 3.8. The probe depth of the polystyrene films was restricted to 9 nm with the X-ray incidence angle of 0.14°, which is below the critical angle of polystyrene films (0.16°). The overall thicknesses of the films were above 16nm, thus ensuring the scattering from the vacuum/surface dominates the scattering pattern. The setup of the instrument makes possible the collection of intensities at values of the in-plane wave vector, \( q_{||} \), up to \( 10^{-3} \) Å\(^{-1} \). The dimension of the beam was 20×20 μm\(^2\), and its coherence lengths were 7 and 90 μm in the horizontal and vertical directions, respectively. The typical intensity of the beam was about \( 1\times10^{10} \) photons/sec. The surface fluctuation dynamics were measured at temperatures 30-60 °C above the values of \( T_{g,\text{bulk}} \) of the cyclic and linear polystyrenes. The off-specular scattering from the film surface was recorded at certain time intervals using a charge coupled device (CCD) camera located 3345 mm downstream of the samples.
Two dynamic modes were used to collect the off-specular diffuse scattering: full frame and kinetic modes. In the full frame mode, the whole area of the CCD camera was used to collect data as a function of time; in contrast, only 1/13 of the CCD active area was used to capture each frame for the measurement when the kinetic mode was used. Examples of scattering patterns captured on the CCD camera using full frame and kinetic modes are shown in Figures 3.9 (a) and (b), respectively. In the full frame or kinetic mode, sequences of speckle patterns were collected over time. Generally, the full frame mode is used for measuring slow surface fluctuations (200 sec < τ < 2000 sec) and kinetic mode is used for measuring fast surface fluctuations (0.1 sec < τ < 500 sec). When the relaxation time is long, a so-called “sleep time”, or time between adjacent frames with no data collection, is increased. During sleep time, a fast beam shutter is kept closed to eliminate x-ray beam exposure to prevent the spot from being damaged. The access to
sleep time provides the chance to extend the time window of accessible relaxation times without further exposure of that sample spot with the x-rays. Since the exposure time on each spot is limited due to beam damage, the dynamics are measured at multiple spots on a sample and the correlation functions from these multiple spots averaged to obtain a correlation function with better statistics. When measuring in the kinetic mode, the active area of the detector is divided into 13 regions. The benefit of this mode is that it is able to measure for shorter times otherwise not accessible due to the readout time of the detector, which is 1.8 seconds. When the active area of the camera is divided into several slices and several patterns captured successively before reading out the detector, the shortest time between frames can be reduced to as short as 0.050 sec. By reducing both the time per frame and the time between each frame, the extended time window of the XPCS measurement can reach down to relaxation times of order 0.1-1 sec, though this sacrifices the $q_{\parallel}$ range probed since a small portion of the CCD camera is used to collect the speckle pattern.
Figure 3.9. CCD images of diffuse scattering collected using (a) full frame and (b) kinetic modes.

The surface fluctuations were characterized by calculating the normalized intensity-intensity time autocorrelation function ($g_2$),

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

where $I(q,t')$ is the scattering intensity at a certain wave vector, $q$, at time $t'$ and angular brackets refer to ensemble averages over time $t'$ and $t$ is the delay time. Reflectivity measurements were carried out before and after the dynamics measurement to calculate the thicknesses of the film and provide one check on possible damage of the sample. The beam damage caused by x-ray exposure at the temperature far above $T_{g,bulk}$ was checked rigorously by comparing the correlation results using the full number of frames with those using half the number of frames, and the suspicious frames were discarded.

Values of the autocorrelation function were calculated using a Matlab based analysis program (xpcs gui, version 730) coded by Zhang Jiang and Michael Sprung of
the University of California San Diego and was made available to users at 8-IDI by the beamline scientists at Argonne National Laboratory. The two dimensional data have to be partitioned to define which intensity is associated with each value of $q$. Since the numbers of the static and dynamic partitions are constant for the analysis, use of different mask sizes results in the incorporation of different length scales of motion. Therefore, the relaxation times calculated using different masks for a given sample under the same conditions can be different, depending on how closely the mask regions have been matched. Therefore, it is necessary to make just one mask for one mode during the analysis, to ensure that the results are consistent.
CHAPTER IV

SYNTHESIS OF MACROCYCLIC POLYSTYRENE

In this chapter, the architecture of the cyclic polystyrenes will be confirmed by comparison of characterization data with those from the α-4-pentenyl-ω-(p-vinylbenzyl) precursor obtained by $^1\text{H}$ NMR and MALDI-ToF mass spectrometry. The glass transition temperatures of the samples determined by differential scanning calorimetry will be reported. The reaction pathway for the synthesis of this kind of macrocyclic polystyrene is depicted in Figure 4.1.

Scheme 4.1. Reaction pathway for macrocyclic polystyrenes.
4.1 NMR

The existence and changes of vinyl group peaks in both the divinylpolystyrene precursors and the macrocyclic polystyrene were verified by the peak positions and peak area integrals using \(^1\)H NMR spectroscopy.

4.1.1 \(\alpha\)-4-pentenyl-\(\omega\)-(\(\rho\)-vinylbenzyl)polystyrene\(^5\)

The \(^1\)H NMR spectrum of the \(\alpha\)-4-pentenyl-\(\omega\)-(\(\rho\)-vinylbenzyl)polystyrene is shown in Figure 4.1. It exhibits terminal vinyl resonances at \(\delta\) 5.2 ppm and \(\delta\) 5.7 ppm, which provide evidence for the formation of the \(\omega\)-(\(\rho\)-vinylbenzyl) chain end (=CH\(_2\)H and =CH\(_2\)H\(_\text{d}^\gamma\)\). The terminal resonance at \(\delta\) 5.7 ppm overlaps with the vinyl resonance from the \(\alpha\)-pentenyl group (-CH=, H\(_b\)). Another vinyl resonance (-CH=, H\(_a\)) from the 5-pentenyl group is clearly observed at \(\delta\) 4.9 ppm. The internal vinyl proton resonance (-CH=, H\(_c\)) at \(\delta\) 6.4 ppm is seen in the aromatic proton resonances areas. The integral ratio of H\(_b\):(H\(_b\)+H\(_d\)):H\(_c\) is around 2:1:2, which is in accordance with the number of the protons expected at each position. From both the chemical shifts and integrals, it is clear that the \(^1\)H NMR spectral analysis is consistent with the formation of \(\alpha\)-4-pentenyl-\(\omega\)-(\(\rho\)-vinylbenzyl)polystyrene precursor.
4.1.2 Macrocyclic Polystyrene

The $^1$H NMR spectrum of the 6k macrocyclic polystyrene is shown in Figure 4.2. The new internal vinyl protons at $\delta$ 6.0 ppm and 6.2 ppm are observed as expected for the structure of the macrocycle, which corresponds to formation of the coupling product with vinyl protons (=CH$_a$- and =CH$_b$-).
The comparison of the $^1$H NMR spectra for the $\alpha$-4-pentenyl-$\omega$-(p-vinylbenzyl) polystyrene with the corresponding macrocyclic polystyrene shows that it is a well-defined macrocyclic polystyrene. The signals for the terminal vinyl protons at $\delta$ 4.9 ppm, 5.7 ppm ($\alpha$-vinyl, red rectangle, Figure 4.1) and 5.7 ppm, have disappeared, while the new vinyl protons at $\delta$ 6.0 ppm and 6.2 ppm (red rectangle, Figure 4.2) have appeared as expected for the structure of the ring topology formed from the metathesis ring-closure reaction. From the comparison of the $^1$H NMR spectra it may be seen that the ring-closure reaction is so efficient that almost all of the $\alpha,\omega$-divinylpolystyrenes coupled.
4.2 Size Exclusion Chromatography

From the analysis of the SEC data, the number average molecular weight ($M_n$) of the α-4-pentenyl-ω-(p-vinylbenzyl)polystyrene is $6,000\pm 30$ g/mol and its polydispersity index (PDI) is $1.01\pm 0.1$, which demonstrates that it is well-defined polystyrene. This result from SEC was taken as the molecular weight of the sample, because the data collected from MALDI-ToF mass spectrometry reflect lower average molecular weight due to the fact that the chains with lower molecular weight are easier to ionize.

4.2.1 Comparison of Macrocycle and its Linear Precursor

The SEC chromatograms of the α-4-pentenyl-ω-(p-vinylbenzyl)polystyrene and macrocyclic polystyrene are compared in Figure 4.3.
Figure 4.3. SEC chromatograms of the 6k α-4-pentenyl-ω-(p-vinylbenzyl)polystyrene and the corresponding macrocyclic polystyrene before and after fractionation.

The chromatogram of the precursor has a small shoulder (5 wt%) that appears at lower elution volume, which may be attributed to the formation of a side-product resulting from lithium-halogen exchange between α-4-pentenylpoly(styryl)lithium and p-vinylbenzyl chloride to from α-4-pentenyl-ω-chloropolystyrene. Once the intermediate α-4-pentenyl-ω-chloropolystyrene formed, it can further undergo Wurtz coupling with α-4-penten-poly(styryl)lithium to form dimer as depicted in Figure 4.4.
Figure 4.4. Mechanism for formation of dimeric product.

The chromatogram of the crude macrocycle (Figure 4.3) also has a shoulder (9 wt%) that appears at lower elution volume. This may be due to the competition from higher molecular weight adducts versus intermolecular reactions, as well as a similar reaction for the dimer procured during termination. Roovers and Toporowskii\textsuperscript{104} demonstrated experimentally that the retention volume of a macrocycle is larger than that of its linear analog in their SEC chromatograms. Here also we see a larger elution volume for the macrocyclic polystyrene than for the α-4-pentenyl-ω-(\textit{p}-vinyl-benzyl)polystyrene, which is consistent with formation of a cyclic polymer. After three fractionations using toluene as the solvent and methanol as the precipitant, the chromatogram (Figure 4.3, blue curve) shows a symmetrical distribution without any shoulder at lower retention volume, which demonstrates that the high molecular weight impurities have been successfully removed.
4.3 Determination of Molecular Weight and Chain Topology using MALDI-ToF Mass Spectrometry

The most definitive characterization method to confirm the formation of macrocyclic polystyrene is MALDI-ToF mass spectrometry. Due to the fact that the macrocyclic polystyrene was produced by the elimination of an ethylene molecule from the divinyl precursor, the molar mass difference between an average mass peak from the macrocyclic polystyrene and the corresponding peak from the linear precursor should be 28.05 m/z, and the numerical calculation will be discussed in the following part.

4.3.1 α-4-Pentenyl-ω-(p-vinylbenzyl)polystyrene

Figure 4.5 shows the MALDI-ToF mass spectrum of the α-4-pentenyl-ω-(p-vinylbenzyl)polystyrene. The calculated average mass for the 46-mer of the α,ω-divinyl precursor is 5085.06 Da \[69.12 (C_5H_9) + 46 \times 104.15 (C_8H_8) + 117.17 (C_9H_9) + 107.87 (Ag^+)\], while the observed peak is at 5085.40 m/z. There are some distributions of weak intensity that appear at 4757.18 m/z on the spectrum, which correspond to the monofunctional impurity α-4-pentenylpolystyrene \[C_5H_9-(C_8H_8)_n-H.Ag^+, 4758.58 Da\]. It probably results from termination reactions with the solvent (THF) or terminating agent. The absence of the peaks corresponding to the dimers seen in the SEC chromatogram is due to the limitation of the scale window. Dimers would appear at around 10k-12k. In summary, the MALDI-ToF mass spectral characterization is in good accord with the efficient synthesis of 6k α-4-pentenyl-ω-(p-vinylbenzyl)polystyrene with controlled
molecular weight, narrow molecular weight distribution and high \( \alpha,\omega \)-vinyl chain-end functionality.

Figure 4.5. MALDI-ToF mass spectrum of the 6k \( \alpha \)-4-pentenyl-\( \omega \)-(\( p \)-vinylbenzyl)polystyrene.

4.3.2 Macrocyclic Polystyrene

To investigate the formation of the macrocyclic structure for the metathesis ring-closure products from the \( \alpha,\omega \)-divinylpolystyrenes quantitatively, MALDI-TOF mass spectrometry has been used, because it has proven to be the most definitive characterization method to confirm the molecular weight of the compound. The mass spectrum of the 6k macrocyclic polystyrene after fractionation, shown in Figure 4.6, shows a monomodal distribution. The calculated average mass of the 47-mer of the
macrocyclic polymer is 5161.16 Da \[158.24 (\text{C}_{12}\text{H}_{14}) + 46 \times 104.15 (\text{C}_8\text{H}_8) + 107.87 (\text{Ag}^+)\], while the observed peak is at 5161.34 \(m/z\). What is more, because the macrocyclic polystyrene was produced by the elimination of an ethylene molecule from the divinyl precursor, the molar mass difference between an average mass peak from the macrocyclic polystyrene and its corresponding peak from the linear precursor should be 28.05 \(m/z\) \([28.05(\text{C}_2\text{H}_4)]\). Actually, the average mass peak (Figure 4.6) of the 47-mer macrocyclic polystyrene is 5161.34 \(m/z\), while the average mass peak (Figure 4.5) of the corresponding linear 47-mer precursor is at 5189.48 \(m/z\). The observed difference is 28.15 \(m/z\). The calculated difference is consistent with the observed one, which means the MALDI-ToF mass spectral result is in excellent agreement with the designed topology of a macrocyclic structure. The MALDI-ToF mass spectrum of the crude macrocyclic polystyrene verified the high efficiency of the ring-closure catalyst, with which the cyclization reaction can produce a well-defined macrocycle with a narrow molecular weight distribution.
4.4 Differential Scanning Calorimetry

The glass transition temperatures of cyclic polystyrenes have been studied before\textsuperscript{53}, but not widely. Therefore, a measurement of $T_g$ for this molecule will add to the existing database of values for well-defined cyclic polystyrenes. The DSC curve is shown in Figure 4.7. The value of $T_g$ was determined by the second scan carried out from 20 °C to 120 °C at the rate of 10 °C/min.
The result for this 6k macrocyclic polystyrene is 98.9±1 °C. It is a bit higher than the value of $T_g$ (97.2±1 °C) of a 7k macrocyclic polystyrene with the same composition and structure already reported in the literature. This may be due to the uncertainty of the machine. The bulk $T_g$ of a 6k linear polystyrene synthesized using anionic polymerization was also measured. The procedure was the same as for the macrocyclic polystyrene, and the value of determined for this linear analog 83.4±1 °C. The result is in reasonable agreement with the value of 89.7±1 °C reported for a 7k linear chain by the previous study. The $T_g$ of the 6k films are supposed to be as same as the bulk $T_g$ when dealing with XPCS data.
CHAPTER V

NEW ROUTE TO SYNTHESIZE MACROCYCLIC POLYSTYRENES

In this chapter, a new method combing anionic polymerization, a linking reaction and metathesis ring-closure chemistry to synthesize a well-defined macrocyclic polystyrene will be confirmed by comparison of characterization data with those from its α, ω-divinylprecursor. Using this new route, the formation of dimeric linear impurities can be eliminated, thus improving the efficiency of cyclization. The reaction pathway for the synthesis of this kind of macrocyclic polystyrenes is depicted in Figure 5.1.

Preparation of α,ω-divinylpolystyrene. Polymerization was initiated by 5-lithio-1-pentene\(^99\) in benzene with twenty equivalents of THF. THF was used to disassociate the aggregates of the initiator and keep the living chain in a low degree of aggregation so that the rate of initiation to propagation was high enough to obtain the product with narrow molecular weight distribution. The living chain ends were terminated with dichlorodimethysilane in benzene. The termination reaction between the living chains and dichlorodimethysilane was quantitative and free of side reactions. The living chains were in excess so that each linking agent could connect two chains. The residual living chains were terminated by ethylene oxide and methanol. Due to the difference of polarity between the linear precursor and the residual chains, the latter with hydroxyl end groups were removed by column chromatography using toluene as eluent.
Scheme 5.1. Reaction pathway for macrocyclic polystyrenes.

5.1 NMR

The existence and changes of vinyl groups in both the divinylpolystyrene precursor and macrocyclic polystyrene were verified by the peak positions and peak area integrals using $^1$H NMR and $^{13}$C NMR spectroscopy.
5.1.1 α,ω-divinylpolystyrene

The $^1$H NMR spectrum (Figure 5.2) of the linear precursor exhibits the characteristic vinyl resonances (–CH=, $H_a$) and (=CH$_2$, $H_b$, $H_{b'}$) at $\delta$ 5.7 ppm and 4.9 ppm, respectively. The integration ratio of the two peaks is consistent with the number of protons in the vinyl groups. The broad peak between $\delta$ -0.1 ppm and -0.9 ppm corresponds to the protons of methyl groups which attach to the silane (– Si(CH$_3$)$_2$, $H_c$). The integration of the peak is in accordance with the number of protons in the methyl groups, which demonstrates the high efficiency of the linking agent. The $^1$H NMR spectrum proves the formation of α,ω-divinylpentenylstyrene.
The $^{13}$C NMR spectrum (Figure 5.3) of the linear precursor shows a pattern similar to that seen in the spectrum of α-4-pentenyl-ω-(p-pentenyl)styrene.\textsuperscript{5} From the integration of the $^{13}$C of vinyl carbon (5) and aromatic carbon (D, E), the calculation of $M_n$ is 5400 g/mol, which is in the acceptable error range of the values from SEC and MALDI-ToF.
mass spectrometry data. Thus, the quantitative $^{13}$C NMR analysis is again consistent with the formation of $\alpha,\omega$-divinylpentenylstyrene.

![Figure 5.3. $^{13}$C NMR spectrum of the $\alpha,\omega$-divinylpolystyrene.](image)

Figure 5.3. $^{13}$C NMR spectrum of the $\alpha,\omega$-divinylpolystyrene.
5.1.2 Macrocyclic Polystyrene

The $^1$H NMR spectrum of the macrocyclic polystyrene is shown in Figure 5.4. Compared to the spectrum of the linear precursor (Figure 5.2), it is obvious that the vinyl resonance at $\delta$ 4.9 ppm has disappeared and that the $\delta$ 5.7 ppm ($\text{–CH=, H}_a$) peak has shifted to the higher field (5.1 ppm) due to the cyclization. The integrations of the peaks of the vinyl and methyl groups deviate from the expected ratio of 2 to 6, which may be due to the fact that the relaxation time of the hydrogen in the vinyl groups is slower than that in the methyl groups. Thus, they do not fully relax.
Figure 5.4. $^1$H NMR spectrum of the macrocyclic polystyrene.

The comparison of the $^{13}$C NMR spectra of the linear precursor (Figure 5.3) and the macrocyclic polystyrene (Figure 5.4) demonstrates the disappearance of vinyl carbon at $\delta$ 114.1 ppm and the shift of the other vinyl carbon from $\delta$ 139.3 ppm to $\delta$ 130.1 ppm due to the metathesis ring-closure reaction. The $^{13}$C NMR spectra together with $^1$H NMR spectra provide clear evidence of the high efficiency of the ring-closure reaction to synthesize the macrocycle.
5.2 Size Exclusion Chromatography

From the analysis of the SEC data, the number average molecular weight of the linear precursor is 4,600 g/mol and its polydispersity index is 1.09, which demonstrates
that it is well-defined polystyrene. The SEC result was taken as the molecular weight of the sample, because the average calculated from MALDI-ToF mass spectrometry is shifted to lower molecular weight due to the fact that the chains with lower molecular weight are easier to ionize.

5.2.1 Comparison of Macrocycle and its Linear Precursor

The SEC chromatograms of the α,ω-divinylpolystyrene and macrocyclic polystyrene are compared in Figure 5.6. The SEC chromatography of α,ω-divinyl polystyrene shows a symmetric, monomodal distribution (Figure 5.6, red curve), which demonstrates the elimination of dimer formation described in previous work by this group.⁵
The SEC chromatogram of the macrocycle exhibits a monomodal distribution (Figure 5.6, blue curve) as well. The molecular weight determined by SEC coupled with light scattering is $M_n = 4,600$ g/mol and the molecular weight distribution measured with a differential refractometer is $M_w/M_n = 1.09$. The retention volume of the macrocyclic polystyrene (blue curve) is larger than that of its linear precursor (red curve), which is consistent with the findings of Roovers and Toporowskii.\textsuperscript{104}
5.3. Determination of Molecular Weight and Chain Topology using MALDI-ToF Mass Spectrometry.

The most definitive characterization method to confirm the formation of macrocyclic polystyrene using the above mentioned procedure is MALDI-ToF mass spectrometry. Due to the fact that the macrocyclic polystyrene was produced by the elimination of an ethylene molecule from the divinyl precursor, the molar mass to charge ratio difference between a monoisotopic mass peak from the macrocyclic polystyrene and its corresponding peak from the linear precursor should be 28.01 \text{ m/z}, and the numerical calculation will be discussed in the following part.

5.3.1 α,ω-Divinylpolystyrene

Figure 5.7 shows the MALDI-ToF mass spectrum of the α,ω-divinylpolystyrene. From the spectrum, a clean and monomodal distribution is observed, which means the chains with hydroxyl end groups have been successfully removed from the product through column chromatography and only the target product is left. The calculated monoisotopic mass for the 33-mer of the α,ω-divinyl precursor is 3737.1 Da \([138.19 (C_{10}H_{18}) +2\times15.00 (CH_3) + 33\times104.06 (C_8H_8) + 106.91 (Ag^+) + 27.98 (Si)]\), while the observed peak is at 3737.2 \text{ m/z}. The MALDI-ToF mass spectral characterization, together with the SEC chromatogram are in good accord with the efficient synthesis of α,ω-divinylpolystyrene with controlled molecular weight, narrow molecular weight distribution and high α,ω-vinyl chain-end functionality.
5.3.2 Macrocyclic Polystyrene

To investigate the formation of the macrocyclic structure for the metathesis ring-closure products from the α,ω-divinylpolystyrenes quantitatively, MALDI-ToF mass spectrometry has again been used. The spectrum of the 4.6k macrocyclic polystyrene after purification by column chromatography to remove the catalyst, shown in Figure 5.8, shows a clean and monomodal distribution. The calculated monoisotopic mass of the 33-mer of the macrocyclic polymer is 3709.1 Da $[110.16 \times (C_8H_{14}) + 33 \times 104.06 \times (C_8H_8) + \ldots]$
106.91 (Ag⁺) + 57.98 (Si(CH₃)₂), while the observed peak is at 3709.2 m/z. What is more, because the macrocyclic polystyrene was produced by the elimination of an ethylene molecule from the divinyl precursor, the molar mass to charge ratio difference between an average mass peak from the macrocyclic polystyrene and its corresponding peak from the linear precursor should be 28.0 m/z [28.0 (C₂H₄)]. Actually, the monoisotopic mass peak (Figure 5.8) of the 33-mer macrocyclic polystyrene is 3709.1 m/z, while the monoisotopic mass peak (Figure 5.7) of the corresponding linear 33-mer precursor is at 3237.1 m/z. The observed difference is 28.0 m/z. The calculated difference is consistent with the observed one, which means that the MALDI-ToF mass spectral result is in excellent agreement with the designed topology of a macrocyclic structure. The MALDI-ToF mass spectra of the purified macrocyclic polystyrene verified the high efficiency of the ring-closure catalyst, with which the cyclization reaction can produce a well-defined macrocycle with a narrow molecular weight distribution. Thus the physical properties of the macrocyclic polystyrenes can be reliably deduced using the product, since the linear impurities formed during the synthesis that can cause dramatic change in the behavior of the cyclic polymers melt have been effectively minimized. From the MALDI-Tof data we estimate that any linear impurities comprise less than 1 wt% of the product.
A new procedure for the synthesis of well-defined macrocyclic polystyrene using anionic polymerization, linking chemistry and a metathesis ring-closure reaction has been investigated. Using this procedure, a macrocyclic polystyrene with controlled molecular weight (4,600 g/mol) and narrow molecular weight distribution ($M_w/M_n = 1.09$) has been synthesized without any obvious linear impurities detected by SEC, $^1$H NMR, $^{13}$C NMR and MALDI-ToF mass spectrometry.
CHAPTER VI

SURFACE SEGREGATION

Surface segregation in binary polymer blends containing nonlinear polymers has been investigated both experimentally and theoretically, and many interesting phenomena have been observed.\textsuperscript{69-79} A SCF theory proposed by Wu \textit{et al.}\textsuperscript{79} predicted that in a blend of linear and cyclic polymers of identical repeat chemistry and comparable molecular weight the cyclic polymers should be enriched at the air/polymer surface regardless of the size of the chains. To test this prediction, our group measured linear/cyclic blends as a function of molecular weight using NR, Surface Layer MALDI-ToF mass spectrometry and Surface ToF-SIMS.\textsuperscript{6, 53} From the analysis of the 2k and 37k blends, it was found that in the 2k blend, the cyclic chains were depleted from the surface, while in the 37k blend, the cyclic chains enriched the surface. To confirm these data, and find out the transition point at which no segregation occurs, another three groups of blends with different molecular weights have been measured. The details of the polystyrenes in the blends studied are listed in Table 1, and the analysis of the data will be discussed in the following sections.
Table 6.1. Macrocyclic polystyrenes and their linear analogs used in blends studied with NR measurements

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_n$ (g/mol)$^a$</th>
<th>PDI$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>hLPS2k</td>
<td>2200</td>
<td>1.05</td>
</tr>
<tr>
<td>hCPS2k</td>
<td>2500</td>
<td>1.05</td>
</tr>
<tr>
<td>dLPS2k</td>
<td>2200</td>
<td>1.07</td>
</tr>
<tr>
<td>hLPS6k</td>
<td>6000</td>
<td>1.02</td>
</tr>
<tr>
<td>hCPS6k</td>
<td>6000</td>
<td>1.03</td>
</tr>
<tr>
<td>dLPS6k</td>
<td>6000</td>
<td>1.02</td>
</tr>
<tr>
<td>hLPS17k</td>
<td>16600</td>
<td>1.02</td>
</tr>
<tr>
<td>hCPS17k</td>
<td>16000</td>
<td>1.06</td>
</tr>
<tr>
<td>dLPS17k</td>
<td>16000</td>
<td>1.02</td>
</tr>
</tbody>
</table>

$^a$ Determined by SEC coupled with a laser light scattering detector (±5%) at 30 °C;

$^b$ Determined by SEC coupled with a differential refractometer detector (±0.03) at 30 °C.

Films were prepared by dissolving hCPS/dLPS or hLPS/dPLS (20/80 wt%) in toluene (EMD, 99.5%) and stirring for at least for 24h. Each solution was filtered with a 0.45μm filter (Whatman, PTFE) five times before an aliquot was spun cast onto an etched silicon wafer. The speed of the rotation was 2000 rpm. The prepared films were then annealed in high vacuum (ca. 1×10$^{-7}$ Pa) at 120 °C for 12h to reach equilibrium. NR data corrected for background were fitted using the software Reflpak, and the entire curve "fits" matched the collected data with a figure of merit, $\chi^2$, of 3 or less. A mass balance was used to check the discrepancy between the overall film composition corresponding to the scattering length density profile derived from the NR data and the overall composition known from how a films was made, and only those fits corresponding to an error less than 2% was accepted. If this criterion was not met some modification to the
film model was made to improve the consistency of the overall composition from the model fit and the known composition.

6.1 Surface Segregation of 2k Blends

The NR curves of the annealed 2k linear/linear blend and cyclic/linear blend films are shown in Figures 6.1 and 6.2, respectively, and their corresponding SLD (Nb) profiles are exhibited in Figures 6.3 and 6.4, respectively. It appears from the SLD profile of the linear/linear blend that hardly any segregation occurs, while in the cyclic/linear blend, the surface composition is 89\% linear polystyrene in volume fraction. The enrichment is in the opposite direction from that expected by the SCFT.
Figure 6.1. Neutron reflectivity of a blend of 2k linear/linear polystyrene (20/80 wt%) blend with the best fit ($\chi^2 = 2.66$).
The surface compositions for these 2k blends deduced from NR measurements are consistent with surface compositions of 78.8% linear for the linear/linear blend and 89.3% linear for the cyclic/linear blend from Surface Layer MALDI-ToF mass spectrometry measurements by Foster and coworkers. This result, which differs from the SCFT prediction, can be rationalized using the modified Wall-PRISM theory, which was originally introduced by Yethiraj and coworkers. The theory can capture the behavior of packing of the two types of chains at both the air/polymer interface and the
substrate/polymer interface when the chain conformation of the cyclic differs away from the Gaussian conformation. Calculations made by our collaborator, David Wu using this theory show that the linear chains are enriched at the air surface of a blend of short linear and short cyclic chains. It is interesting to note that at the blend/substrate interface no segregation of either species is required to fit the data from either blend. Since the Wall-PRISM theory treats the air/blend as essentially a hard wall, the two interfaces must not be enthalpically equivalent.

Figure 6.3. SLD profile of a blend of 2k linear/linear polystyrenes (20/80 wt%) annealed at 120 °C.

Figure 6.3. SLD profile of a blend of 2k linear/linear polystyrenes (20/80 wt%) annealed at 120 °C.
The beauty of the NR measurement is its ability to access the film composition as deep as 100 nm, which enables the study of the behavior at the interface with the solid substrate. At that interface, both of the species do not show obvious segregation. However, the roughness of the transition layer between the linear/linear blend and the substrate is larger than that roughness for the cyclic/linear blend, which may be due to the difference between the architectures of the two hydrogenous species.
6.2 Surface Segregation of 6k Blends

It is interesting to study the surface segregation of cyclic/linear blends as a function of molecular weight. The NR curves of the 6k linear/linear blend and cyclic/linear blend films are shown in Figures 6.5 and 6.6, respectively, and their corresponding SLD profiles are exhibited in Figures 6.7 and 6.8, respectively. With increasing molecular weight, the enrichment of the dLPS to the surface of the linear/linear blend increases, which is expected because the isotopic effect becomes more important as molecular weight increases. As the isotopic preference for the d-linear chain increases this effect will further offset the tendency of the cyclic chains to go to the surface expected from the SCFT. However, even though the isotopic driving force for the d-linear chain to go to the surface is stronger at the 6k molecular weight, the surface composition of the cyclic/linear blend actually drops, from 89% d-linear to 83% d-linear. This is in accordance with our expectation that there should be a move toward the SCFT predicted behavior as the cyclic chains become more Gaussian in their conformations.
Figure 6.5. Neutron reflectivity of a blend of 6k linear/linear polystyrenes (20/80 wt%) with the best fit ($\chi^2 = 2.69$).
Figure 6.6. Neutron reflectivity of a blend of 6k cyclic/linear polystyrenes (20/80 wt\%) with the best fit ($\chi^2 = 2.47$).

The surface composition for the 6k linear/linear blend fits in with the trend seen for the 2k and 37k linear/linear blends. Also the result of the surface segregation for the 6k cyclic/linear blend agrees with the tendency observed with the 2k and 37k cyclic/linear blends studied previously.\textsuperscript{53} Thus it is reasonable to predict that the transition molecular weight, at which the surface segregation in the hCPS/dLPS blend film disappears, lies between 6k and 37k.
Figure 6.7. SLD profile of a blend of 6k linear/linear polystyrenes (20/80 wt%) annealed at 120 °C.
Figure 6.8. SLD profile of a blend of 6k cyclic/linear polystyrenes (20/80 wt%) annealed at 120 °C.

The interface segregation of both the samples again can be derived from the SLD profiles. The interface at the substrate appears to be broader for the 6k cyclic/linear blend than for the 2k cyclic/linear blend according to the best fit. Also, the interface for the 6k cyclic/linear blend seems thicker than that for the 6k linear/linear blend. These results should be checked using complementary methods. Investigating the behavior of a blend with 16k cyclic and linear chains should better define the location of this crossover molecular weight.
6.3 Surface Segregation of 16k Blends

In the last section, the surface enrichment of the cyclic/linear blend by linear chains became weaker as molecular weight was increased from 2k to 6k, so the 16k group should be the most interesting samples to investigate. The NR curves of the 16k linear/linear blend and cyclic/linear blend films are shown in Figures 6.9 and 6.10, respectively, and their corresponding SLD profiles are exhibited in Figures 6.11 and 6.12, respectively. With this additional increase in molecular weights of the species, any surface segregation of the cyclic/linear blend becomes hard to detect because it is even weaker than that for the 6k cyclic/linear blend. The SLD profile of the linear/linear blend once more shows that the enrichment in dLPS increases with molecular weight, which is consistent with both previous investigations in our group\textsuperscript{107,108} and work by others.\textsuperscript{61,63,64}
Figure 6.9. Neutron reflectivity of a blend of 16k linear/linear polystyrenes (20/80 wt%) with the best fit ($\chi^2 = 2.75$).
Figure 6.10. Neutron reflectivity of a blend of 16k cyclic/linear polystyrenes (20/80 wt%) with the best fit ($\chi^2 = 2.91$).

So the enrichment of the surface of the cyclic/linear blend disappears for a molecular weight of about 16k. Apparently, at this molecular weight the driving force for the cyclic chains to enrich the surface to minimize the system's free energy equals the driving force for the deuterated chains to enrich the surface.
This balance is achieved as a result of the non-Gaussian behavior of the cyclic chains decreasing in importance as molecular weight increases. However, the form of the reflectivity curve is not sensitive to small differences in the surface segregation for surface concentrations of dLPS around 80% in volume fraction. So it would strengthen the determination of the crossover molecular weight to have data from a complementary method such as Surface Layer MALDI-ToF mass spectrometry or STOF-SIMS mass spectrometry to verify the degree of surface enrichment for the 16k cyclic/linear blend.
Figure 6.12. SLD profile of a 16k cyclic/linear polystyrene blend (20/80 wt%) annealed at 120°C.
7.1 Surface Fluctuations of Melt Macro cyclic Polystyrene Films

In this chapter, the surface height fluctuations of melt macro cyclic polystyrene films on silicon wafers will be presented and the effect on them of confinement when decreasing the thickness of the film will be discussed. The surface relaxation times of CPS films using the 6k macro cyclic polystyrene samples described in Chapter 5 have been systematically investigated as a function of film thickness to find out the thickness at which the confinement effect begins to manifest itself. We identify the thickness at which confinement becomes significant as the thickness at which the universal scaling of the surface relaxation times, $\tau$, with thickness $h$, predicted by the hydrodynamic continuum theory (HCT)\textsuperscript{14} is lost.

Characterization of the 6k macro cyclic polystyrene by $^1$H NMR, SEC chromatogram and MALDI-ToF mass spectrometry described in Chapter 4 confirmed the molecular structure. A 6k linear polystyrene analog was also synthesized by anionic polymerization using (sec)butyl-lithium as the initiator and terminating with a hydrogen from methanol. The samples measured at the APS are listed in Table 7.1.
**Table 7.1. Macrocyclic polystyrene and its linear analog used in the XPCS measurements**

<table>
<thead>
<tr>
<th></th>
<th>CPS 6k</th>
<th>LPS 6k</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (nm)</td>
<td>$M_n^a\approx6000$ g/mol</td>
<td>$M_n^a\approx6000$ g/mol</td>
</tr>
<tr>
<td>16</td>
<td>20</td>
<td>17</td>
</tr>
<tr>
<td>20</td>
<td>24</td>
<td>38</td>
</tr>
<tr>
<td>24</td>
<td>28</td>
<td>77</td>
</tr>
<tr>
<td>28</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>42</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>120</td>
<td></td>
</tr>
<tr>
<td>PDI$^b$</td>
<td>1.03</td>
<td>1.02</td>
</tr>
<tr>
<td>$T_g$</td>
<td>98.9°C</td>
<td>83.4°C</td>
</tr>
</tbody>
</table>

$^a$ Determined by SEC coupled with a laser light scattering detector (±5%) at 30 °C;  
$^b$ Determined by SEC coupled with a differential refractometer detector (±0.03) at 30 °C;  
$^c$ Determined by DSC (±1°C).

Films were prepared by creating polymer solutions in toluene (EMD, 99.5%) with various concentrations (1 to 3 wt%). Each solution was filtered with a 0.45μm filter (Whatman, PTFE) five times before it was spun cast onto an etched silicon wafer. The speed of the rotation was 2000rpm. The prepared films were then annealed in high vacuum (ca. $1\times10^{-7}$ Pa) at 120°C for 12h. The intensity-intensity auto correlation functions, $g_2$, from all the linear and macrocyclic samples (examples shown in Appendix B) were analyzed using a single-exponential decay functional form,

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

with speckle contrast, $\beta$. Fits were also done to a stretched exponential shape and a comparison of the relaxation times resulting from these two types of fitting proved a rough assessment of the degree to which the shape of the correlation function was captured by the single exponential shape. For some ranges of $q_0$ with some films of cyclic chains, full frame mode data suggested that a stretched exponential or two exponential shape might be more appropriate for capturing the correlation function.
behavior. However, for the first analysis that is presented here, only relaxation times extracted using the single exponential shapes have been considered.

7.1.1 Thickness Dependence of Surface Fluctuations of Melt Macroyclic Films

According to the hydrodynamic continuum theory by Jäckle\textsuperscript{14} the surface fluctuations of viscoelastic films are overdamped capillary waves. The characteristic relaxation time of these waves is a function of film viscosity, surface tension, film thickness and wave vector. In a supported film with the thicknesses, $h$, under a non-slip boundary condition at the melt/substrate interface, the surface relaxation time, $\tau$, and the data should collapse onto a universal curve of $\tau/h$ vs. $q|h$, given by

$$\frac{\tau}{h} = \frac{2\eta[\cosh^2(q,h) + q^2h^2]}{\gamma q \sqrt{\sinh^2(q,h) \cosh(q,h) - q^2h^2}},$$

where $\eta$ is the film viscosity and $\gamma$ is the surface tension. In this theory, the entire film is assumed to behave uniformly with depth, so the surface viscosity of the film is taken to be the same as it is for the bulk. So once the behavior of a melt sample can be regarded as that of a single layer, data for films of the same polymer, but with different thicknesses can be collapsed onto a single curve. Jiang \textit{et al.}\textsuperscript{12} found this scaling of $\tau$ with $h$ for melt linear polystyrene films for chain molecular weight of 220k when the thickness of the film is greater than $4R_g$. Wang \textit{et al.}\textsuperscript{13} also found this sort of scaling for films of 17k CPS for film thicknesses greater than 40 nm, but the normalized relaxation times for a film of thickness 22 nm were larger than those expected from the predicted scaling.
The variations of surface relaxation times with $q_{\parallel}$ for the melt CPS6k films with thickness are shown in Figure 7.1. The dashed curve for the 28 nm thick film was obtained by allowing the ratio $\eta/\gamma$ to vary in order to fit the HCT. The value of $\eta$ implied by the fitted value of this ratio was $1030 \pm 100$ Pa s, as discussed below. This compares reasonably with a value of $1300$ Pa s interpolated for data in reference 110. This value of $\eta/\gamma$ obtained from the data for the 28 nm thick film was then used to calculate the curves that would be expected from the HCT for the films of the other thicknesses. From the figure, it is obvious that the model captures very well the shape of the data when the film is thicker than 28 nm. However, when the film thickness is 24 nm, the observed relaxation time is clearly higher than the predicted curve.

Deviation from the curve expected from the HCT using $\eta/\gamma$ from the 28 nm thick film may be due to the fact that the interaction between the film and substrate becomes dominate when the film is thin enough.\(^9^3\) The confinement effect becomes much stronger when the film thickness decreases further, as the gaps between the 16 nm and 20 nm data and the corresponding HCT model curves are wider than that for the 24 nm thick film. The 24 nm thickness of the film is equivalent to approximately $17R_g$ ($R_g$=1.4 nm) for these small molecules. So the confinement effect manifests itself for these 6k cyclic chains at a thickness in terms of $R_g$ that is much larger than that seen for linear chains of 220k molecular weight ($R_g$=8.5 nm).\(^1^2\) The absolute thickness at which these confinement effects are seen is similar to the 22 nm thickness seen by Wang et al.\(^1^3\) for 17k cyclic chains. In her work, there is no systematic change in the change in the shape of the curve of $\tau$ vs. $q_{\parallel}$ when its value exceeds that expected by the HCT. This suggests that the source of the confinement here could be different than the pinning or tethering effect.
proposed by Jiang et al.\textsuperscript{12} This is reasonable, because in the case of the long linear chains, entanglements would be expected to play a role in the confinement effect.

Figure 7.1. \(\tau\) vs. \(q_{||}\) for CPS6k films with thicknesses 16, 20, 24, 28 and 60 nm at 150 °C, as marked, shown with symbols. The dashed curve through the data for the 28 nm film was obtained from a least squares fit of the HCT to the data. Using the value of \(\eta/\gamma\) from this fit, the other dashed curves were calculated for the other films thicknesses. Symbols and dashed curves of the same color are to be compared.

7.1.2 Temperature Dependence of Surface Fluctuations of Melt Macro cyclic Films

The temperature dependence of the surface fluctuation relaxation time was studied for all the films and here we consider that dependence for the 28 nm thick film,
which displayed a behavior of $\tau$ vs. $q_{||}$ that was consistent in shape with that expected from the HCT. When the temperature is varied, the data at all temperatures for the 28 nm sample can be described well with the HCT, as shown in Figure 7.2. This again is consistent with the argument that when the thickness is 28 nm or more for the CPS6k sample, there is no confinement effect, and all the behavior of the surface dynamics of the melt films can be described using overdamped capillary waves.

Figure 7.2. $\tau$ vs. $q_{||}$ for a 28 nm thick CPS6k film at temperatures 140, 150 and 160 °C as marked, and curves obtained by fitting the HCT expression (dash curves) by allowing the ratio of $\eta/\gamma$ to vary as a fitting parameter.
7.1.3 Comparison of Surface Fluctuations of Melt Macrocyclic Films with Universal Scaling

Another way of showing the confinement effects is to plot the data from the melt films of various thicknesses in the form of $\tau/h$ vs. $q|h$. Such a plot is presented in Figure 7.3 for one temperature. It becomes clear that the data from films of thickness 24 nm or less do not collapse onto the universal behavior at 140 °C.

Figure 7.3. $\tau/h$ vs. $q|h$ for CPS6k films with thicknesses of 16, 28, 42 and 120 nm at 140 °C. The dashed curves represent a least squares fit to the HCT using just the data for 28 and 42 nm.

For the higher temperatures of 150 and 160 °C the trend of increasing deviation from the universal curve with smaller thickness is arguably clearer. Figures 7.4 and 7.5
present the normalized surface fluctuation relaxation times of the melt films of various thicknesses in the form of $\tau/h$ vs. $q_{||}h$ at 150 and 160 °C. It is clear that the deviation from the expected scaling due to the confinement effect varies with temperature. The data show that in the range of thickness for which the confinement effect occurs, its magnitude depends on the thickness of the film. When the film is 24 nm thick, the data start to deviate slightly from the HCT prediction curve, and the gap between the data and prediction grows when the film becomes thinner. So the deviation for the 16 nm thick film from the predictions is quite large.

![Graph showing $\tau/h$ vs. $q_{||}h$ for CPS6k films with thicknesses of 16, 20, 24, 28, 42 and 60 nm at 150 °C. The dashed curves represent least squares fits to the HCT for the data from the 28, 42 and 60 nm thick films.](image)

**Figure 7.4.** $\tau/h$ vs. $q_{||}h$ for CPS6k films with thicknesses of 16, 20, 24, 28, 42 and 60 nm at 150 °C. The dashed curves represent least squares fits to the HCT for the data from the 28, 42 and 60 nm thick films.
Figure 7.5. $\tau/h$ vs. $q/l$ for CPS6k films with thicknesses of 16, 20, 24, 28 and 60 nm at 160 °C. The dashed curves represent least squares fits to the HCT using the data from the 28 nm and 60 nm thick films.

Although the data of the CPS6k films thinner than 28 nm lie above the HCT model curves, the slopes of the data curves for these thicknesses are almost the same as those of the curves for the other thicknesses. Due to this, the data from the films of these small thicknesses can be fitted with the functional form from the HCT by just using an effective viscosity higher than the bulk value. One possible reason for this phenomenon could be that the glass transition temperature of the cyclic chain film is increasing when the thickness is decreasing. Such a change in $T_g$ would be in the opposite direction from that seen for linear chain films. So it would be very interesting to study the glass
transition temperature of the cyclic polymer thin film as a function of thickness, and this will be investigated in research following up on this thesis research.

7.2 Surface Dynamics of Melt Linear Polystyrene Films

In order to compare with the results from the CPS6k samples, surface fluctuations of melt LPS6k films with various thicknesses were also measured at various temperatures. Data for linear and cyclic analogs should be compared not at a given value of temperature, \( T \), but rather at a fixed value of \( T - T_{g,\text{bulk}} \). The \( T_{g,\text{bulk}} \) of all samples were measured using DSC as described in Section 4.4, and here the value for \( T_{g,\text{bulk}} \) of the CPS6k is taken as 99 °C, while the value for the LPS6k is 84 °C.

The data for melt LPS6k films of 17, 38 and 120 nm thicknesses are plotted together in Figure 7.6 in the form of \( \tau/h \) vs. \( q_{\parallel}/h \). Data from the LPS6k films with three different thicknesses collapse onto the universal curves for the temperatures at which data were collected, and there is no obvious confinement effect observed. This means the HCT theory using a non-slip condition captures the features of the surface fluctuations of LPS6k samples when the thickness of the film is larger than 17 nm. The molecular weight of the LPS6k samples is far below the entanglement molecular weight for linear polystyrene, and the thinnest film has a thickness of approximately \( 10R_g \). According to the contention of Jiang et al.\(^\text{12} \) that \( 4R_g \) represents the thickness at which confinement effects set in for long linear chains, no confinement effect may be expected even for this 17 nm thick film. However, both this thickness relative to \( R_g \) (10\( R_g \)) and the absolute thickness (17 nm) are smaller than the values at which confinement effects were seen for the cyclic chains of 6k molecular weight (17\( R_g \), 24 nm) or cyclic chains of 17k molecular weight.
weight \(9R_g, 22\) nm). Thus the films of short linear chains seem less prone to confinement than are the films of the cyclic chains. This may due to the fact that the linear chains pack better than their cyclic analogs for small molecular weights, thus perhaps the linear chains are less affected by the interaction between the film and the substrate, and less sensitive to the confinement effect.

Figure 7.6. \(\tau/h\) vs. \(q_{||} h\) for LPS6k films with thicknesses of 17, 38 and 120 nm at 110, 120, 130 and 140 °C. The dashed curves represent least squares fits to the HCT.

When comparing data in Figure 7.3 with that in Figure 7.6, at the same temperature (140 °C), one finds that the surface dynamics of the cyclic polystyrene films are one order of magnitude slower than those of films of the linear counterparts. When comparing the surface fluctuations of cyclic and linear polystyrene films at the same value of \(T - T_{g,\text{bulk}}\),
however, it is found in Table 7.2, that the surface of the melt linear film moves more slowly than that of its cyclic analog.

Table 7.2 Comparison of thickness-normalized surface relaxation times for 6k linear and 6k cyclic melt films for thicknesses within the region of universal scaling

| $T-T_g$ (°C) | $\tau/h$ at $q||h = 0.2$ | $T-T_g$ (°C) | $\tau/h$ at $q||h = 0.2$ |
|-------------|-----------------|-------------|-----------------|
| 61.1        | 0.0023          | 51.1        | 0.0071          |
| 56.6        | 0.0070          | 46.6        | 0.0328          |
| 36.6        | 0.3840          | 26.6        | 4.0424          |

7.3 Viscosities Derived from the XPCS Data

As mentioned in the previous two sections, the surface dynamics of the melt macrocyclic polystyrene films thicker than 28 nm and the melt linear polystyrene films thicker than 17 nm can be fitted well by the HCT theory, simply by allowing the ratio of $\eta/\gamma$ to be a fitting parameter. So if the surface tension of these films is known, their viscosities can be calculated according to the HCT formula using the least squares fits. In order to have surface tension values for the macrocyclic polystyrene films that were consistent with those use for the linear ones, the surface tension data were inferred from published results using a calculation introduced by Koberstein$^{104}$ and also used by Wang.$^{13}$ We can also take advantage of the observation that the change in surface tension
with temperature seems not to be dependent on architecture\textsuperscript{77}, and therefore the same coefficient for temperature dependence (−0.068 mN/(m°C)) can be used for both architectures. Values calculated for surface tensions in this way are listed in Table 7.3.

Table 7.3. Calculated surface tensions of 6k macrocyclic polystyrene and its linear analog at different temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>γ\text{linear} (mN/m)</th>
<th>γ\text{cyclic} (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>110</td>
<td>33.4</td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>32.8</td>
<td></td>
</tr>
<tr>
<td>130</td>
<td>32.2</td>
<td></td>
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<tr>
<td>140</td>
<td>31.5</td>
<td>32.3</td>
</tr>
<tr>
<td>150</td>
<td></td>
<td>31.6</td>
</tr>
<tr>
<td>160</td>
<td></td>
<td>31.0</td>
</tr>
</tbody>
</table>

At a given temperature the surface tension for the cyclic chain is slightly higher than that for the linear analog. This difference is caused by the absence of chain ends in the macrocyclic polystyrene. The apparent viscosities of the melt CPS6k and LPS6k films were calculated from the values of $\eta/\gamma$ used to fit the data of $\tau$ vs. $q$ and using the calculated surface tensions in Table 7.3. The resulting values for the viscosities are listed in Table 7.4 and compared with bulk rheology values of the 6k cyclic polystyrene interpolated from the literature\textsuperscript{110}. The results from XPCS are within 30% of the values extrapolated from the literature at 150 and 160 °C for the cyclic chain. For 140 °C the agreement is not as good, but still within the factor of two agreement seen by Kim \textit{et al.}\textsuperscript{10} For the 6k linear chains the agreement is within 10% at 110 and 120 °C, but at 130 and 140 °C the values from XPCS are a factor or two and three, respectively, below the bulk values.\textsuperscript{111} Since the literature values are interpolated we choose not to infer much from these moderate discrepancies over narrow temperature ranges.
Table 7.4 Viscosities derived from fits to the HCT of XPCS data for the 60nm thick 6k macrocyclic polystyrene film and 77 nm thick linear analog film at various temperatures

<table>
<thead>
<tr>
<th>Temperature (℃)</th>
<th>η&lt;sub&gt;linear&lt;/sub&gt; (Pa×s)</th>
<th>η&lt;sub&gt;linear, lit&lt;sup&gt;a&lt;/sup&gt;&lt;/sub&gt; (Pa×s)</th>
<th>η&lt;sub&gt;cylic, expt&lt;/sub&gt; (Pa×s)</th>
<th>η&lt;sub&gt;cylic, lit&lt;sup&gt;b&lt;/sup&gt;&lt;/sub&gt; (Pa×s)</th>
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<tr>
<td>110</td>
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<td></td>
</tr>
<tr>
<td>130</td>
<td>6300</td>
<td>12000</td>
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<td>140</td>
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<td></td>
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<tr>
<td>160</td>
<td></td>
<td>330</td>
<td>590</td>
<td></td>
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</tbody>
</table>

<sup>a</sup> Interpolated from reference 111;
<sup>b</sup> Interpolated from reference 110.
CHAPTER VIII

CONCLUSION

In this thesis research four different aspects of macrocyclic polystyrenes have been investigated. In the first part, a well-defined macrocyclic polystyrene of molecular weight 6,000 g/mol has been synthesized for the first time using a combination of anionic polymerization and the metathesis ring closure method. This material made possible the measurements of surface segregation and surface fluctuations in the last two parts of this thesis. Characterization of the macrocyclic polystyrene using $^1$H MNR, SEC and MALDI-ToF mass spectrometry demonstrated that the method used is highly efficient. The elimination of ethylene from each molecule during the cyclization makes it possible to prove the cyclization of the linear precursor.

The second part of the research focused on the new synthesis of a well-defined macrocyclic polystyrene of molecular weight 4,600 g/mol using the combination of anionic polymerization, linking chemistry and metathesis ring closure. Although the synthetic route in the first part was an efficient way to synthesize well-defined macrocyclic polystyrenes, it did produce high molecular weight impurities during the termination step when making the linear precursor. Using dichlorodimethysilane as a
coupling agent enabled the formation of a high purity macrocyclic polystyrene (as indicated by $^1$H MNR, $^{13}$C NMR, SEC chromatogram and MALDI-ToF mass spectrometry) that did not require purification. Since the purity of macrocyclics has become a major issue in research on their bulk rheological properties, a means of making macrocyclics free of linear contaminants is a major step forward also for the study of surface fluctuation dynamics.

In the third part, a crossover in the surface segregation behavior of blends of linear and cyclic polystyrenes was investigated with 2k, 6k and 17k cyclic/linear blend films. Neutron reflectrometry was used to study the molecular weight at which the behavior crosses over from surface enrichment by the linear chain, which is anticipated by the PRISM theory, to surface enrichment by the cyclic chain, which is anticipated by a SCFT. For the 2k molecular weight, the composition inferred from the NR data matched well with the composition measured using Surface Layer MALDI-ToF mass spectrometry.\textsuperscript{6} With the increase of the molecular weights from 2k to 6k to 17k, the enrichment of the surface of the cyclic/linear blends by deuterated linear chain becomes weaker and weaker and is undetectable with NR at 17k. So the molecular weight at which the crossover occurs is close to 17k. Since the deuteration of the linear chain also tends to drive the linear chain to the surface and this effect becomes stronger with increasing molecular weight, the crossover in absence of the isotopic labeling is probably at a molecular weight somewhat less than 17k. To confirm the results from the NR, it is essential to measure the same blends using complementary techniques.
The final part of the research addressed the surface fluctuations of melt 6k cyclic polystyrene films and how confinement effects appear when decreasing the thicknesses of the films. Melt 6k cyclic films of thickness equal to or greater than 28 nm showed the universal scaling of the surface fluctuation dynamics with film thickness expected from the HCT. When the thickness decreased to 24 nm, which is around $17R_g$ for the 6k cyclic chains, the surface fluctuations are slower than expected from the universal curves. That is, the apparent film viscosity is a factor of five times higher than the bulk value at 140 °C. Even larger deviations were observed when the thickness of the film was 20 and 16 nm, respectively. The deviation also grew with increase in temperature from 140 to 150 °C, but did not necessarily grow further with a temperature increase to 160 °C. In contrast, when the thickness of the linear polymer film was decreased to 17 nm, which is less than $17R_g$ of the linear coils, no confinement effect was observed. This comparison suggests that the chain architecture is very important for determining the thickness at which confinement effects appear. In research following up on this thesis research it will be interesting to investigate the confinement effects for cyclic polymers with different molecular weights to see if the thickness at which these effects appear is $R_g$ dependent, or whether perhaps it is does not change with $R_g$ in this unentangled regime. Ultimately we would like to understand how the presence of the substrate interface perturbs the melt surface dynamics away from those expected for a simple viscous melt.
REFERENCES


119


101. Piranha solution is corrosive, so acid-resistant gloves, protective goggles, and lab coats are required when handling the piranha solution.


APPENDICES
APPENDIX A

DSC DATA FOR 6k LINEAR POLYSTYRENES

A.1 DSC data for 6k linear polystyrenes.

Figure A.1. DSC scan for LPS6k.
APPENDIX B

DATA ANALYSIS OF XPCS

B.1 Autocorrelation functions of 42 nm 6k melt cyclic polystyrene film at 140 °C.

Figure B.1. Autocorrelation functions (blue curve: single exponent, red curve: stretched exponent) of CPS6k at 140 °C obtained at several values of in-plane wave vector (film thickness, $h = 42$ nm) from data obtained in kinetic mode. The relaxation time corresponding to the fit with the single exponential is given as the first time in the title for each plot. The second time is for the stretched exponential fit. For this sample these two values very little because the shape of the correlation function as captured in this range of time is fit reasonably well by a single exponential shape.
B.2 Autocorrelation functions of 16 nm 6k melt cyclic polystyrene film at 140 °C.

Figure B.2. Autocorrelation functions (blue curve: single exponent, red curve: stretched exponent) of CPS6k at 140 °C obtained at several values of in-plane wave vector (film thickness, $h = 16$ nm) obtained using full frame mode. The relaxation time corresponding to the fit with the single exponential is given as the first time in the title for each plot. The second time is for the stretched exponential fit. For this sample these two values differ substantially because the shape of the correlation function is not represented well by a single exponential shape.
B.3 Autocorrelation functions of 77 nm 6k melt linear polystyrene film at 120 °C.

Figure B.3. Autocorrelation functions (blue curve: single exponent, red curve: stretched exponent) of LPS6k at 120 °C obtained at several values of in-plane wave vector (film thickness, \( h = 77 \) nm). The relaxation time corresponding to the fit with the single exponential is given as the first time in the title for each plot. The second time is for the stretched exponential fit. For this sample these two values are very close because the data are very well fit by a single exponential shape.