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The Stuctural, Mechanical, and Osmotic Properties of Acrylic Triblock Copolymer Gels Determined by Self-Consistent Mean Field Theory and Experiment

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ABSTRACT

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In recent years, research has expanded the uses of triblock copolymer gels to a wide variety of applications including everything from ceramics processing to regenerative medicine and drug delivery. The research presented in this dissertation focuses on a physically crosslinked, block copolymers gel system in a selective solvent. This system undergoes a rapid thermally reversible gel transition, from a viscous liquid at elevated temperatures to an elastic solid at room temperature. The research presented in this text was motivated by a desire to develop a more detailed understanding of the interplay between the structural, osmotic, and mechanical properties that determine the properties of physically crosslinked triblock copolymer networks. A more refined understanding of the forces at work in such a system will provided a basis for the design of future systems with specific predetermined properties. Self-consistent field theory is a useful tool in modeling complex polymeric systems. A SCFT based model of acrylic triblock copolymer gels was formulated and used to simulate the equilibrium properties of acrylic triblock copolymers for a range of temperatures, volume fractions, and two different midblock architectures. Theoretical results are compared to experimental rheometric, SAXS, swelling, and osmometry data. Both SCFT and experiment showed that between 55 °C and 80 °C the gel structure undergoes considerable rearrangement. Rheometry provided mechanical characterization of the acrylic triblock copolymer gels and showed that the visco-elastic gel to liquid transition occurs between 65 °C and 80 °C. Osmotic pressure measurements demonstrated that the complete dissolution of the endblock aggregate network occurs between 75 °C and 80 °C, but is only detectable when the elastic restoring force plays a large role in determining osmotic properties when compared to the volume fraction of osmotically active polymer. In conjunction with SCFT, the experimental results obtained provide a more detailed understanding of the relationship between the mechanical, structural, and osmotic properties of acrylic triblock copolymers.

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Contents

ABSTRACT	3
Acknowledgements	5
List of Figures	9
List of Tables	13
Chapter 1. Introduction	14
1.1. Research Motivation	14
1.2. Outline of Objectives and Research	16
Chapter 2. Background	20
2.1. Physically Crosslinked Triblock Copolymer Gels	20
2.2. Osmotic Properties of Polymer Gels	24
Chapter 3. Self-Consistent Field Theory Simulation of Acrylic Triblock Copolymers	28
3.1. Self Consistent Field Theory Background	28
3.2. Theoretical Formulation	33
3.3. The Validity of the Unit Cell Approximation	43
3.4. Results of SCFT Simulations for ABA Symmetric Triblock Copolymers	48
3.5. Self-consistent Field Theory Summary	67

Chapter 4. Mechanical, Structural, and Osmotic Characterization of Acrylick	
Triblock Copolymers	70
4.1. Materials	70
4.2. Rheometry	72
4.2.1. Rheometry Experimental Method	72
4.2.2. Rheometry Analysis Method	72
4.3. Swelling Measurements	73
4.4. Small Angle X-ray Scattering	74
4.4.1. SAXS Experimental Methods	74
4.4.2. SAXS Analysis Methods	75
4.5. Vapor Pressure Osmometry	80
4.5.1. Vapor Pressure Osmometry Background	80
4.5.2. Vapor Pressure Osmometry Experimental Method	85
4.5.3. Vapor Pressure Osmometry Calibration Method	86
Chapter 5. Experimental Results and Discussion	89
5.1. Temperature Dependant Properties of Acrylic Triblock Copolymer Gels	90
5.2. Volume Fraction Dependant Properties of Acrylic Triblock Copolymer Gels	102
5.3. Swelling Measurement Results	108
5.4. Vapor Pressure Osmometry Results	111
5.5. Experimental Results Summary	114
Chapter 6. Future Work	118
References	122

List of Figures

A schematic of the structural origins of acrylic triblock copolymer	
mechanical properties adapted from Drzal et al. , 2003 $[1]$	23
Illustration of the Unit Cell Approximation	32
Illustration of the self-consistent field theory algorithm developed for	
the study of block copolymers	40
A schematic representaion of the phase diagram of a symetric Triblock	
copolymer	44
Free energy curves calculated for a symetric ABA triblock copolymer	
near the order-disorder transition	45
Free energy curves for a symetric ABA triblock copolymer near the	
sphere to cylinder transition	46
Free energy curves for a symetric ABA triblock copolymer near the	
sphere to cylinder transition	47
Comparison of the free energies of spherical and cylindrical phases as a	
function of χN	48
System size vs. free energy from 50 $^{\circ}\mathrm{C}$ to 70 $^{\circ}\mathrm{C}$ for the Short midblock	
polymer at $\phi = 0.15$	49
	A schematic of the structural origins of acrylic triblock copolymer mechanical properties adapted from Drzal et al. , 2003 [1] Illustration of the Unit Cell Approximation Illustration of the self-consistent field theory algorithm developed for the study of block copolymers A schematic representaion of the phase diagram of a symetric Triblock copolymer Free energy curves calculated for a symetric ABA triblock copolymer near the order-disorder transition Free energy curves for a symetric ABA triblock copolymer near the sphere to cylinder transition Free energy curves for a symetric ABA triblock copolymer near the sphere to cylinder transition Comparison of the free energies of spherical and cylindrical phases as a function of χN System size vs. free energy from 50 °C to 70 °C for the Short midblock polymer at $\phi = 0.15$

3.9	Temperature vs. the SCFT calculated equilibium volume per micelle	50
3.10	SCFT calculated volume fraction profiles for each polymer component	52
3.11	SCFT calculated, total polymer volume fraction profiles for both long	
	and short midblock polymers from 30 $^{\circ}\mathrm{C}$ to 70 $^{\circ}\mathrm{C}$	54
3.12	SCFT calculated Temperature vs. Bridging fraction for both long and	
	short midblock polymer	56
3.13	Temperature vs. PnBA equivalent volume fraction of polymer for both	
	long and short midblock polymers	58
3.14	Background normalized electron scattering length density profiles from	
	$30^{\rm o}{\rm C}$ to $70^{\rm o}{\rm C}$ for both long and short midblocks	60
3.15	Temperature vs. SCFT calculated PMMA aggregate radius	64
3.16	Temperature vs. the average SCFT calculated electron scattering length	
	density [eu]	65
3.17	Comparison of simulated scattering data calculated using SCFT volume	
	fraction profiles and a step function approximation for short (\mathbf{a}) and	
	long (b) midblock polymers	66
3.18	Comparison of temperature vs. maximum scattering intensity calculated	
	using a trapazoidal rule approxiamtion of SCFT calculated volume	
	fraction profiles or a step function approximation for short (\mathbf{a}) and long	
	(b) midblock polymers	68
4.1	The chemical structures of PMMA (\mathbf{a}) and PnBA (\mathbf{b})	71

4.2	Illustration of the physical meaning of Percus-Yevic fitting parameters	79
4.3	Representative SAXS scattering data and data fit	80
4.4	Schematic illustration of a vapor pressure osmometer	82
4.5	Temperature vs. osmometer signal for PnBA homopolymer callibration data	87
4.6	Osmometer signal to PnBA homopolymer volume fraction calibration curves	88
5.1	Representative storage and loss modulus modulus master curves	
	for acylic triblock copolymer gels generated by time-temperature superposition	91
5.2	Temperature vs. viscosity curves for several acrylic triblock copolymers	93
5.3	Master viscosity curve obtained from gel temperature normalized data	94
5.4	Temperature vs. SAXS maximum scattering intensity	96
5.5	Comparison of SCFT prediction and experimental data for temperature vs. maximum scattering intensity	98
5.6	Comparison of SCFT prediction and experimental data for temperature)
	vs. aggregation number	101
5.7	Comparison of SCFT prediction and experimental data for polymer	
	volume fraction vs. plateau modulus	103
5.8	Volume fraction vs. nearest neighbor spacing determined from room	
	temperature SAXS data.	105

5.9	Volume fraction vs. aggregation number at room temperature for both	
	long and short midblock polymers	107
5.10	A photograph of short midblock polymer gels after one week of ageing	108
5.11	Initial volume fraction vs. final volume fraction for long and short	
	midblock polymer gels after swelling in pure solvent	110
5.12	Vapor pressure osmometry results for the long midblock polymer	112
5.13	Vapor pressure osmometry results for the short midblock polymer	113
5.14	Illustration of the relationship between gel structure, mechanical, and	
	osmotic properties of an acrylic triblock copolymer gel.	116

List of Tables

3.1	Polymer end- and midblock degrees of polymerization used in SCFT	
	calculations	42
4.1	Polymer end- and midblock degree of polymerization and PMMA weight	
	fraction	71
5.1	Rheometrically determined plateau moduli and gelation temperatures	95
5.2	Experimental shear moduli and SCFT predicted shear moduli as well as	3
	the parameters used to derive the SCFT moduli	104

CHAPTER 1

Introduction

1.1. Research Motivation

The self-assembly of triblock copolymers is a topic of continuing interest in the scientific community. Triblock copolymers are technologically important and scientifically useful. Today, they are common in industrial applications ranging from car bumpers to electronic components [2]. The widespread use of block copolymers is a result of their ability to self-assemble into complex microstructures that combine the materials properties of their various blocks. This often results in materials with superior properties to homopolymers and polymer blends [3]. When swollen with solvents, block copolymers often form gels. In recent years, research has expanded the uses of triblock copolymer gels to a wide variety of applications including everything from pressure sensitive adhesives [4, 5] to ceramics processing [6, 7]. More recently, polymer gels have become increasingly important in the areas of regenerative medicine and drug delivery [8-17]

The theoretical understanding of the self-assembly of block copolymers into complex microphases has advanced in parallel with their increasing importance. In many cases it is possible to predict and understand the microstructure of block copolymers through the use of self-consistent field theory (SCFT) [18–24]. Advances in polymer physics have gone hand in hand with advances in polymer chemistry. Synthetic methods for the production of block copolymers have expanded from basic living anionic polymerizations to include

free radical polymerization methods such as: atom transfer radical polymerization [25, 26], nitroxide mediated controlled radical polymerization [27], and reversible addition-fragmentation chain transfer polymerization [28].

The ever expanding toolkit of polymer synthesis methods allows the production of a wide variety of polymers with specific architectures. This has made possible the synthesis of block copolymers specifically for the purpose of creating polymer gels. On a fundamental level polymer gels are simply a crosslinked network of polymer that is swollen by a solvent. However, thanks to the growing number of available synthetic methods the crosslinking mechanism can be ionic, chemical, or physical. The result is a plethora of polymer systems with a variety of gelation triggers, including temperature changes, pH, and salinity [7].

The research presented in this dissertation focuses on a physically crosslinked block copolymers gel system. When triblock copolymers are dissolved in midblock selective solvents they can form polymer gels through the association of the less soluble endblocks. These endblock aggregates act as physical crosslinks for the network formed by the solvent swollen midblocks [1, 29]. The properties of these gels are highly dependent on the polymer-solvent interactions.

If the thermodynamic interactions between the solvent and polymer end-blocks have the appropriate temperature dependence, the gelation process will be temperature-controlled, rapid and reversible. This is the case for triblock copolymers with poly(methyl methacrylate) (PMMA) end blocks and a poly(n-butyl acrylate) (PnBA) midblock dissolved in alcohol [1,29,30]. Previous research proposes that the temperature dependant mechanical response of these solutions is determined by two characteristic transition temperatures [1]. The first of these is the critical micelle temperature. Below this temperature the PMMA endblocks will aggregate to form a physically crosslinked network. Once this network is formed the viscosity of the solution is controlled by the rate of exchange of the endblocks between micelles [29]. As the temperature is further decreased a glass transition temperature is reached for the PMMA aggregates. The presence of this glass transition results in a very strong temperature dependence for the relaxation times of the polymer gels [29].

The mechanical properties of polymer gels also depend on their osmotic properties [31–33]. The intent of this dissertation is to elucidate the interplay between mechanical, structural, and osmotic properties in determining the physical properties of a triblock copolymer gel. In conjunction with SCFT the experimental work presented here leads to an improved understanding of thermally reversible, physically crosslinked, gel networks. The detailed picture of the interaction between structure, mechanical, and osmotic properties that emerges from this research will become part of the basis for predictive models that can be used to design polymer gels with specific properties.

1.2. Outline of Objectives and Research

The goal of research presented in this text was motivated by a desire to develop a more detailed understanding of the interplay between the structural, osmotic, and mechanical properties that determine the physical behavior of physically crosslinked triblock copolymer networks. A more refined understanding of the forces at work in such a system will provided a basis for the design of future systems with specific predetermined properties.

Chapter 2 of this text begins with a background on the specific acrylic triblock copolymer gels system used in this study. Acrylic triblock copolymers in alcohol solvent are a good choice as a model system for two main reasons. First of all, the endblock interactions which control gel formation are temperature tunable. Second, a basic understanding of their structural and mechanical properties already existed in literature. This information provided a base from which a more detailed understanding of structural and mechanical properties could be built. A brief background on endblock driven thermally reversible phase transitions and what is already known about this transition in acrylic triblock copolymer gels is included in chapter 2.

One characteristic of acrylic triblock systems of particular interest was the concept of a critical micelle temperature. This is the temperature at which polymer endblocks aggregate to form a physically crosslinked polymeric gel. Therefore, one of the main objectives of this work was to explore the structural and mechanical properties of acrylic triblock copolymer gels in the temperature range where this aggregation transition is thought to occur. Also of interest was the possibility of using osmotic properties measurements to monitor the state of endblock aggregates. The osmotic properties of these systems, which play a significant role in determining mechanical properties, had not previously been studied in detail.

Chapter 2 continues by providing additional background on the osmotic properties of gels. It has been known for some time that the osmotic and mechanical properties of gels are closely related. A basic model for the relationship between the quantity of osmotically active polymer and the mechanical properties of a polymer gel in determining the total osmotic pressure is discussed.

Developing a detailed understanding of the properties of triblock copolymer gels required the development of a model that provides detailed information about some of the structural features, which are difficult to probe experimentally. These features include the size and volume fraction of solvent present in endblock micelles. Chapter 3 describes an SCFT model for studying multi-block copolymer melts, which was adapted to study triblock gels. Also presented in Chapter 3 are the results of SCFT simulations for two different triblock architectures at a single volume fraction and a variety of temperatures. SCFT results were then used to predict some experimentally relevant properties, such as bridging fraction and the maximum scattering intensity obtained from small angle x-ray scattering measurements as a function of temperature.

Chapter 4 provides a detailed description of the experimental methods and procedures used to measure the physical properties of acrylic triblock copolymer gels. The methods used to characterize gels included rheometric techniques to measure mechanical properties, small angle x-ray scattering to determine gel structure, and gel swelling measurements as well as vapor pressure osmometry to measure osmotic properties. The details of the fit model used to interpret SAXS data is included in the description of SAXS experimental methods. Also, presented in Chapter 4 is a background on vapor pressure osmometry, which is an unfamiliar technique to many researchers.

The results and discussion of the experiments described in Chapter 4 are presented in Chapter 5. When experimental data is combined with the knowledge gained from SCFT simulation a detailed understanding of the interplay between gel structure, osmotic properties, and mechanical properties emerges. Rheological measurements indicate that the flow properties and transitions from an elastic gel, to a visco-elastic gel, to a liquid, are controlled by the state of endblock aggregates. The temperatures at which these mechanical transitions occur are relatively insensitive to volume fraction and midblock architecture. However, the relative magnitude of mechanical properties, such as shear modulus and zero shear viscosity is effected by midblock degree of polymerization and the total volume fraction of polymer. Small angle x-ray scattering experiments provided insight into the structural evolution of gels as a function of temperature. The nearest neighbor distance between aggregates was found to depend heavily on volume fraction and midblock architecture. The scattering intensity was also shown to decrease rapidly from 55 °C to 80 °C, which is indicative of the swelling of endblock aggregates. Swelling measurements allowed assessment of the osmotic properties of gels and highlighted the importance of midblock degree of polymerization in determining osmotic properties. Lastly, direct measurements of osmotic pressure confirmed the importance of gel mechanical properties, the degree of midblock stretching, and the volume fraction of osmotically active polymer in determining gel osmotic properties.

Chapter 6 describes the future direction of this work and areas where additional experiments could improve the predictive capability of an SCFT-based model for designing physically crosslinked thermally reversible gels. Additional small angle scattering experiments designed to study the density and size of PMMA endblock aggregates would be particularly useful for improving SCFT. SCFT calculations that attempt to account for the kinetic trapping of endblock aggregate structure at low temperatures would also improve the utility of the SCFT calculations, as their current form does not predict the room temperature behavior of triblock gels.

CHAPTER 2

Background

2.1. Physically Crosslinked Triblock Copolymer Gels

When swollen in a midblock selective solvent, triblock copolymers in solution can exhibit mechanical properties similar to crosslinked polymer gels; this occurs due to polymer endblock aggregation. The resulting endblock aggregates are bridged by solvated midblocks, creating a physically crosslinked polymer network [**34–39**]. In some cases, mechanical properties are found to be highly temperature dependant [**1**,**38**,**40**]. In these systems the mechanical properties of triblock copolymer gels are generally found to fall into three distinct ranges as a function of temperature: the first is an elastic or rubbery regime, where gels have an elastic mechanical character; the second is a plastic range, where gels behave as visco-elastic solids; the third is the viscous range where the system behaves as a viscous polymer solution, rather than a gel.

The temperature dependant behavior of these gels can be explained by the changing nature of the Flory-Huggins interaction parameter between the solvent and endblock as a function of temperature. In 1984, Wantanabe et al. explained these temperature regimes through the use of transient network theory [41]. They proposed that in the elastic temperature range, endblock ends are essentially fixed in aggregates due to extremely unfavorable endblock-solvent interactions: stress relaxation in this range would occur through an endblock pull out mechanism. In the intermediate plastic regime, the solvent-polymer interaction is not as unfavorable and endblocks become mobile, exchanging between aggregates to accommodate stresses. The flow of endblocks in what is otherwise a networked solid is a somewhat unusual characteristic of these physically crosslinked systems [42]. Finally, viscous or liquid-like mechanical behavior occurs when the solvent-endblock interaction is favorable enough that endblock aggregation is no longer required to minimize the free energy of the polymer system: instead of forming a physically crosslinked network, the triblocks behave as a homogeneous, disordered solution. Subsequent research expanded on these concepts and demonstrated their applicability to a variety of triblock copolymer-solvent systems [39, 43–49].

Symmetric, ABA architecture, PMMA-PnBA-PMMA triblock copolymers in alcohols are a particularly interesting subset of gel-forming triblock copolymers. The poly(methyl methacrylate) endblocks of these polymers exhibits an upper critical solution temperature in alcohols, which leads to gels with a rapid, thermally reversible transition in mechanical properties. At room temperature, these PMMA-PnBA alcohol mixtures are elastic gels; if warmed to a moderate temperature, above ~ 80 °C, the PMMA-PnBA gel will become a viscous liquid. These properties lead to investigations of the possibility of using PMMA-PnBA-PMMA tricblock copolymer gels as pressure sensitive adhesives and binders for gel casting ceramics [5–7, 50, 51].

In conjunction with the investigation of novel applications, the basic structure-properties relationships that give rise to thermally reversible properties were studied. In 1999, Flanigan, Crosby, and Shull used small angle x-ray scattering to investigate the evolution of gel microstucture as a function of temperature and solvent evaporation [**30**]. Drawing on the previous work with acrylic triblock systems, Drzal and Shull published a detailed investigation into the origins of mechanical strength and elasticity thermally reversible acrylic triblock copolymer gels in 2003 [1]. The authors concluded that, in acrylic triblock copolymer gels the rapid nature of the transition from viscous liquid to elastic solid is due to an endblock critical micelle temperature(CMT), that is above - but relatively close to - the glass transition temperature (T_g) of the endblocks [1]. Figure 2.1 is adapted from this 2003 paper by Drzal et al. and schematically illustrates the structure-mechanical properties relationship in acrylic triblock gels and their relationship to critical temperatures. This schematic generally agrees with the model of physically crosslinked networks proposed by Wantanabe in 1984 for other triblock copolymer systems [41]. Above the CMT the triblock copolymer solution will behave as a low viscosity liquid; as the temperature decreases below the CMT the endblocks will aggregate, forming a network and taking on the properties of a visco-elastic solid. Further decrease in temperature to below the T_g results in improved creep resistance and mechanical behavior similar to that of an elastic solid. Drzal and Shull were able to confirm from their study, which focused mainly on rheometry and dynamic scanning calorimetry results, the existence of a glass transition temperature near 36 °C and were further able to show that aging time effected the creep resistance and the DSC measured glass transition temperature. Aging time did not appear to impact the location of the higher temperature visco-elastic solid to liquid transition. Drzal and Shull also proposed that the CMT could be estimated from the known temperature dependence of the interaction parameter of PMMA in butanol. In an equilibrium system, the chemical potential, μ_s , of solvent and swollen midblock was assumed to be zero. Therefore, it is possible to solve for the relationship between the PMMA-solvent interaction parameter, χ , and the equilibrium volume fraction of solvent



Figure 2.1. A schematic of the structural origins of a crylic triblock copolymer mechanical properties adapted from Drzal et al. , 2003 $[\mathbf{1}]$

in the PMMA end blocks, ϕ_s , using the Flory-Huggins expression for chemical potential shown below:

(2.1)
$$\mu_s = \ln \phi_s + (1 - \phi_s) + \chi \left(1 - \phi_s\right)^2$$

Combined with the temperature dependence of the interaction parameter, they estimated that the CMT for PMMA-PnBA-PMMA triblock copolymer in 1-buanol is 82.5 °C.

Detailed investigations of the structures-properties relationship in acrylic triblock copolymers continued with work by Seitz et al. published in 2007. In this paper, SAXS data, in combination with rheometric data, was used to characterize PMMA-PnBA-PMMA triblock copolymer gels in 2-ethylhexanol and to investigate the relationship of polymer architecture to rheometric properties. Seitz et al. 's main conclusions were fourfold. First of all, the number of endblocks per micelle, or aggregation number, was strongly correlated with endblock length. Second, a dramatic decrease in SAXS scattering intensity is observed in the same 20 °C temperature region as the rheometric liquid to sold transition. Third, the rheometric properties of acrylic triblock gels appear to vary smoothly, from that of an elastic gel to liquid-like behavior. Lastly, stress relaxation times were found to depend strongly on the volume fraction of polymer and the endblock degree of polymerization. In combination, these conclusions supported Drzal and Shull's previous interpretation of the structure properties relationship in PMMA-PnBA-PMMA acrylic triblock gels. However, their conclusions also suggest that an experimental examination of the visco-elastic solid to liquid transition, utilizing alternative techniques to SAXS and rheometry, could further improve understanding of these systems.

2.2. Osmotic Properties of Polymer Gels

As outlined in the previous section, a physical gelation of PMMA-PnBA-PMMA polymers can be observed with rheometry. However, questions about the correlation between the physical gelation temperature, critical aggregation temperature, and SAXS observations remained. A goal of this dissertation is to investigate the use of osmotic pressure measurements to evaluate the state of aggregation in the PMMA domains of acrylic triblock copolymers. Gel networks, including acrylic triblock copolymer gels, will swell or deswell upon immersion in pure solvent. The balance between osmotic swelling forces that tend to expand the gel and elastic restoring forces that oppose this swelling, can be expressed in terms of two components of the overall osmotic pressure:

(2.2)
$$\Pi_{Total} = \Pi_P + \Pi_{El}$$

Here Π_{Total} is the total osmotic pressure, Π_{El} is the elastic contribution to the pressure, and Π_P is the contribution from the quantity of solvated polymer. Π_P is taken to be equivalent to the osmotic pressure of a solution of un-crosslinked high molecular weight polymer of the same volume fraction. For a semidilute solution, the volume fraction of polymer, ϕ_p can be approximated as a simple power law [52],

(2.3)
$$\Pi_P = \frac{k_B T}{\xi^3} = \frac{k_B T}{a_0^3} \phi_p^{9/4}$$

where ζ is the correlation length, and a_0 is an effective segment size. The elastic contribution to the osmotic pressure can be expressed in terms of the free energy change per unit volume by the equation below:

(2.4)
$$\Pi_{El} = -V \frac{\partial}{\partial V} \Delta f_{El}$$

where V is volume and Δf_{El} is the elastic free energy density. Under low strain, acrylic triblock copolymer gels can be approximated as neo-Hookean materials and thus Δf_{El} can be expressed as:

(2.5)
$$\Delta f_{El} = \frac{G\left(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3\right)}{2}$$

where G is the shear modulus of the material and λ_x , λ_y , λ_z are the principle extension ratios. For an incompressible, isotropic, gel at equilibrium Equation 2.5 can be simplified to

(2.6)
$$\Delta f_{El} = \frac{3G}{2} \left[\left(\frac{V}{V_0} \right)^{\frac{2}{3}} - 1 \right]$$

where V_0 is the volume of the unswollen gel. Combining Equations 2.4 and 2.6 at equilibrium $(V = V_0)$, we obtain the below result [53]:

(2.7)
$$\Pi_{El} \simeq -V \frac{\partial}{\partial V} \left[\frac{3G}{2} \left(\left(\frac{V}{V_0} \right)^{\frac{2}{3}} - 1 \right) \right]_{V=V_0} = -G$$

As shown in Equation 2.7, the osmotic contribution due to elasticity in a gel at equilibrium with pure solvent is equivalent to the shear modulus of the material. Furthermore, since pure solvent has no elasticity and zero osmotic pressure, the osmotic and elastic terms of the total osmotic pressure of a gel at equilibrium with pure solvent must be equal and opposite as expressed below:

(2.8)
$$\Pi_{Total} = \Pi_P + \Pi_{El} = \frac{k_B T}{a_0^3} \phi_p^{9/4} - G = 0$$

This strong connection between the mechanical and osmotic properties of swollen networks and gels has been well documented for a number of chemically crosslinked, entangled, and pH-sensitive gels [31–33]. The loss of the physical network in acrylic triblock gels as endblock aggregates dissolve into solution at elevated temperatures should result in a change in osmotic pressure.

CHAPTER 3

Self-Consistent Field Theory Simulation of Acrylic Triblock Copolymers

3.1. Self Consistent Field Theory Background

Self consistent field theory (SCFT) is a powerful method of modeling the equilibrium behavior of polymer melts and concentrated polymer solutions. The basis of SCFT was developed by Edwards in 1965 [54] who showed an asymptotic solution to the probability of a particular segment of a polymer passing through a particular point in space under the influence of a field. Since then, SCFT has been used to describe many features of polymer systems, including the density profiles of polymer brushes [55,56] and the complex phase behavior of block copolymers [18–20,23,57–62]. Modern computational capabilities have further extended the application of SCFT by allowing increasingly complex problems to be solved with calculation-intensive, numerical solutions [63–68]. For a detailed introduction to SCFT, see Chapter 2, "Self-Consistent Field Theory and Its Applications", by Mark Matsen in volume one of the Soft Matter series edited by Gromper and Schick [24]. The basics of SCFT are presented here to provide context for the simulations discussed in subsequent sections.

The robust utility of SCFT is a result of the limited number of assumptions made in its formulation. The first of these assumptions is that the polymer being studied can be modeled with a simple, coarse-grained, Gaussian model [24]. The nonspecific scaling behavior of polymers is what makes this possible. In a melt or concentrated solution, polymers are known to follow random walk statistics. An example is the radius of gyration of a homopolymer melt system. The radius of gyration, R_g , is known to scale as

$$(3.1) R_g = a \left(\frac{N}{6}\right)^{1/2}$$

regardless of the specific chemistry involved. The proportionality constant or segment size, a, will be different for different polymers, but the scaling behavior as a function of N, the degree of polymerization will remain constant [52].

The second assumption of most SCFT formulations is that monomer-monomer interactions may be accounted for using basic Flory-Huggins theory with an incompressibility constraint [69]. It is possible to modify SCFT to use a more complex model for molecular interactions, but that is outside the scope of this work. The use of the Flory-Huggins theory is possible due to the large difference in molecular versus atomic size scales in polymers. Every polymer in a melt or concentrated solution is in contact with hundreds of others. There are so many interaction points, that they minimize the effects of individual atomic interactions. Fluctuations on the atomic scale have little effect on the overall polymer chain. Therefore, the combination of all the various interactions between a polymer and its surroundings can be approximated as a combination of various chemical potential fields.

This leads to the final assumption of SCFT, the mean field, or saddle point approximation [70,71]. The mean field approximation assumes that the chemical potential field can be well approximated by a single average or mean field. The saddle point approximation allows one to determine the state of a polymer system by self-consistently solving for the mean field via the method of steepest decent.

Unfortunately, SCFT cannot model all polymeric systems accurately. For example, SCFT has difficulties in systems where thermal fluctuations approach the size scale of the polymer chain [72]. Systems near critical points are another example of a case where the basic assumptions of SCFT break down [73–75]. Various methods can be used to compensate for these problems, and the subject is an active area of research [76–81]. Another relevant weakness of SCFT is that it is best used to examine equilibrium states. However, it is well known that polymer systems can have very slow kinetics and remain trapped in non-equilibrium or metastable states for intervals significantly longer than experimental times [24]. Indeed, previous work with ABA architecture PMMA-PnBA-PMMA triblock copolymers has shown that introducing isotactic PMMA will drastically slow down the exchange kinetics within endblock aggregates. The isotactic homopolymer complexes with the syndiotactic polymer endblocks, resulting in pronounced aging effects in the material properties [30].

In this work the effect of additives on the endblock configuration was not examined. However, it is expected that at low temperatures, below the glass transition of PMMA, there maybe some disagreement between SCFT and experiment as the slow kinetics of the polymer system trap it in a non-equilibrium configuration. As long as one is aware of these pitfalls, it is possible to compare SCFT and experimental results.

Although it is unconventional, it is possible to apply SCFT to solvated polymer systems, as solvent molecules are generally small molecules. One would expect that as the molecular and atomic scales converged the decreasing number of inter- and intra-molecular interactions would invalidate the mean field approximation. Fortunately it has been shown that even at relatively low polymer volume fractions, as long as polymer-polymer interactions are the main factor in determining the properties of the solution, SCFT will remain valid [60,82–85]. More specifically, SCFT is valid for polymer systems that are in the semi-dilute or concentrated regimes, but not the dilute regime [86]. Experimental evidence presented in Section 4.5.3 shows that the osmotic pressure of calibration solutions with similar volume fractions of polymer to those studied experimentally and with SCFT are well fit by Flory-Huggins theory, rather than by a linear Van't Hoff dilute solution type relationship.

In the theoretical formulation developed in the next section, one additional assumption is made. It is assumed that for spherical, cylindrical, or lamellar symmetric systems it is possible to approximate the full three-dimensional structure of the system by collapsing the problem into one dimension. In essence, the unit cell approximation replaces a packing structure with a spherically symmetric reflecting boundary condition, as illustrated in Figure 3.1. The first part of the figure **a**, illustrates a full 2-dimensional system. Part **b** shows the new unit cell after application of the unit cell approxiamtion. This practice is known as the unit cell approximation and is often employed in complicated, periodic systems where the full three-dimensional SCFT would otherwise be to computationally intensive [**24**, **87**–**89**]. When collapsed to one dimension, the modified diffusion equation derived by Edwards in 1965, is

(3.2)
$$\frac{\partial q(r,n)}{\partial n} = \frac{a^2}{6} \left\{ \frac{\partial^2 q(r,n)}{\partial r^2} + \frac{C}{r} \frac{\partial q(r,n)}{\partial r} \right\} - w(r,n) q(r,n)$$



Figure 3.1. Illustration of the Unit Cell Approximation

where C is dependant on system symmetry, C = 0 for planar symmetry, C = 1 for cylindrical symmetry, and C = 2 for spherical symmetry. The partition function, q(r, n)describes the probability that a polymer segment, n, is located at a particular position, r, in space. The mean field, w(r, n), is a function of both the local chain composition, dependant on n, and the composition of the surrounding environment. The variable, a, is the polymer segment size.

The form of Equation 3.2 should be familiar to students of physics and is essentially equivalent to a one dimensional form of the Schrödinger wave equation where the wave function is equivalent to partition functions, $\Psi(r,t) = q(r,n)$, and the potential term is equivalent to the mean field, U(r,t) = w(r,n), though the various constant terms are situation specific. In the case of the acrylic triblock copolymer gels studied, the volume fraction profile is of greater interest than the overall three dimensional organization of the PMMA rich aggregates. Previous work suggests that the organization of the aggregates is random under the processing conditions used. [1,30] Given this, the unit cell approximation serves to simplify the problem, while still providing the pertinent information. Nonetheless, it was instructive to compare SCFT results using the UCA to a full three dimensional calculation. The results of this comparison are described in Section 3.3.

3.2. Theoretical Formulation

In order to better identify and connect key features of experimental results concerning acrylic triblock copolymers, it was necessary to develop a detailed theoretical understanding of gel systems. To this end, self-consistent field theory was employed. This section describes the specific theoretical formulation used, a modified version of the formulation developed by Nunalee and Shull for use in polymer melt systems [23]. Additionally, the input parameters for the calculations were chosen such that the SCFT model corresponds to the experimental system of acrylic triblock copolymers described in Chapters 4 and 5. The starting point for the theoretical formulation used is the Flory approximation of the free energy per unit volume, f, of a homogeneous mixture of polymers

(3.3)
$$f = \frac{k_b T}{\nu_0} \left\{ \sum_k \frac{\phi_k \ln \phi_k}{N_k} + \frac{1}{2} \sum_{m \neq n} \chi_{mn} \phi_m \phi_n \right\}$$

where T is temperature, v_0 is the reference volume, N is the degree of polymerization, Φ are the volume fractions as a function of radial distance from the aggregate center, and χ_{mn} are the various Flory-Huggins interaction parameters. The subscript k refers to a particular component. In our system k can be polymer (p) referring to triblock copolymer or solvent (s). The subscripts m and n refer to the actual chemical species. In the acrylic triblock copolymer gels studied, there are three chemical constituents. These are butanol (b), PMMA (A), and PnBA(B). In this case v_0 is the molar volume of butanol, 91.5 cm³ per mol. To determine the free energy, it is necessary to determine the volume fractions as a function of distance from the endblock aggregate center. The chemical potential is derived using functional calculus from the equation for free energy, Equation 3.4. [24]

(3.4)
$$\frac{\mu_k}{k_b T} = \ln \phi_k + 1 - N_k \sum_k \frac{\phi_k}{N_k} + \frac{1}{k_b T} \sum_{j=1}^{N_k} w_p(j)$$

The first three terms of this expression represent the entropy of component k, while the last term represents the enthalpic contribution due to polymer-polymer interactions, with

(3.5)
$$\frac{w_p(j)}{k_b T} = \frac{1}{2} \sum_{m \neq n} \{ \phi_m - g_m(j) \} \chi_{mn} \{ g_n(j) - \phi_n \}$$

where j is an index for each polymer segment going from j = 1 at one end of a polymer chain to N_k . The Flory interaction parameters, χ_{mn} , are assumed to be independent of polymer composition. The functions $g_m(j)$ describe the average composition of segment jin component k. In the case of a system where the exact composition of a polymer chain is unknown, such as a random or gradient copolymer, $g_m(j)$ describes the probability of a segment j being a particular composition [23]. For a well defined polymer, such as a symmetric ABA tri-block copolymer in solvent, $g_m(j)$ and $g_n(j)$ act similarly to a delta function such that

(3.6)
$$g_A(j) = \begin{cases} 1 & 1 < j \le \frac{N_A}{2} \\ 0 & \frac{N_A}{2} < j \le \frac{N_A}{2} + N_B \\ 1 & \frac{N_A}{2} + N_B < j \le N_A + N_B \end{cases}$$

(3.7)
$$g_B(j) = \begin{cases} 0 & 1 < j \le \frac{N_A}{2} \\ 1 & \frac{N_A}{2} < j \le \frac{N_A}{2} + N_B \\ 0 & \frac{N_A}{2} + N_B < j \le N_A + N_B \end{cases}$$

where the possible values for the subscripts m and n are A for the endblocks, B for the midblock. Here N_A is the total degree of polymerization of the endblocks and N_B is the midblock degree of polymerization.

To proceed further, it is necessary to find expressions for the volume fractions in equations 3.3 through 3.5. This is accomplished by making use of the basis of SCFT: that partition functions can be used to describe the statistics of polymer chains. These partition functions specifically describe the location of a polymer chain segment, n, at a particular point in three dimensional space, r, with respect to a reference point. It has previously been established that the acrylic triblock copolymer system consists of spherically symmetric micelles. This allows the vector r to be collapsed into a onedimensional scalar via the unit cell approximation. In this formulation, r is the distance from the micelle center. It is possible to approximate r with the discrete variable, i, by dividing the volume normally described by r into layers. The width of each layer, i, is equivalent to the statistical segment length of a polymer repeat unit. The continuous variable, n, can be also approximated discretely with the previously defined polymer segment index, j.

In this formulation, each component, k, is described by two partition functions, $q_{k1}(i, j)$ and $q_{k2}(i, j)$, which start at opposite ends of a polymer chain. These distribution functions must obey the connectivity of a polymer chain and initial conditions that $q_{k1}(i, 0) =$ $q_{k2}(i, 0) = 1$. An additional reflective boundary condition was applied in the case of the acrylic triblock copolymer system such that q(0, j) = q(1, j) and also that at the system size, i_{max} , $q(i_{max}, j) = q(i_{max+1}, j)$. The equations below satisfy all the necessary requirements

$$q_{k1}(i,j) = \{\lambda_{-1}q_{k1}(i-1,j-1) + \lambda_0 q_{k1}(i,j-1) + \lambda_{+1}q_{k1}(i+1,j-1)\} \exp\left\{-\frac{w(i,j)}{k_b T}\right\}$$
(3.9)
$$q_{k2}(i,j) = \left\{\lambda_{-1}q_{k2}\left(i-1,j-1\right) + \lambda_{0}q_{k2}\left(i,j-1\right) + \lambda_{+1}q_{k2}\left(i+1,j-1\right)\right\}\exp\left\{-\frac{w\left(i,j\right)}{k_{b}T}\right\}$$

where the variables λ_{-1} , λ_0 , and λ_{+1} are the transitional probabilities of the polymer and are equivalent to the number of nearest neighbor sights in layers i - 1, i, and i + 1. For a spherically symmetric system we can describe these translational probabilities in terms of the contact area between layers. This gives

(3.10)
$$\lambda_{-1}(i) = \frac{S(i-1)}{6(V(i) - V(i-1))} = \frac{(i-1)^2}{2(i^3 - (i-1)^3)}$$

(3.11)
$$\lambda_{+1}(i) = \frac{S(i)}{6(V(i) - V(i-1))} = \frac{i^2}{2(i^3 - (i-1)^3)}$$

(3.12)
$$\lambda_0(i) = 1 - \lambda_{-1}(i) - \lambda_{+1}(i)$$

where $S(i) = 4\pi i^2$ is the surface area between layers and $V(i) = (4/3)\pi i^3$ is the volume contained in *i* layers. As stated earlier, the term w(i, j) represents the mean field acting on a polymer chain and is dependent on both the local composition of a chain and the surrounding composition. The mean field used in this SCFT formulation is

$$w(i,j) = \frac{\mu_k - 1}{N_k} - \Delta w(i) + w_{ext}(i,j) = w_p(i,j) - k_b T \sum_k \frac{\phi_k(i)}{N_k} - \Delta w(i) + w_{ext}(i,j)$$

This function is based on the chemical potential with $w_p(i, j)$ representing the enthalpy of polymer-polymer interactions. The term $w_p(i, j)$ is equivalent to equation 3.5. The second term describes the conformational entropy of the system, while the third term, $\Delta w(i)$, enforces the incompressibility of the system according to

(3.14)
$$\frac{\Delta w(i)}{k_b T} = \zeta \left\{ 1 - \sum_k \phi_k(i) \right\}$$

where ζ is inversely proportional to the bulk incompressibility of the system. The incompressibility parameter, ζ , is chosen to be large enough to correspond to the incompressibility limit where ζ is infinity. The last term represents any external field acting on the system, such as, interactions with a surface or an applied stress. In the SCFT formulation used here, no external field was necessary thus, $w_{ext} = 0$. In order to fully solve for the volume fraction of a chemical species, n, in component, k, it is helpful to further constrain the partition functions, equations 3.8 and 3.9, such that $q_{k1}(i, j) = q_{k2}(i, N_{k-j})$. For a given junction point, j, the partition functions must now describe the possible polymer configurations on either side of the junction point. Summing over all the possible junction points of the two partition functions gives the volume fraction of chemical species, n, in component, k, for a particular layer, $\phi_{km}(i)$,

(3.15)
$$\phi_{km}(i) = \frac{1}{N_k} \sum_{j=1}^{N_k} q_{k1}(i,j) q_{k2}(i,N_k-j) g_m(j)$$

The over all volume fractions of the various components, ϕ_k , or chemical species, ϕ_n , can be found by summing the relevant volume fraction profiles as defined by equation 3.15 over all layers and then normalizing by the total system volume.

To simulate a polymer system of a given size, i_{max} , the system of equations consisting of equations 3.4 through 3.15 are solved numerically in a recursive process until self consistency is achieved. The system size is then decreased by i - 1 and again solved self-consistently. The system size that gives the lowest free energy corresponds to the equilibrium system.

SCFT calculations were carried out using a FORTRAN program written by the Shull group. The self-consistency algorithm used by this software is summarized schematically in Figure 3.2. The starting point is an initial guess for the volume fraction distribution of each component, ϕ_k and the chemical potential, μ_k , of each component based on past experience or previous calculation. From this information, the incompressibility condition, Δw , is calculated. Copies of these values are stored as separate variables referred to as "images" or ϕ_{image} and Δw_{image} .

New values for the volume fraction of polymer are calculated from partition functions using equation 3.16 based and the initial values for Δw , the volume fractions and chemical potentials. These new volume fraction profiles, ϕ , along with the volume fraction profiles stored as new ϕ_{image} values, are then used to calculate new initial volume fractions. The variation between the original and new volume fractions is controlled via a relaxation parameter, λ_{vol} , according to equation 3.16

(3.16)
$$\phi(i) = \lambda_{vol}\phi_{image}(i) + (1 - \lambda_{vol})\phi(i)$$

where λ_{vol} is a small value, typically on the order of 10^{-4} . From this new initial volume fraction profile a new value for Δw is calculated using equation 3.14. Δw and Δw_{image} are then used to update Δw , making use of another relaxation parameter, λ_w ,

(3.17)
$$\Delta w = \lambda_w \Delta w_{image} + (1 - \lambda_w) \Delta w$$



Figure 3.2. Illustration of the self-consistent field theory algorithm developed for the study of block copolymers

This brings the calculations full circle. These calculations are iterated until the difference in free energy calculated from the initial and image volume fractions is a small value, typically less than 10^{-5} .

One of the results obtained from SCFT calculations is the bridging fraction. The bridging fraction, f_b , is defined as

(3.18)
$$f_b = \frac{\phi_{bridges}}{\phi_{total}} = 1 - \frac{\phi_{loops}}{\phi_{total}}$$

where $\phi_{bridges}$ is the volume fraction of triblock copolymers whose endblocks are in separate endblock aggregates and ϕ_{total} is the total volume fraction of triblock chains. The alternative configuration is for both endblocks to be located in the same aggregate causing the polymer midblock to form a loop. Calculation of the bridging fraction is achieved by adding an additional step to the recursive SCFT algorithm described in the previous paragraph. Once the equilibrium system size is determined, a new calculation is carried out for twice the equilibrium system size. In the standard calculation, the equilibrium system size is half the distance from an aggregate center to the center of its the nearest neighbor. Doubling the system size results in an SCFT calculation for the full distance between aggregate centers. An additional constraint that $q_{k1}(I,0) = 0$ is applied for all *i* between i = 1 and $i = 2i_{max}$. This constraint forces the SCFT calculation to count only those polymer chains that begin and end in the same aggregate. The resulting loop volume fraction profile, ϕ_{loop} , can be used to calculate the bridging fraction via equation 3.18.

Polymer	PMMA N _k per block	PnBA N _k per block
Short midblock	231	1225
Long midblock	212	328
Solvent	1-Butanol	

Table 3.1. Polymer end- and midblock degrees of polymerization used in SCFT calculations

In order for SCFT results to be relevant to the actual polymer systems studied in Chapters 4 and 5, calculation parameters had to be chosen correctly. The degree of polymerization for the various components was determined based on the molar volume of butanol, 91.5g per cm³. This gives the degrees of polymerizations for each block of the acrylic triblock copolymers studied summarized in Table 3.2. The temperature dependant properties of polymer solutions were captured via variation in the Flory-Huggins interaction parameters. To simulate a particular temperature, chi parameters for PMMA with butanol and PnBA with butanol were chosen based on knowledge of the chi parameter, temperature-dependence of high molecular weight homopolymers. The chi parameter of PMMA with PnBA was assumed to be 0.05 for all temperatures. The interaction parameter for the PnBA homopolymer was determined from estimates of the θ temperature using cloud point measurements of 77k molecular weight PnBA homo polymer in 1-butanol and equation 3.19

(3.19)
$$\chi = \left(\frac{1}{2}\right) \left(\frac{T-\theta}{T} - 1\right)$$

which should be valid for solutes relatively close to the θ solvent condition. This gave a chi parameter range of 0.50 through 0.41 for 30 °C through 95 °C for PnBA in butanol. Values

for the chi parameter of PMMA in butanol as a function of temperature were determined based on the relationship described by Drzal and Shull, where $\chi = 1.4508 - 0.0115 * T$, and ranged from 1.11 through 0.36 from 30 °C through 95 °C [1].

3.3. The Validity of the Unit Cell Approximation

A comparison of the unit cell approximation to a full three-dimensional simulation will illustrate the strengths and weaknesses of the former. Matsen and Thompson, in a 1999 paper, simulated the equilibrium phase behavior of symmetric ABA triblock copolymers melts. Figure 3.3 is a schematic reproduction of a portion of the phase diagram derived by Matsen and Thomson for the case where the endblock and midblock have the same polymer segment size. In this figure, N is half the total polymer degree of polymerization and f_A is the fraction of N segments in each endblock. These units are chosen such that the triblock phase diagram could be directly compared to phase diagrams for diblock molecules. The variable χ is the AB interaction parameter.

In order to test the validity of the unit cell approximation used in the simulations in this study, the phase behavior of a symmetric triblock copolymer was replicated along the $f_A = 0.25$ axis, marked in Figure 3.3 by a dashed line. The total degree of polymerization of the triblock, 2N, was chosen to be 1000. The chi parameter was varied to give the appropriate variations in χN . From the original plot by Matsen, it is expected that two phase transitions will be observed along the $f_A = 0.25$ axis with increasing χN . A transition from a disordered melt state to a spherical phase is expected near $\chi N = 16$. A second transition from spherical to cylindrical phase morphology is expected near $\chi N =$

18.



Figure 3.3. A schematic representation of the phase diagram of a symetric Triblock copolymer

To determine the equilibrium phase it is necessary to simulate both spherical and cylindrical geometries. The geometry that results in the lower free energy minimum per lattice site, $k_b T/v_0$, for a given χN is the equilibrium phase. The SCFT calculations using the unit cell approximation were found to agree with Madsen's 1999 paper. Figure 3.4 shows free energy curves for a spherical geometry with χN above, below, and near the disorder to spherical phase transition. To determine the sphere to cylinder phase transitions, we generated free energy curves for still higher values of χN . Figure 3.5 compares free energy curves above and below the sphere to cylinder phase transition. At $\chi N = 17.5$ the spherical geometry produces the lower minimum free energy; however, at



Figure 3.4. Free energy curves calculated for a symetric ABA triblock copolymer near the order-disorder transition

 $\chi N = 19$ the cylindrical geometry produces the lower free energy. The phase boundary is located at the χN where cylindrical and spherical geometries give equivalent free energy minima. This occurs at $\chi N = 18.425$ as is illustrated by Figure 3.6, where f_c is the free energy calculated assuming a cylindrical geometry and f_s is the free energy calculated assuming a sphereical geometry.

Bridging fractions were also calculated using the methods described in Section 3.2., and the results are shown in Figure 3.7. These bridging fractions are found to agree with those determined by Madsen and Thomson. In general, the bridging: fraction in



Figure 3.5. Free energy curves for a symetric ABA triblock copolymer near the sphere to cylinder transition

the spherical case is ~0.8. This is well above the cylindrical bridging fraction of ~0.67. It is important to note that the bridging fraction decreases slightly with increasing χN . The discontinuous change of the bridging fraction that accompanies the transition from spherical to cylindrical geometry is a feature of a first order phase transition. The close agreement between the results of a full three-dimensional simulation and those obtained via the unit cell approximation provide confidence that the SCFT formulation described in Section 3.2 can be used to model a network of acrylic triblock copolymer micelles.



Figure 3.6. Free energy curves for a symetric ABA triblock copolymer near the sphere to cylinder transition



Figure 3.7. Comparison of the free energies of spherical and cylindrical phases as a function of χN

3.4. Results of SCFT Simulations for ABA Symmetric Triblock Copolymers

SCFT results were obtained using the methods described in Section 3.2 for both the long and short midblock architectures. The degrees of polymerization used are described in Table 3.2. Calculations were carried out for volume fractions of 0.10, 0.15, and 0.20 acrylic triblock in butanol. Only results for a volume fraction of 0.15 will be discussed in detail. The changing χ parameters used to capture temperature variation were described at the end of Section 3.2. The volume fractions 0.15 proved most useful in interpreting the experimental results that will be described in Chapter 5 and which are described here in



Figure 3.8. System size vs. free energy from 50 °C to 70 °C for the Short midblock polymer at $\phi = 0.15$

detail. These results provide insight into the structure of individual micelles: specifically, the volume fraction profiles of the individual components, bridging fraction, and expected small angle x-ray scattering behavior.

SCFT calculations were carried out for both long and short midblock polymers with χ parameters capturing temperature variation from 30 °C to 80 °C. For each temperature, SCFT calculations were iterated for a range of system sizes. The system size with the minimum free energy for a given architecture and temperature is the equilibrium system. Figure 3.8, is representative of the free energy per unit volume, f, curves calculated for a given architecture and temperature the location of free energy min-



Figure 3.9. Temperature vs. the SCFT calculated equilibium volume per micelle

ima. Free energy increases as a function of temperature while the equilibrium system size decreases steadily. At temperatures above 70 °C, free energy calculations exhibit almost no curvature, and volume fraction profiles indicate convergence to the trivial solution: a homogenous distribution of each component. This is in agreement with the observation that at temperatures above 75 °C to 80 °C, the experimental acrylic triblock gels studied become homogenous solutions.

The trend of equilibrium system size as a function of temperature can be summarized by plotting temperature versus equilibrium micelle volume as in Figure 3.9. Equilibrium micelle volume, V_M , is calculated according to

$$(3.20) V_M = \frac{4}{3}\pi r_{\max}^3$$

where the r_{max} is the radius of the system calculated to have the minimum free energy for a given volume fraction and temperature. As temperature increases, the equilibrium volume per micelle decreases, as does aggregation number: the number of polymer chains per endblock-rich aggregate. Aggregation number, M, can be calculated from the equilibrium micelle volume by

(3.21)
$$M = \frac{2\rho\phi_{poly}N_{av}}{Mw}V_M$$

where ρ is the density of the triblock copolymer, ϕ_{poly} is the volume fraction of polymer in solution, Mw is the triblock molecular weight, and N_{av} is Avagadro's number. It is clear from Figure 3.9 that equilibrium micelle volume decreases more rapidly with temperature in the short midblock polymer system than long midblock polymer system. To understand why this occurs, it is helpful to compare the volume fraction profiles of the two chemical components, PMMA and PnBA, of both systems. Figure 3.10 shows the volume fraction profiles for long and short midblock polymer micelles at 50 °C. Horizontal scales are provided in nanometers and also as the radius normalized by the unperturbed radius of gyration of each individual triblock. At 50 °C, we see that each micelle consists of a PMMA core surrounded by a PnBA corona. Despite an unfavorable PMMA-butanol interaction parameter, $\chi_{AS} = 0.876$, the volume fraction of solvent in the PMMA rich regions is fairly high, approximately 0.4. The radii of the PMMA-rich regions are similar



Figure 3.10. SCFT calculated volume fraction profiles for each polymer component

in both polymer systems, with average PMMA fractions near 0.6. This result is expected because the degree of endblock polymerization is similar for both polymers.

The difference in PnBA content between the two polymers studied is apparent in the volume fraction profile for PnBA. For the short midblock, the volume fraction of PnBA in the aggregate coronal region drops off to almost zero near, r_{max} , the equilibrium system radius. In contrast, the long midblock system shows only a slight decrease in the PnBA volume fraction profile. Evaluating these volume fraction profiles in terms of unperturbed radius of gyration, we see that the long midblock system equilibrium size is less than 2.5 times the unperturbed radius of gyration. Therefore, polymers in a bridging conformation in the short midblock system are more stretched than those of the long midblock system.

The temperature dependence of the local volume fractions of each component is compared in Figure 3.11, which shows total polymer volume fraction profiles for both long and short midblock polymers at a range of temperatures. Several trends are observed. As expected, the overall volume fraction of PMMA in the micelle core and the total system size steadily decrease with increasing temperature. As described in Section 3.2, a reflecting boundary condition was applied; thus, these trends imply that the system reorganizes to form many small micelles rather than fewer large micelles.

Both systems appear to have similar volume fractions of PMMA in core regions at the same temperature. The core region of the long midblock polymer is slightly more PMMA-rich. This is explained because the degree of polymerization is of the endblock slightly higher in the long midblock polymers. The size of the PMMA-rich regions in both polymers is similar below 50 °C. However, above this temperature, the size of the PMMA-rich region for the short midblock polymer continues to increase as temperatures



Figure 3.11. SCFT calculated, total polymer volume fraction profiles for both long and short midblock polymers from 30 $^{\circ}{\rm C}$ to 70 $^{\circ}{\rm C}$

decrease. In the long midblock system, the radius of the PMMA rich region remains relatively constant, though the volume fraction of PMMA continues to increase.

The short and long midblock SCFT simulations also exhibit different behavior in the PnBA-rich coronal region. The volume fraction of PnBA at the system radius, r_{max} , steadily increases with decreasing system size from approximately zero at 30 °C to 0.1 at 70 °C. Simply put, as the system size increases, the midblocks can fill the space with less-stretched conformations. In the long midblock system, the midblocks are less sensitive to temperature, with the PnBA volume fraction at the reflective boundary varying from ~0.1 at 30 °C to ~0.13 at 70 °C.

It should also be noted that the unfavorable interaction between PMMA and PnBA, appears to contribute significantly to the phase separation behavior of the acrylic triblock system. This is evident in that, at all temperatures below 70 °C, PnBA is largely excluded from PMMA-rich regions, although the interaction with solvent becomes increasingly favorable.

Calculations of the bridging fraction confirm that the observed temperature dependence of the PnBA volume fraction at the maximum system size correlates to changes in the bridging fraction. The bridging fraction, as a function of temperature, is plotted for both polymers in Figure 3.12. As expected, the bridging fraction in the short midblock system is more temperature dependant than that of the long midblock system. At 30 °C less than 5% of the midblock chains form bridges, while more than 50% of the chains form bridges in the long midblock polymer. As temperature increases, the bridging fraction for the two systems converges. In both cases, bridging fraction does not exceed 80% before



Figure 3.12. SCFT calculated Temperature vs. Bridging fraction for both long and short midblock polymer

the order-disorder transition. This is significant as the bulk modulus of the gels formed by these triblock copolymer networks depends on the bridging fraction.

Mean field calculations also provide information about the osmotic pressure of a solution. Osmotic pressure is thermodynamically defined as

(3.22)
$$\Pi = \frac{-\Delta\mu_0}{V_0^0}$$

where $\Delta \mu_0$ is the chemical potential of the solution relative to pure solvent and V_0^0 is the molar volume of the solvent. The chemical potential of a system is determined during SCFT calculations. However, rather than expressing changes in chemical potential as osmotic pressure, it is useful to quantify changes in terms of the volume fraction of a solution of midblock homopolymer with equivalent chemical potential. Expressing osmotic pressure as equivalent to a homopolymer volume fraction allows closer comparison to the experimental results. Experimental values for osmotic pressure were determined relative to homogenous solutions of midblock polymer of known volume fraction. Instrument variables, choice of theoretical model for osmotic pressure, and the determination of additional physical quantities based on the chosen model can introduce considerable variability in the calculated osmotic pressure. Expressing solution osmotic pressure in terms of equivalent volume fractions compensates for possible errors, see Chapter 4 for a detailed explanation.

Figure 3.13 shows the variation in equivalent PnBA volume fraction as a function of temperature for both long and short midblock polymers. Both polymers show "u" shaped curves. This indicates that osmotic pressure is affected by competing contributions as a function of temperature. In homopolymer solution with a set volume fraction, osmotic pressure should scale nearly linearly with temperature. Variation in the polymer-solvent interaction parameter makes a smaller contribution. Further more, osmotic pressure is expected to continuously increase with increasing temperature. SCFT suggests this is not the case with the triblock copolymers, implying that polymer architecture and the resulting self-assembly must account for this unusual temperature dependence. See Chapter 4 for a more in-depth discussion of osmotic pressure in triblock systems.

Figure 3.13 also demonstrates that the osmotic pressure of the short midblock system has a stronger temperature dependence than the long midblock system. This can be explained by the fact that the relative PMMA content is much higher in the short



Figure 3.13. Temperature vs. PnBA equivalent volume fraction of polymer for both long and short midblock polymers

midblock system than in the long midblock system. Therefore, the total osmotic pressure is more dependant on the temperature dependant PMMA-Butanol interaction parameter. Further more, the variation in entropic contribution to chemical potential from variation in polymer configuration is much greater in the short midblock systems, as we know from bridging fraction calculations.

SCFT calculations can also be used to simulate small angle x-ray scattering results. Small angle x-ray scattering is a useful tool for studying the structure of polymer melts and gels. The intensity of scattered x-rays in reciprocal space, I(q), is the square of the scattering amplitude, A(q),

(3.23)
$$I(q) = |A(q)|^{2} = \left| \int_{V} \rho(r) e^{-iqr} \right|^{2}$$

where q is the scattering vector. Scattering amplitude can be expressed as the Fourier transform of the electron scattering length density, $\rho(r)$, over the illuminated volume as a function of the position vector, r, as expressed in equation 3.23. Assuming incompressibility and no volume change upon mixing, it is a simple process to convert volume fraction profiles of the various chemical components of a spherical system to electron scattering length densities. This is done by computing the weighted average of electron density as a function of position or

(3.24)
$$\rho(r) = r_e \sum_{m=A,B,S} n_m(r)$$

where r_e is the electron scattering length, and $n_m(r)$ is the local electron density per component. The subscripts correspond to those defined in Section 3.2 for the various polymer blocks and solvent. The specific expression for average electron density is related to the volume fraction of a component by

(3.25)
$$n_m(r) = \phi_m(r) \cdot \frac{N_{av}\rho_m e_m}{Mw}$$

where N_{av} is Avagadro's number, ρ_m , is the component density, e_m , is the number of electrons per component molecule, and Mw is the component molecular weight.

Converting the volume fraction profiles for both polymers to electron scattering length density gives the data shown in Figure 3.14. The electron density profiles in Figure 3.14



Figure 3.14. Background normalized electron scattering length density profiles from 30 $^{\circ}{\rm C}$ to 70 $^{\circ}{\rm C}$ for both long and short midblocks

have been background subtracted using the scattering length density at the reflection boundary, or $\rho_{(r_{max})}$. This prevents erroneous step boundaries in the electron density profile. Only fluctuations in scattering length density give rise to x-ray scattering at the reflecting boundary. These electron scattering length density profiles are similar in shape to the triblock copolymer volume fraction profiles shown in Figure 3.11. The PMMA endblock-rich regions are more prominent in scattering length density profiles as PMMA is significantly more electron dense than the solvent and aggregates to significantly higher local volume fractions than the PnBA midblock.

This system is useful; however, in an actual polymeric system, the scattering intensity would also be modified by interference between the scattered waves of neighboring particles. This scattering function is most heavily dependant on the nearest neighbor distance, but also depends on the actual organization of the scattered particles. The previous use of the unit cell approximation in these SCFT calculations provides a good estimate of the average nearest neighbor distance, but further information as to the aggregate organization is lost. Therefore, calculations of the expected SAXS results are limited to the case of a single triblock aggregate. Only the form factor of this aggregate, without an additional structure factor, is considered in calculating the scattering intensity. Further discussion on this topic can be found in Chapters 4 and 5.

In order to calculate the scattering amplitude, the three-dimensional Fourier transform of the scattering length density must be carried out. The spherical symmetry of SCFT-simulated triblock copolymer micelles allows the conversion of the three dimensional Fourier transform, equation 3.23, to a one dimensional integral:

(3.26)
$$A(q) = \int_{V} \rho(r) \frac{4\pi r^2 \sin(qr)}{qr} dr$$

The SCFT calculations provide discretized volume fraction profiles, which obviously results in discretized scattering length density profiles. It is therefore necessary to approximate the integral in equation 3.26 with the trapezoidal rule

(3.27)
$$A(q) = \sum_{i=0}^{i_{\max}} (r_i - r_{i-1}) \left(\frac{f(r_i) + f(r_{i-1})}{2} \right)$$

where i represents the layer indices used to determine distance from the aggregate center in the SCFT calculations. The function, f, refers to the scattering density profile as a function of position multiplied by the spherical Fourier transform term:

(3.28)
$$f(r_i) = \rho(r_i) \frac{4\pi r_i^2 \sin(qr_i)}{qr_i}$$

An alternative approach to this numerical integration is to approximate the PMMA-rich region as a spherical particle of constant density. In this case, spherical symmetry allows the collapse of the electron scattering length density to a one dimensional step function

(3.29)
$$\rho(r) = \begin{cases} \rho_0 & r \le r_0 \\ 0 & r > r_0 \end{cases}$$

where r_0 is the radius of the particle. Substituting equation 3.29 into equation 3.26 and performing the integration yields equation 3.30.

(3.30)
$$A(q) = \rho_0 \left(\frac{4\pi r_0^3}{3}\right) \left\{ \frac{3}{(qr_0)^3} \left[\sin(qr_0) - qr_0 \cos(qr_0) \right] \right\}$$

Appropriate values for aggregate radii are required in order to approximate the SCFT calculated polymer aggregate. Approximate aggregate radii were chosen to correspond to the electron scattering length density profiles with the steepest slope. These points are highlighted with dots on each curve in Figure 3.14.

Figure 3.15 directly compares the r_0 values for both long and short midblocks as a function of temperature. It also further elucidates the trends in PMMA aggregate size observed in Figure 3.11. Above 50 °C, both systems behave similarly, though the long midblock aggregates tend to be slightly smaller. Below 50 °C, the two systems display distinct behavior. Aggregate size in the long midblock system remains constant from 30 °C to 50 °C, while aggregate size in the short midblock system begins to increase more rapidly with temperature. The solid sphere density, ρ_0 , required for step function approximation was calculated by averaging electron scattering length density as a function of radius to 90% of the idealized sphere radius. These idealized scattering length densities are plotted as a function of temperature in Figure 3.16. Using either the trapezoidal rule or step function approximations to compute the scattering intensity gives similar results. Figure 3.17 shows a comparison of the intensity curves as a function of scattering vector for both long and short midblock polymers at 30 °C using both of the previously described calculation methods. Below a scattering vector of 0.2nm^{-1} , the trapezoidal rule gives a steeper decay in intensity with increasing scattering vector. It also yields a higher intensity



Figure 3.15. Temperature vs. SCFT calculated PMMA aggregate radius

than the step function approximation. In the short midblock system there is a clear discrepancy in the location of discontinuities in the intensity curve between the trapezoidal rule and step function methods. In contrast, both methods provide almost identical results in the long midblock systems. The reason for this phenomenon can be understood from the scattering length density profiles. The uneven midblock distribution in the short midblock system leads to significant deviation of the scattering length density profile from a step like function. In the long midblock system, the even distribution of endblocks



Figure 3.16. Temperature vs. the average SCFT calculated electron scattering length density [eu]

leads to a more step like profile in scattering length density, even though the magnitude of the density contrast is less than that of the short midblock polymer. In the short midblock system, it is expected that the more even distribution of the PnBA component in the inter-aggregate space with increasing temperature will improve agreement between the two calculation methods.

The variation in the maximum scattering intensity is expected to decrease with temperature and to eventually vanish once the homogenous solution state is reached and



Figure 3.17. Comparison of simulated scattering data calculated using SCFT volume fraction profiles and a step function approximation for short (\mathbf{a}) and long (\mathbf{b}) midblock polymers

variations in local density become to small to be observed in the SAXS regime. Calculations of the scattering intensity for q = 0.05 as a function of temperature for both polymers with the trapezoidal rule is shown in Figure 3.18a. The results obtained using the step function approximation are shown in Figure 3.18b. With either method the long and short midblock systems behave similarly. The long midblock system gives slightly lower intensities than the short midblock system, except at 70 °C using the trapezoidal rule method. In both cases an intensity drop of approximately one order of magnitude is observed.

3.5. Self-consistent Field Theory Summary

Self-consistent field theory can be a very useful tool in modeling complex polymeric systems. Appropriate choice of input parameters allows comparison to experimental results and provides insight into the phenomena at work. This Chapter provided a basic background to SCFT calculations as well as a detailed description of the specific SCFT formulation used to model an acrylic triblock copolymer system. The validity of the unit cell approximation with regards to SCFT calculations of the networks of triblock copolymer aggregates was explored. The unit cell approximation was found to agree closely with full three-dimensional calculations, although some structural information is lost.

Simulation of acrylic triblock copolymer micelles with different midblock molecular weights yielded several interesting results. First, volume fraction profiles for equilibrium states were determined over a range of temperatures. These profiles show that the PMMA endblock aggregates in acrylic triblock-butanol systems are swollen with solvent even near room temperature. Volume fraction profiles also make clear that the degree



Figure 3.18. Comparison of temperature vs. maximum scattering intensity calculated using a trapazoidal rule approxiamtion of SCFT calculated volume fraction profiles or a step function approximation for short (\mathbf{a}) and long (\mathbf{b}) midblock polymers

of midblock stretching varies significantly between the two experimental systems. This gives rise to significant differences in bridging fraction between long and short midblock systems which, in turn, directly impacts mechanical properties. Additionally, it was also possible to estimate the osmotic pressure of each system, which showed unusual temperature dependence and suggests that the magnitude of osmotic pressure changes are greater in the short midblock system. Lastly, volume fraction profiles were converted to electron scattering length density and used calculate small angle x-ray scattering intensity. Interestingly, the long midblock system was found to provide less electron scattering density contrast, and thus a lower maximum scattering intensity, but could be more closely approximated as a spherical particle of uniform density than the short midblock system. These results and a detailed look at volume fraction profiles as a function of temperature proved valuable in interpreting experimental results in Chapter 5.

CHAPTER 4

Mechanical, Structural, and Osmotic Characterization of Acrylick Triblock Copolymers

A variety of experimental methods were used to probe the mechanical, structural and osmotic properties of acrylic triblock copolymer gels. Rheometric measurements of both long and short midblock gels provided information on the temperature dependence of gel mechanical properties. Swelling measurements provided initial insights into the osmotic properties of the systems and established a useful framework for interpreting small angle x-ray scattering and osmometry results. Small angle x-ray scattering provided direct structural measurements of gels as a function of temperature and also of equilibrium and as cast gels. Vapor pressure osmometry measured the osmotic properties of the triblock gels as a function of temperature. The details of the methods employed are described in the following sections.

4.1. Materials

All gels were prepared by dissolving poly(b-methyl methacrylate-b-n-butyl acrylateb-methyl methacrylate) triblock copolymers in 1-butanol at temperatures between 80 °C and 90 °C. The chemical structures of poly(methyl methacrylate), abbreviated as PMMA, and poly(n-butyl acrylate), abbreviated as PnBA, are shown in Figure 4.1. Both polymers used to make gels were of similar architecture, that is, both are ABA symmetric triblock copolymers. Their different midblock molecular weights are summarized in Table 4.1.



Figure 4.1. The chemical structures of PMMA (a) and PnBA (b)

Polymer	PMMA N _k per block	PnBA N _k per block
Short midblock	231	1225
Long midblock	212	328
Solvent	1-Butanol	

Table 4.1. Polymer end- and midblock degree of polymerization and PMMA weight fraction

Here after, the polymer with N = 116 for the PnBA block will be referred to as the long midblock polymer, while the polymer with N = 31 will be referred to as the short midblock polymer. Both polymers were provided by Kuraray Co. and used as received.

Polydispersity was measured via size exclusion chromatography using polystyrene standards. The polydispersity index of long midblock polymer was 1.39, while that of the short midblock polymer was 1.18 [29]. Control solutions were prepared from the 77,000 molecular weight PnBA homopolymer in 1-butanol. PnBA homopolymer was purchased from Polymer Source Inc., Montreal, Canada. Gels were stirred and maintained at

elevated temperatures overnight in sealed containers to ensure even mixing of copolymer and solvent prior to experiments. Butanol was chosen as a solvent for its high vapor pressure, which is advantageous for vapor pressure osmometry, while still acting as a sufficient solvent for PnBA to form homogenous gels at room temperature when cooled from a disordered state.

4.2. Rheometry

4.2.1. Rheometry Experimental Method

All rheometry was done with a Paar Physica MCR-300 rheometer using a double-gap cuvette fixture (DG26.7) with a Peltier temperature control stage. Samples were heated above 70 °C to ensure liquid-like behavior and then poured into a warmed fixture. Sample solutions were added quickly to prevent solidification until properly loaded. Oscillatory isothermal angular frequency sweeps over a range of 0.1 to 100 s^{-1} were obtained every 5 °C from 25 °C to 70 °C with 5 minutes allowed between measurements for thermal equilibration of the sample. Stress was controlled such that strains remained in the linear viscoelastic regime. For constant rotation temperature ramps, heating and cooling rates of 1 °C per minute, with a constant strain rate of 50 s⁻¹, were used to obtain the viscosity of the samples from 70 °C to 95 °C. Viscosity data for pure butanol was also obtained with similar constant rotation experiments from 25 °C to 90 °C.

4.2.2. Rheometry Analysis Method

The concept known as time-temperature superposition (TTS) was used to analyze the data for gels in the viscoelastic regime. Time-temperature superposition states that all
relaxation times have the same temperature dependence; thus, time and temperature are interchangeable. Put another way, the temperature dependant properties, such as storage and loss modulus, will have the same value for long times at low temperatures or short times at high temperatures. For temperature changes where this holds true, data can be shifted along either temperature or time axis via shift factors based on a reference temperature. If plotted in this manner, the data will collapse to form a master curve. TTS allows you to define relaxation times for any valid temperature using the equation below

(4.1)
$$\tau = \frac{\eta_0 a_T}{G_0}$$

where τ is the relaxation time, a_T is the shift factor, η_0 is the zero shear viscosity, and G_0 is the plateau modulus. The zero shear viscosity is determined from low frequency behavior where the system behaves similarly to a liquid, while the plateau modulus is determined from high frequency behavior where the system behaves more like an elastic solid. The zero shear viscosity, η_0 , is defined as

(4.2)
$$\eta_0 = \lim_{\omega \to 0} \frac{G''(\omega)}{\omega}$$

where G'' is the loss modulus, and ω is frequency.

4.3. Swelling Measurements

Samples for swelling experiments were prepared by casting solutions into plastic washers (2.5 mm thick, 10.4 mm diameter) sandwiched between glass slides. Once the gels had cooled they were removed from the washers and immersed in pure 1-butanol inside sealed containers. Room temperature samples were stored in a lab hood at approximately 25 °C, while low temperature samples were stored in a laboratory refrigerator with a nominal temperature of 0 °C. At various intervals the gels were removed from solvent, lightly dried on both sides with filter paper, weighed, and immediately returned to their solvent baths. The initial volume fraction, final weight, and initial weight were used to determine the final volume fraction of gel. After times greater than 20 days, the swelling ratios of the gels became constant indicating that equilibrium had been reached.

4.4. Small Angle X-ray Scattering

4.4.1. SAXS Experimental Methods

Small angle X-ray scattering (SAXS) experiments were preformed at Argonne National Labs' Advanced Photon Source on the DuPont-Northwestern-Dow Collaborative Access Team beam line (DND-CAT, Sector 5) in collaboration with Steven Weigand, Michelle Seitz and Andy Schoch. Samples for room temperature studies were prepared by casting heated solutions into polyethylene washers (1.6 mm thick, 7.6 mm in diameter) and sealed with a 3 μ m kapton layer on either side. Some gels were allowed to swell in pure butanol before being sealed with kapton. Sealed unequilibrated samples were heated to melting and allowed to cool within two hours of measurements to eliminate stress and edging effects. Samples for temperature ramp experiments were loaded into 1.5 mm and 2 mm diameter boron-rich capillary tubes. Heating and cooling of the samples was controlled via a Linkham THMS 600 hot stage. Temperature was monitored with thermocouples inside a copper block in direct contact with boron-rich capillaries. Samples were heated and cooled at 2 to 4 °C per minute. Isotropic scattering patterns were collected on a

2D detector over a scattering vector range of $0.1 - 1 \text{ nm}^{-1}$ and then integrated over all azimuths to generate one-dimensional data.

4.4.2. SAXS Analysis Methods

Analysis of SAXS patterns began with azimuthal integration of the 2D SAXS patterns. Since all samples were isotropic amorphous gels, the 2D scattering patterns appeared as diffuse, circularly symmetric rings allowing for azimuthal integration. The integrated intensity was normalized by azimuthal angular range, collection time, and incident beam transmitted intensity measured via a photo diode on the detector beam stop. Before fitting, background subtraction was performed. The background used for the temperatureramp samples was the highest temperature data for the same sample, because at high temperatures samples were homogeneous solutions. The result is a background subtraction that removes scattering due to the beam stop, capillary tube, and low scattering vector background associated with solvated polymer. In the case of room temperature samples, background subtraction was less accurate. The scattering data from blank samples consisting of an empty kapton, windowed cell were used for background subtraction.

The background subtracted data was fitted using a Percus-Yevick amorphous hard sphere model. The basis of this model was first developed by Jerome Percus and George Yevick, who developed a statistical mechanics method for approximating the classical many body system using the Fourier components of particle density as fundamental coordinates [90]. The correlation functions they developed were applied to the analysis of small angle scattering techniques, which are sensitive to variations in scatter density [91]. This model method was first applied to a block copolymer system by David Kinning and Edwin Thomas in 1984 [92]. The Shull research group has used this method on several occasions to interpret SAXS of acrylic triblock copolymer gels [29, 30]. For full derivations of the structure and form factors used see publications by Kinning and Thomas as well as Mschenko et al. [92] [93] In order to provide background for later discussions, the model used for data fitting is derived in the following paragraphs.

The derivation begins with the standard general expression for scattering intensity as a function of scattering vector

$$(4.3) I(q) = KNP(q)S(q)$$

where q is the scattering vector, I is the scattering intensity, N is the total number of scatterers, K is a contrast factor based on scattering mechanism, P(q) is the form factor describing the shape of the scatters, and S(q) is the structure factor describing the organization of the scatterers. In this case K is the difference in electron density between PMMA aggregates and the surrounding PnBA-solvent mixture. To determine the form factor, one assumes that the scatterers will be spherical PMMA aggregates with some polydispersity and a less dense coronal region at the block junction between the PMMA and PnBA. The form factor becomes a function of the scattering vector, average aggregate radius, and an interface width describing the error function type smearing of the aggregate surface

(4.4)
$$\langle P(q,r_0,\sigma)\rangle = \int_0^\infty \frac{1}{\sigma \left(2\pi\right)^{1/2}} \exp\left(-\frac{\left(r-r_0\right)^2}{2\sigma^2}\right) P(q,r) dr$$

where r_o is the average aggregate size, r is the radius from the aggregate core, and P(q, r)is the standard spherical form factor. Sigma, σ , is related to the interfacial width, t, by

(4.5)
$$t = (2\pi)^{1/2} \sigma$$

The standard spherical form factor is

(4.6)
$$P(q,r) = \left(\frac{4\pi r_0^3}{3}\right)^2 \left\{\frac{3}{(qr_0)^3} \left[\sin\left(qr_0\right) - qr_0\cos\left(qr_0\right)\right]\right\}^2$$

The structure factor, S(q), describes the spatial distribution of the scattering aggregates. The structure factor is chosen based on a liquid like distribution of amorphous hard spheres. In this system, each aggregate is assumed to be the center of a fictitious hard sphere. The distribution of aggregates is described by the size and volume fraction of these hard spheres. This form factor is derived from the correlation function developed by Percus and Yevick and is described by the following system of equations

(4.7)
$$S(q, R_{hs}, \eta) = \left[1 + 24\eta \frac{G(A)}{A}\right]^{-1}$$

(4.9)

$$G(A) = \frac{\alpha}{A^2} (\sin A - A \cos A) + \frac{\beta}{A^3} [2A \sin A + (2 - A^2) \cos A - 2] + \frac{\gamma}{A^5} \{-A^4 \cos A + 4 [(3A^2 - 6) \cos A + (A^3 - 6A) \sin A + 6]\}$$

(4.10)
$$\alpha = \frac{(1+2\eta)^2}{(1-\eta)^4}$$

(4.11)
$$\beta = -6\eta \frac{\left(1 + \frac{\eta}{2}\right)^2}{\left(1 - \eta\right)^4}$$

(4.12)
$$\gamma = \frac{1}{2}\eta \frac{(1+2\eta)^2}{(1-\eta)^4}$$

where η is the volume fraction of hard spheres and R_{hs} is the fictitious hard sphere radius.

The fitting program used to analyze the SAXS results was written by Michelle Seitz with some minor modifications. The program uses the Levenberg-Marquardt algorithm to fit the data by minimizing the χ^2 of the theoretical intensity

(4.13)
$$I(q) = KN \langle P(q, r_0, \sigma) \rangle S(q, R_{hs}, \eta)$$

and the normalized intensity data. Absolute intensity calibrations were not done during measurements as they were prohibitively time consuming given the constraints of the allocated beam time and number of samples in addition to other experimental complications. As a result information relating to K and N is lost in a single normalization constant. This leaves four fit parameters: r_0 , σ , η , and R_{hs} . Figure 4.2 is a schematic showing the relationship between the various fit values and the actual physical structure of the gel. Figure 4.3 shows an example of scattering data and a fit based on the Percus-Yevick type model. The data shown is a room temperature sample of 0.15 volume fraction long midblock gel. This plot is labeled to show which portions if the I(q) curve are influenced most heavily by the various model parameters. The location of the main scattering peak



Figure 4.2. Illustration of the physical meaning of Percus-Yevic fitting parameters

is most strongly influenced by the hard sphere radius, R_{hs} , while the width of this peak is largely dependant on the hard sphere volume fraction, η . The shoulder location and slope of the curve from q = 0.3 to 0.5 nm^{-1} depends on both the hard sphere radius and the scattering core radius. The slope, shape, and location of secondary shoulders in the tail region, q > 0.5, depend on the aggregate core radius, r_0 and σ .

It was possible to accurately fit both R_{hs} and η from the main scattering peak. However, obtaining highly accurate fits of the tail region, q > 0.3, was not possible. The scattering intensity in the tail and shoulder regions was low, resulting in large effects from



Figure 4.3. Representative SAXS scattering data and data fit

background subtraction. For a given sample it was often possible to obtain equally good fits for a range of r_0 and σ , but a single set of R_{hs} and η . Essentially, the tail regions did not have sufficiently defined features to fit well. The specific results of SAXS scattering data will be discussed in more depth in the results and discussion section.

4.5. Vapor Pressure Osmometry

4.5.1. Vapor Pressure Osmometry Background

There are a several ways to measure the osmotic pressure of solutions. Osmometry can be preformed using membrane based methods or utilizing the relatedness of the solutions' colligative properties. Several varieties of osmometer are commercially available. The majority of these systems are for medical diagnosis and are biased on freezing point depression or boiling point elevation of aqueous solutions. Vapor pressure osmometry is appropriate for this experiment because the instrument is more versatile and can be used effectively with a variety of organic solvents over a large temperature range.

Most vapor pressure osmometers consist of a pair of thermistors suspended above a solvent bath in a temperature controlled chamber. Droplets of various solutions can be introduced onto the thermistors via preloaded syringes. These instruments monitor temperature changes in the sample droplet driven by the difference in vapor pressure between the sample droplet and the surrounding environment. Vapor pressure is directly related to the amount and type of solute in solution and thus the osmotic pressure.

Before a sample droplet is introduced, the osmometer chamber is allowed to saturate with solvent vapor at the solvent's equilibrium partial pressure for the specified temperature. A droplet containing solutes will have a lower vapor pressure than that of pure solvent. To achieve short-term pseudo-equilibrium, the temperature of the droplet must rise until the chemical potential and vapor pressure of the sample and surrounding environment are equivalent.

This occurs through conductive heat transfer and condensation of the solvent vapor on the droplet. The temperature change of the sample is monitored against a reference droplet of pure solvent via the thermistor probe as shown in Figure 4.4. The vapor pressure with its temperature dependence can be directly related to osmotic pressure. Below is a more rigorous exploration of the relationships between vapor pressure, temperature and osmotic pressure.



Figure 4.4. Schematic illustration of a vapor pressure osmometer

The colligative properties of solutions arise from deviations from the chemical potential of pure solvent. The chemical potential of a solution, $\mu_0(T, P)$, is defined as

(4.14)
$$\mu_0(T,P) = \mu_0^0(T,P) + RT_0 \ln a_0$$

where μ_0^0 is the chemical potential of the pure solvent, R is the gas constant, T_0 is the ambient temperature in Kelvin, and a_0 is the activity of the solution. Rearranging we arrive at Equation 4.15

(4.15)
$$\Delta \mu_0 = \mu_0(T, P) - \mu_0^0(T, P) = RT \ln a_0$$

The osmotic pressure, Π , is defined as the chemical potential difference between two solutions over the molar volume of the solvent or

(4.16)
$$\Pi = \frac{-\Delta\mu_0}{V_0^0}$$

where V_0^0 is the molar volume of the pure solvent. Substituting equation 4.14 into equation 4.15 gives equation 4.16

(4.17)
$$\Pi = \frac{-RT_0}{V_0^0} \ln a_0$$

Additionally, the activity of a solution can be expressed as a ratio of partial pressures, where P(T) is the vapor the solution and $P_0(T)$ is the vapor pressure of pure solvent at a given temperature

(4.18)
$$a_0 = \frac{P(T)}{P_0(T)}$$

Substituting into equation 4.16 gives the relationship shown below

(4.19)
$$\Pi = \frac{-RT_0}{V_0^0} \ln\left(\frac{P(T)}{P_0(T)}\right) = \frac{-RT}{V_0^0} \left[\ln\left(P(T)\right) - \ln\left(P_0(T)\right)\right]$$

The temperature dependence of Π can be expanded around $T = T_0$ using a standard Taylor series

$$P_0(T) = P_0(T_0) + \left(\frac{dP_0(T)}{dT}\right)_{T=T_0} (T_f - T_0) + \frac{1}{2} \left(\frac{d^2 P_0(T)}{dT^2}\right)_{T=T_0} (T_f - T_0)^2 + \dots$$

where T_0 is the temperature of the pure solvent at equilibrium, and T_f is the final temperature perature of the solution droplet. The expansion is possible because the final temperature of the droplet and the initial temperature are close to one another. The second order and higher terms can be neglected as these terms will be very small. For example, $(T_f - T_0)^z$ is very small when z is two or greater. Thus, only the first derivative of the solvent vapor pressure with respect to temperature needs to be found [94]. The Clausius-Clayperon relation can be used to determine the required derivative

(4.21)
$$\left(\frac{dP_0(T)}{dT}\right)_{T=T_0} = \left(\frac{\Delta H}{RT_o^2}\right)P_0\left(T_0\right)$$

where R is the gas constant and ΔH is the enthalpy of vaporization of the solvent. Substituting equations 4.19 and 4.20 into equation 4.18 gives the expression below

(4.22)
$$\Pi = \frac{-RT_0}{V_0^0} \ln\left(\frac{P(T_f)}{P_0(T_0) + \left(\frac{\Delta H}{RT_o^2}\right)P_0(T_0)(T_f - T_0)}\right)$$

The activity of the system approximated at one. This assumption is valid if solute concentration is sufficiently small. Under these circumstances, equation 4.21 can be greatly simplified to give equation 4.22.

(4.23)
$$\Pi = \frac{\Delta H}{V_0^0} \frac{(T_f - T_0)}{T_0}$$

It can now be noted that the osmotic pressure can be approximated from physical constants of the solvent and the temperature difference of the solution droplet [95]. At 75 °C the heat of vaporization of butanol is 47.43kJ·mol⁻¹ and the molar volume is 91.94 $cm^3 \cdot mol^{-1}$. Using these values and estimating the osmotic pressure of a 0.15 volume fraction solution of Poly(tert-butyl acrylate) homopolymer as 7720 Pa (based on deGennes scaling theory), the temperature change observed in a vapor pressure osmometer is only 0.0052 degrees Kelvin. Similar expressions can be derived using a number of physical quantities based on the specific measurement apparatus and a mean field theory approach to osmotic pressure. Details of this approach, as well discussions on the theory and design of vapor pressure osmometers can be found in the text book by Kenji Kamide and Toshiaki Dobashi and papers by the same authors and others [94, 96–100].

4.5.2. Vapor Pressure Osmometry Experimental Method

Vapor pressure osmometry measurements were performed with a Knauer K-7000 vapor pressure osmometer. A schematic of the vapor pressure osmometer is shown in Figure 4.4. Samples of varying concentration were heated to above 70 °C and loaded into the osmometer syringes. The osmometer was then allowed to equilibrate at the desired temperature for at least 30 minutes prior to taking a measurement. The osmometer has six sample ports, two of which were used for triblock samples of varying concentration, two for 77,000 molecular weight PnBA control solutions, and two for pure solvent. By comparing the osmometer signal of triblock samples and homopolymer for a given volume fraction of triblock copolymer at a given temperature. For both long and short midblock polymers this technique could only be applied to temperature ranges between 65 °C and 95 °C. At low temperature the sample viscosity was to high to be properly transferred to the

osmometer thermistors. As the boiling point of the solvent is approached, temperatures above 95 °C, measurements became unreliable.

A minimum of five measurements was taken for each sample. Additionally, measurements were not recorded until six minutes after droplets were exchanged on the sample thermistor. This allowed the sample enough time to reach pseudo-equilibrium as droplet replacement initially causes a large fluctuation in osmometer signal. The osmometer cap was also over heated by 2 °C to compensate for heat loss from the exposed portions of the sample syringes and syringe ports.

4.5.3. Vapor Pressure Osmometry Calibration Method

As stated in the previous section the osmometer was calibrated using solutions of 77k molecular weight PnBA homopolymer. Calibration measurements were carried out simul-taneously with actual measurements. Plotting temperature versus signal for the various solutions of PnBA used for osmometer calibration gives Figure 4.5. Osmometer signal should be directly proportional to osmotic pressure as shown by equation 4.23

(4.24)
$$Signal = A\left(\frac{-RT}{V_o^o}\right)\left(\ln\left(1-\phi\right) + \left(1-\frac{1}{n}\right)\phi + \chi\phi^2\right)$$

where R is the gas constant, T is temperature, V_0^0 is the solvent molar volume, n is the polymer degree of polymerization, χ is the polymer solvent interaction parameter, and ϕ is the polymer volume fraction. In this case the right hand side of the equation is the Flory-Huggins theory expression for the osmotic pressure of a polymer solution. The variable, A, is an instrument-imposed scaling factor that converts the osmotic pressure to the measured osmometer signal. As both equation 4.24 and Figure 4.5 demonstrate,



Figure 4.5. Temperature vs. osmometer signal for PnBA homopolymer callibration data

polymer signal is essentially linearly proportional to temperature, assuming that χ is not temperature-dependant. This assumption is valid for PnBA in butanol over the temperature range in which osmometry was performed. Therefore, it was possible to fit linear trendlines to the data in Figure 4.5. Plotting these trend lines as a function of volume fraction for separate temperatures gives the data points in Figure 4.6. Fitting these points using, A, the osmotic pressure to signal conversion constant, as the only fit parameter, gives the solid trend lines in Figure 4.6. Using these curves it is possible to convert SAXS signal to an equivalent volume fraction of PnBA homopolymer.



Figure 4.6. Osmometer signal to PnBA homopolymer volume fraction calibration curves

CHAPTER 5

Experimental Results and Discussion

This chapter will discuss the results of experiments used to characterize the structure of acrylic triblock copolymer gels as well as their mechanical and osmotic properties. A background discussion of the detailed connections between the mechanical and osmotic properties of gel systems is available in Chapter 2 of this text.

Previous work on acrylic triblock systems proposed a basic model for the structural evolution of these physical networks as a function of temperature, as is outlined schematically in Figure 2.1. Above a critical temperature, the solvent polymer solution behaves as a viscous liquid. Below this critical temperature range, a network of endblock aggregates connected by polymer midblocks results in visco-elastic mechanical behavior. In this state, endblock aggregates can still rearrange. This is believed to be the main stress-relaxation mechanism [1, 29].

If cooling continues, the endblock aggregates become kinetically trapped resulting in a detectable glass transition [1]. These endblock aggregates will under go some physical ageing over long periods, but structural evolution is localized in the endblock aggregates [1, 30]. Once endblocks have become kinetically trapped, these gels have highly elastic properties in which stress relaxation occurs through network failure, though the detailed mechanisms of gel fracture are unknown and continue to be a subject of study in the Shull research group. The experiments presented here addressed two goals: first, to more clearly identify the temperature range at which physical network breakdown occurs and second, to further elucidate the processes that result in a rapid, thermo-reversible transition from a viscoelastic solid to a viscous liquid. Rheometry and small angle x-ray scattering provided initial information regarding the critical transition temperature range and mechanical properties of the triblock copolymers. Combined, rheometry and SAXS indicate that network breakdown occurs between 70 °C and 85 °C. These two techniques also show that the swelling of endblock aggregates as temperature increases precedes the drastic change in mechanical properties by at least 15 °C. Gel swelling measurements provided insight into the osmotic forces underlying the mechanical properties. Osmotic pressure measurements narrowed the temperature regime where complete network breakdown occurs to between 75 °C and 80 °C. However, a clear osmotic signal of network failure was only observable in the short midblock system at one of the measured volume fractions. This phenomenon appears anomalous; however, it can be understood by combining the results of the experimental techniques with the predictions made by SCFT.

5.1. Temperature Dependant Properties of Acrylic Triblock Copolymer Gels

Rheometry provided the initial characterization of the temperature-dependant of mechanical properties of acrylic triblock copolymer gels. Frequency sweep studies over a range of temperatures showed that the transition from liquid to visco-elastic behavior was dependant on time and temperature. Time-temperature superposition was possible for both long and short midblock systems between 40 °C and 70 °C for volume fractions of 0.1 to 0.2. This suggests a single relaxation mechanism in this regime, because multiple



Figure 5.1. Representative storage and loss modulus modulus master curves for acylic triblock copolymer gels generated by time-temperature superposition

relaxation mechanisms are unlikely to share the same temperature dependence. Figure 5.1 shows two examples of the resulting master curves. Some deviation from ideal be-

havior, characterized by an upturn in loss modulus, is observed at long relaxation time in the long midblock example indicating that multiple relaxation mechanisms may be at work. The short midblock system exhibits imperfect time-temperature super position at temperatures above 50 °C. This may be due to solvent evaporation despite the use of a sample enclosure.

Despite these deviations at long relaxation times, TTS remains valid for those intermediate relaxation times where the transition from viscous liquid to visco-elastic solid occurs. Thus, it was possible to determine values for viscosity from plateau modulus and shift factors. When combined with rotational rheology, viscosity was determined for a large temperature range as seen in Figure 5.2. A knee in the temperature versus viscosity curve for both polymers is observed between $68 \,^{\circ}\text{C} - 80 \,^{\circ}\text{C}$. At temperatures below $\sim 68 \,^{\circ}\text{C}$, the polymer viscosity increases rapidly with decreasing temperature. Above $\sim 68 \,^{\circ}\text{C}$, the viscosity of the polymer solution changes behavior, becoming similar to that of pure solvent by $80 \,^{\circ}\text{C}$. Above $80 \,^{\circ}\text{C}$, viscosity is only weakly temperature dependant. The location of the viscosity behavior transition appears to be independent of midblock length and only weakly dependant on volume fraction between $\phi = 0.1$ and 0.2. The actual magnitude of the viscosity does depend on midblock length and volume fraction.

During the process of calculating the zero shear viscosities from TTS master curves, it was necessary to calculate relaxation times for each sample as a function of temperature. In the temperature range where TTS is possible, all samples exhibit a similar power law dependence on temperature. This suggests that the relaxation times can be collapsed into a single master curve using a temperature shift. To do this, a suitable reference



Figure 5.2. Temperature vs. viscosity curves for several acrylic triblock copolymers

temperature must be selected. This temperature is determined by selecting the temperature at which the relaxation time is 0.1 seconds. At this relaxation time acrylic triblock solutions exhibit distinctly gel like mechanical properties thus, the reference temperature is designated T_{gel} . Figure 5.3 shows the master curve which results from the temperature shift of relaxation times based on T_{gel} . The collapse of relaxation times to a master curve confirms that the scaling behavior is similar for both long and short midblock polymers for volume fractions from 0.1 to 0.2. The plateau moduli and gel temperatures for each sample shown in Figure 5.3 are tabulated in Table 5.1. These rheometry results are in



Figure 5.3. Master viscosity curve obtained from gel temperature normalized data

agreement with results obtained by Seitz et al. In their 2006 paper with identical polymers in 2-ethyl hexanol, they concluded that below the critical micelle temperature, but above the endblock aggregate glass transition temperature, the mechanical properties of acrylic triblock gels are controlled by endblock interactions. Physical network breakdown must occur in the 68 °C to 80 °C temperature range, but cannot be further defined with rheometry.

Mechanical properties measurements provide secondary information about the gel's structural state. However, it is possible to probe polymer structure directly via small angle x-ray scattering (SAXS). Both room temperature and temperature-controlled SAXS

Polymer	ф	G₀ [Pa]	T _{gel} [°C]	
Short midblock	0.10	603	54	
Short midblock	0.15	3150	56	
Short midblock	0.20	10000	58	
Long midblock	0.10	1600	55	
Long midblock	0.15	1890	59	
Long midblock	0.20	4980	58	

Table 5.1. Rheometrically determined plateau moduli and gelation temperatures

measurements for several concentrations of long and short midblock polymers in butanol were carried out at Argonne National Labs Advanced Photon Source. The resulting SAXS patterns were azimuthally integrated, and were fit using a Percus-Yevick hard sphere model as described in Chapter 4. Scattering is attributed to electron density contrast due to the formation of dense aggregates of the PMMA endblocks while the PnBA midblocks remain in solution [29, 43].

Temperature ramp SAXS experiments give insight into the structural evolution of the triblock copolymer gels. The scattering intensity of the main peak in the SAXS data decreases as a function of increasing temperature. Temperature versus the maximum scattering intensity for volume fractions of 0.05, 0.01, 0.15 for the short midblock polymer and 0.10 and 0.15 for the long midblock polymer is shown as a semi-logarithmic plot in Figure 5.4. A rapid decrease in the intensity of the scattering peak, is observed beginning



Figure 5.4. Temperature vs. SAXS maximum scattering intensity

by 55 °C for both long and short midblock polymers. By 80 °C, no further decrease in scattering is observed as scattering features are indistinguishable from the background. This transition is broader than that seen for identical acrylic triblock copolymers in 2-ethyl hexanol by Seitz et al.

The abrupt drop in scattering intensity suggests a structural transition. As discussed in Chapters 3 and 4, the magnitude of scattering intensity from a spherical particle is largely dependant on electron density contrast, though changes in the particle size also play a role. The observed drop in scattering intensity is attributed to a decrease in the density of PMMA aggregates as the PMMA-solvent interaction becomes more favorable at elevated temperatures [29]. The loss of electron density as a result of aggregate swelling explains the broadening seen in the maximum intensity drop off of butanol-based gels versus 2-ethyl hexanol-based gels. 2-ethyl hexanol is a marginally better solvent for PMMA than butanol at room temperature. Thus, it is expected that gels prepared using the former solvent will provide reduced density contrast and reach a solution state more rapidly than gels prepared with butanol.

When compared to mechanical properties as measured by rheometry, structural evolution of triblock copolymer gels begins well before the transition from visco-elastic behavior to liquid-like behavior. This correlation explains the relatively steep temperature dependence of viscosity prior to the transition to solvent-like mechanical properties. As stated earlier, the drop in scattering intensity is attributed to swelling of the endblock aggregates with solvent. Swelling of endblock aggregates is associated with increased endblock mobility, which results in a decrease in the zero shear viscosity.

Rheometry also indicates that the complete break down of endblock aggregates appears to occur between 68 °C and 80 °C. At these temperatures, maximum scattering intensity reachs a lower bound. Unfortunately, it is not possible to correlate the lower plateau in maximum scattering intensity directly to the dissolution of endblock aggregates. This is because detectable scattering peaks are only barely above background. It is not possible to determine if the loss of a scattering peak is due to instrument limitations or an actual loss of polymer endblock aggregates. A careful SAXS study using absolute intensity measurements and comparison to parallel techniques, such as small angle neutron scattering, could resolve this question. All that can be said, is that electron density contrast due to PMMA aggregation is lost between 65 °C and 80 °C for the long and short



Figure 5.5. Comparison of SCFT prediction and experimental data for temperature vs. maximum scattering intensity

midblock polymers at the concentrations shown in Figure 5.4. This agrees with rheometric data, but does not further narrow the temperature range in which the network failure must occur.

The maximum scattering intensity was predicted from SCFT-calculated volume fraction profiles in Chapter 4. A direct comparison of the SCFT-predicted maximum scattering intensity and actual scattering data for a short midblock gel ($\phi = 0.15$) is shown in Figure 5.5. SAXS data is not normalized by absolute intensity and the SCFT prediction does not account for multiple particles. These differences can be eliminated using a single proportionality factor to arbitrarily shift the SCFT predictions along the intensity axis. This results in good agreement between SCFT predictions and the SAXS data between $55 \,^{\circ}$ C and $65 \,^{\circ}$ C. Below $55 \,^{\circ}$ C, SCFT deviates significantly from the SAXS data. It is likely that this is caused by kinetic trapping of endblocks below $55 \,^{\circ}$ C in the experimental system, which is not accounted for by equilibrium SCFT calculations. Indeed, the gel temperature for a volume fraction of 0.15 for the short midblock, as determined from relaxation times, is $56 \,^{\circ}$ C. It may be possible to simulate this behavior with SCFT by setting the system size for calculations below $55 \,^{\circ}$ C equal to the equilibrium system size at $55 \,^{\circ}$ C. The inaccuracy of the SCFT predictions above $65 \,^{\circ}$ C are likely due to inadequacies in the models used for the Flory interaction parameters, unreliability of SAXS data at low electron contrast, and kinetic limitations of the experimental polymer in reaching equilibrium at the experimental heating rate. To summarize, between $50 \,^{\circ}$ C and $65 \,^{\circ}$ C the SCFT-calculated maximum scattering intensity appears to closely mimic experimental behavior. This confirms that endblock aggregate swelling, which manifests as changes in the diameter and electron density of the endblock aggregates, is responsible for the decrease in scattering intensity.

It is experimentally difficult to determine the actual size of a PMMA endblock aggregate with SAXS. An alternative measure of the size of an endblock aggregate and its density is aggregation number or, the number of endblocks per aggregate. This quantity is particularly useful as it is indicative of endblock mobility and the rearrangement of gel structure, which may or may not be occurring as the density and radius of endblock aggregates changes with temperature. Endblock aggregation number can also be extracted from the height and width of the primary scattering peak seen on the SAXS curve. This feature is largely derived from the interference of waves scattered from multiple particles which is accounted for by the structure factor. Features such as the radius of PMMA-rich domains are fit using the particle form factory and are difficult to determine as their contribution to the SAXS scattering pattern is overshadowed by the structure factor scattering term. A more detailed discussion of small angle x-ray scattering can be found in Section 4.4. Aggregation number is calculated from the volume per micelle according to the equation 3.21, from Chapter 3.

(5.1)
$$M = \left(\frac{2\rho\phi_{poly}N_{av}}{Mw}\right)V_m$$

where ρ is the polymer density, ϕ_{poly} is the over all volume fraction of polymer, Mw is the molecular weight of the polymer, and V_m is the volume per micelle [29]. The volume per micelle can be calculated from SAXS data by

(5.2)
$$V_m = \frac{4\pi R_{hs}^3}{3\eta}$$

where R_{hs} and η are the hard sphere radius and hard sphere volume fractions, respectively. These terms are extracted from SAXS data via the Percus-Yevick model as described in Chapter 4. For SCFT predictions, the volume per micelle is taken simply as twice the equilibrium system size cubed or

$$(5.3) V_m = (2r_{\max})^3$$

Temperature versus aggregation number for both SAXS experiments and SCFT calculations for the short midblock polymer ($\phi = 0.15$) are shown in Figure 5.6. Below 50 °C, SCFT data predicts a much larger aggregation number than is measured experimentally. Again, this is because SCFT calculations do not capture the kinetic trapping of endblock



Figure 5.6. Comparison of SCFT prediction and experimental data for temperature vs. aggregation number

aggregates. Above 50 °C, calculated and experimental aggregation numbers are of similar magnitude, although SCFT-calculated aggregation numbers decrease more rapidly as a function of temperature than experimental aggregation numbers. A possible explanation for this trend is that the kinetics of rearrangement of the polymer structure during the gel to liquid transition may have been to slow to reach equilibrium configurations during the temperature ramp experiments. This may also explain the deviation between the calculated and experimental trends in maximum scattering intensity.

5.2. Volume Fraction Dependant Properties of Acrylic Triblock Copolymer Gels

In order to narrow the temperature range of aggregate dissolution it was necessary to find an alternative to mechanical and scattering methods. Measurements of osmotic properties proved fruitful in this regard. In order to accurately interpret osmotic properties measurements it is helpful to examine the room temperature properties of triblock copolymer gels as a function of volume fraction. Osmotic and mechanical properties of gels are highly dependent on polymer volume fraction as discussed in Chapter 2.

The rheometric data provide an estimate of the elastic contribution to the osmotic pressure. Recalling the relationships discussed in Chapter 2, the osmotic pressure of a neo-hookian gel network at equilibrium should be zero as the swelling pressure and the shear modulus of the material are perfectly balanced. While most of the studied gels are not at equilibrium, the plateau modulus still provides an estimate of the order of the osmotic pressure. The shear modulus of a neo-hookian gel is directly proportional to bridging fraction according to

(5.4)
$$G = A f_b \left(\frac{\phi_p \rho RT}{Mw}\right) \frac{d^2}{R_0^2}$$

where G is the shear modulus, f_b is the bridging fraction, ϕ_p is the polymer volume fraction, ρ is the polymer density, R is the gas constant, and Mw is the polymer molecular weight [**39**]. The variable r_0^2 is the mean squared end-to-end distance in an equilibrium solution. The variable d is the average distance between crosslinks and was taken to be equivalent to D, the nearest neighbor spacing. This formulation does not account for the non-point like physical crosslinking in a bridged aggregate system. The variable A, is



Figure 5.7. Comparison of SCFT prediction and experimental data for polymer volume fraction vs. plateau modulus

a prefactor introduced to compensate for this effect and is chosen such that the SCFTbased modulus agrees with the experimental values at a volume fraction of 0.2. SCFT calculations indicated a strong temperature dependence on bridging fraction for the short midblock system. The plateau moduli from rheometry and SCFT at 40 °C for both long and short midblock gels at volume fractions between 0.075 and 0.2 are plotted in Figure 5.7. This plot shows that the plateau modulus of the short midblock polymer decreases more rapidly as a function of volume fraction than that of the long midblock.

Theoretical SCFT values agree well with experimental modulus. The bridging fractions calculated from SCFT also provide some insight as to why the short midblock system

Polymer	φ	G₀ [Pa]	G _{SCFT} [Pa]	f _b	d [nm]	Α
Short	0.20	9050	9048	0.2933	34.6	0.812
Long	0.20	4990	4994	0.5937	41.1	0.763
Short	0.15	3070	3134	0.1135	37.9	0.812
Long	0.15	2940	3795	0.5437	43.2	0.763
Short	0.10	601	92	0.0035	45.3	0.812
Long	0.10	1570	2212	0.4753	43.2	0.763
Short	0.075	129	-	-	-	-
Long	0.075	975	-	-	-	-

Table 5.2. Experimental shear moduli and SCFT predicted shear moduli as well as the parameters used to derive the SCFT moduli

shows a steeper drop in modulus than the long midblock system. SCFT calculations show that bridging fraction decreases more rapidly with decreasing volume fraction in the short midblock system. SCFT calculated shear moduli, bridging fractions, and nearest neighbor spacing are tabulated for comparison with experimental values in Table 5.2. The prefactor, A, used to ensure agreement of SCFT calculated values and experimental data at a volume fraction of 0.2, was 0.812 for the short midblock and 0.763 for the long midblock. SCFT does not account for kinetic trapping of the endblock aggregates, a fact which accounts for the divergence of SCFT calculations from experimental values.



Figure 5.8. Volume fraction vs. nearest neighbor spacing determined from room temperature SAXS data.

The average aggregate spacing, D, clearly plays an important role in mechanical properties. This value can be extracted from SAXS measurements using the equation below:

$$(5.5) D = \left(\frac{4\pi}{3\eta}\right)^{1/3} R_{hs}$$

Shown in Figure 5.8 is the average aggregate spacing at room temperature for both long and short midblock polymers as a function of volume fraction, as determined from both SAXS data and SCFT. Across all volume fractions, the average aggregate spacing is higher in the long midblock system than the short midblock system. The spacing in the long midblock system also increases rapidly as volume fraction decreases, where as aggregate spacing only increases by a few nanometers over the studied volume fraction range. This is direct evidence that the midblocks of the short midblock gels are more highly stretched than in the long midblock gels. Estimating from the standard length and angle of an SP3 hybridized C-C bond, the fully stretched midblock length of the long midblock polymer is 228.5nm. In contrast, the fully stretched midblock of the short midblock polymer is 61nm.

At room temperature for $\phi = 0.15$, SAXS data gives a center-to-center aggregate spacing of 39nm for long midblock gels and 27nm for short midblock gels. Extension ratios, 0.171 and 0.443 for the long and short midblocks respectively, are calculated from the aggregate spacing values and estimated fully-stretched lengths. Clearly, the midblocks in the long midblock system are in a less-extended conformation. As volume fraction decreases, the elastic restoring force should be much higher for the highly-stretched midblocks. Additionally, a highly-stretched conformation is entropically unfavorable; thus, it should result in an increased bridging fraction. The competition between these factors plays a major role in determining the osmotic and mechanical properties of polymer gels.

Despite very different average aggregate spacing, both the long and short midblock polymers show similar behavior in aggregation number as a function of volume fraction as is shown in Figure 5.9. The average aggregation number is slightly higher in the long midblock polymer but always within 10 endblocks of the short midblock polymer. Seitz et al. observed that in 2-ethyl hexanol the rheometric response of acrylic triblock copolymer gels appears to be endblock controlled, that is to say, relaxation times in the temperature dependant transition regime observed with SAXS correlate strongly with endblock length [29].



Figure 5.9. Volume fraction vs. aggregation number at room temperature for both long and short midblock polymers

Combining the knowledge gleaned from examining both temperature and volume fraction dependant properties of acrylic triblock copolymer gels provides a picture of how the interplay between endblock and midblock properties gives rise to gel characteristics. Both long and short midblock gels have similar rheometric properties and aggregation numbers. This implies that flow properties, such as the relaxation time, are temperature and endblock controlled. The elastic properties of the system are heavily influenced by midblock conformations. Thus, it is expected that osmotic properties will depend on both midblock and endblock properties. Any explanation of osmotic properties measurements will have



Figure 5.10. A photograph of short midblock polymer gels after one week of ageing

to take into account the state of both endblocks and midblocks. The swelling measurements described in the next section provide additional insight into the role of midblock length in determining osmotic properties.

5.3. Swelling Measurement Results

When discussing the osmotic properties of triblock copolymers, it is helpful to start from a few simple observations of sample behavior. The photograph above, Figure 5.10, shows a series of short midblock gels that were cast at the labeled volume fractions and allowed to age for one week. A transition from deswelling to swelling is indicated by increasing turbidity with decreasing volume fraction. Low concentration solutions appear opaque and milky after a week of aging, while high concentration solutions remain transparent. The turbid appearance of low concentration gels is the result of light scattering
due to microscopic inhomogenities that develop upon deswelling. Deswelling behavior indicates that, for the short midblock system, low volume fraction gels contain more solvent than is required to reach equilibrium concentration at room temperature. In these cases, the elastic restoring force of the network must exceed the osmotic swelling pressure, thus solvent is expelled by the gel network. At high volume fractions, the gels remain transparent as there is not enough solvent to swell the gel and reduce osmotic pressure to the point where it is balanced by the elasticity of the gel network. The osmotic pressure must remain elevated and exceeds the elastic restoring force at these higher volume fractions.

These trends in osmotic pressure can be quantified with swelling measurements where samples of polymer gels at various initial polymer volume fractions are immersed in pure solvent and allowed to equilibrate. The equilibrium polymer volume fractions of short and long midblock gels, as a function of initial volume fraction at 0 °C and 25 °C in 1-butanol, are shown in Figure 5.11. The results show that the long and short midblock systems do have different osmotic behaviors at room temperature. The long midblock system exhibits a much greater degree of swelling than the short midblock system, as indicated by equilibrium polymer volume fractions (ϕ_{eq}) that are smaller than the initial volume fractions (ϕ_0). The delineation of the swelling and deswelling regimes is indicated by the dashed line. In contrast to long midblock solutions, the short midblock systems fall in the deswelling regime at low temperature and actually go from deswelling to swelling behavior with increasing initial volume fraction at 25 °C. This characteristic is in agreement with the turbidity trend observed in Figure 5.10.

The equilibrium volume fraction for the short midblock system is about 0.2: the intersection of the short midblock 25 °C trendline and the dashed line indicating zero swelling.



Figure 5.11. Initial volume fraction vs. final volume fraction for long and short midblock polymer gels after swelling in pure solvent

For the long midblock system, the equilibrium concentration appears to be about $\phi = 0.05$ volume fraction at 0 °C and $\phi = 0.03$ at 25 °C. Increasing temperature shifts the equilibrium volume fraction for both gels toward lower polymer volume fractions. As stated previously, at equilibrium swelling the total osmotic pressure of the gel is zero relative to the osmotic pressure of pure solvent, because the osmotic contributions due to swelling and network elasticity are perfectly balanced. The volume fraction of polymer at which this occurs is determined by the midblock length and the quantity of osmotically active polymer in solution, which is a function of temperature-dependant interaction parameters. The shorter the midblock length, the higher the equilibrium volume fraction will be at a given temperature. Essentially, the shorter the midblock, the smaller the volume of

solvent that can be accommodated before the midblock reaches a highly stretched conformation where elasticity counteracts swelling. This occurs in spite of greater solvent accommodation by PMMA aggregates with increasing temperature.

5.4. Vapor Pressure Osmometry Results

Direct measurements of osmotic pressure agreed with the model for the relationship between triblock architecture and osmotic properties as proposed in Section 5.3. The measurement of osmotic pressure was achieved using vapor pressure osmometry (VPO). The use of VPO was restricted to temperatures above 65 °C because at lower temperatures the solutions have high viscosity. Nevertheless, it was possible to probe the behavior of the gels in the temperature regime corresponding to the onset of the structural transition observed by SAXS and the mechanical properties transition observed with rheometry. Appropriate calibration curves allowed conversion of the observed signal in the case of triblock polymers to an equivalent PnBA concentration. Plots of the equivalent PnBA concentration as a function of temperature for long and short midblock polymers at various concentrations are shown in Figures 5.12 and 5.13. It is important to keep in mind that the relatively small changes in equivalent volume fraction correspond to larger osmotic pressure changes because osmotic pressure scales as a power law of polymer volume fraction.

VPO measurements show that the proportion of PMMA in the triblock solution has a large effect on the osmotic pressure of the final solution as does midblock length. For the long midblock polymer, 30 wt.% PMMA, the equivalent PnBA concentrations are close to the actual volume fraction of solution for volume fractions of 0.05 and 0.10. At a volume



Figure 5.12. Vapor pressure osmometry results for the long midblock polymer

fraction of 0.15, greater variation in the osmotic pressure is observed. Below 80 °C, the equivalent PnBA volume fraction is 0.01 - 0.02 less than the actual volume fraction. Above 80 °C, there is an increase in the equivalent PnBA concentration to near that of the actual volume fraction of triblock. This suggests that above 80 °C at a volume fraction of 0.15 almost all the PMMA is osmotically active. This is consistent with the theta temperature of PMMA in 1-butanol which is known to be 82.7 °C [1]. The osmotic pressure of the long midblock polymer appears to be dominated by the quantity of osmotically active polymer. Some variation is observed for a volume fraction of 0.15, but not 0.10 or 0.05. This indicates that the magnitude of the osmotic pressure change as a result of network dissolution is too small to be observed by VPO at gel volume fractions of 0.10 and 0.05. A



Figure 5.13. Vapor pressure osmometry results for the short midblock polymer

lack of pronounced change in osmotic pressure with increasing temperature demonstrates that elastic restoring force is playing a minimal role in determining the osmotic pressure at the observed volume fractions and temperatures. This is despite a clear mechanical properties change in the experimental temperature regime.

The temperature dependence of the PnBA equivalent volume fraction of the short midblock polymer is shown in Figure 5.13. Across a temperature range of $65 \,^{\circ}\text{C} - 90 \,^{\circ}\text{C}$, at both the 0.10 and 0.15 volume fractions, the PnBA equivalent volume fraction is 0.02 – 0.05 less than the actual triblock volume fraction. Further more, there is a distinct increase in the equivalent PnBA volume fraction from 75 $\,^{\circ}\text{C}$ to 80 $\,^{\circ}\text{C}$. The short midblock triblock copolymer is ~60 wt.% PMMA, almost twice the PMMA content of the long

midblock polymer. Therefore, for equivalent volume fractions and temperatures, there is less osmotically active polymer in a solution of the short midblock polymer as compared to the long midblock polymer. The contribution to the total osmotic pressure by dissolved polymer must be proportionally less in the short midblock. The sudden increase in osmotic pressure observed by VPO corresponds to the complete loss of scattering peaks as well as the end of the viscosity behavior transition regime observed in the rheometric data. Given this temperature correspondence and the increased importance of network elasticity in determining the osmotic pressure in short midblock gels, the observed osmotic pressure change is attributed to the complete loss of network structure as a result of endblock dissolution. This effectively narrows the location of the dissolution of the physical aggregate network to a five degree temperature range.

5.5. Experimental Results Summary

The structural and osmotic properties of PMMA-PnBA-PMMA acrylic triblock copolymer gels in 1-butanol were investigated using a variety of techniques. Rheometry, SAXS, swelling measurements, and vapor pressure osmometry were used to develop a detailed understanding of gel structure and properties evolution as a function of temperature and volume fraction. The following is a brief summary of what was learned from each technique.

Rheometry provided mechanical characterization of the acrylic triblock copolymer gels and showed that the visco-elastic gel to liquid transition occurs between 65 °C and 80 °C. Rheometric results obtained for butanol-based gels were found to agree with observations by Seitz et al. for the same polymers in 2-ethyl hexanol. Analysis of rheometric results also indicated that many flow properties and the temperature at which elasticity is lost due to break up of the polymer network is controlled by endblock properties. The magnitudes of mechanical properties, such as shear modulus, are controlled by the total volume fraction of polymer and the midblock degree of polymerization.

Small angle x-ray scattering provided basic structural information about the gel microstructure, such as the average nearest neighbor distance between aggregates. Below 55 °C the gel networks show only slight variation with temperature. However, between 55 °C and 80 °C SAXS data shows the gel structure undergoes considerable rearrangement, which is attributed to the swelling and dissolution of endblock aggregates.

Swelling measurements provided additional context for interpreting the results of direct measurements of osmotic pressure. They also highlighted the important role that midblock degree of polymerization plays in determining the osmotic properties of acrylic triblock gels. The results of swelling experiments were combined with structural and mechanical results to explain osmotic pressure measurements of acrylic triblock copolymer gels. Osmotic pressure measurements demonstrated that the complete dissolution of the endblock aggregate network occurs between 75 °C and 80 °C, but is only detectable when the elastic restoring force plays a large role in determining osmotic properties when compared to the volume fraction of osmotically active polymer.

When all these results are combined, a more detailed understanding of the relationship between the mechanical, structural, and osmotic properties of acrylic triblock copolymers is obtained. This more detailed understanding is summarized in Figure 5.14, which schematically illustrates gel structure as a function of temperature and the relationship between gel structure and osmotic properties. SCFT predictions were also found to agree



Figure 5.14. Illustration of the relationship between gel structure, mechanical, and osmotic properties of an acrylic triblock copolymer gel.

well with experimental results. Modification of SCFT results to account for kinetic effects and the modification of SCFT parameters based on experimental data should result in an improvement in the predictive capabilities of SCFT when modeling triblock copolymer networks. This tool combined with a deeper understanding of how acrylic triblock architecture and composition determine the properties of a physically crosslinked network will allow the design of future gel systems with specific properties.

CHAPTER 6

Future Work

The purpose of the research presented in this dissertation was to develop a more nuanced understanding of the interplay of mechanical, osmotic, and structural characteristics of acrylic triblock copolymers, which give rise to their thermally reversible properties. SCFT simulations of two acrylic triblock copolymers with similar endblock degrees of polymerization, but varying midblock degrees of polymerization, were compared to experiment and found to agree within the temperature range of the visco-elastic solid to viscous liquid transition. Using SCFT results as a guide, it was possible to explain osmotic properties measurements, which provided insight as to the temperature range of the critical micelle transition. A clearer understanding of the role played by midblock degree of polymerization in determining mechanical and osmotic properties was also obtained. However, disagreement between SCFT results and experiment occurred at temperatures where endblock aggregates become elastically trapped. A clear goal for future research is to improve the agreement between SCFT predictions and experiment.

As observed in Chapter five, good agreement is obtained between experimental and theoretical predictions of SAXS maximum scattering intensity as a function of temperature, plateau modulus, and inter-aggregate spacing. The best agreement between theory and experiment is obtained at polymer volume fractions of 0.15 or greater and temperatures between $55 \,^{\circ}$ C and $65 \,^{\circ}$ C. Deviations between experiment and theory are observed

at both lower volume fractions and temperatures. This is believed to be the result of a failure of SCFT calculations to capture the kinetic trapping of endblocks. Kinetic trapping of endblocks fixes the room temperature aggregation number at the equilibrium value of aggregation number for the glass transition temperature. The endblock aggregates may expel some solvent, but they cannot rearrange to equilibrate to the equilibrium structure. Lower volume fractions, less than 0.15, are more sensitive to this error as smaller changes in aggregation number will result in larger changes in equilibrium spacing and bridging fraction.

A possible solution for the over prediction of nearest neighbor spacing and bridging fraction at low volume fractions and temperatures, is to run SCFT simulations at system sizes other than the equilibrium system size. Instead, one would calculate the volume fraction profile with the appropriate temperature dependant chi parameters, but setting the system size to the equilibrium system size determined for the glass transition temperature. The temperature used to fix the system at the appropriate glass transition temperature would have to be determined experimentally from rheometric behavior or temperature dependent SAXS intensity measurements.

The interaction parameters used in SCFT simulations could also be improved. A direct measurement of the PMMA-PnBA interaction parameter would helpful. Additionally, refinement of the temperature dependence of the solvent-polymer interaction parameters would be helpful. 1-butanol was used as the solvent in both experiment and theory in this dissertation, because of its high vapor pressure and known temperature dependant interaction parameter with PMMA. However, for gel processing applications 2-ethylhexanol is the preferred solvent. The PMMA-solvent interaction parameter could be determined for a variety of alcohols, or other selective solvents, using a number of standard methods. These include cloud point measurments, sedimentation methods, viscometric methods, and small angle scattering methods.

Another area where additional experimental results would be useful in improving our understanding of physically networked block copolymers, would be in refining small angle scattering experiments. The small angle x-ray scattering experiments presented in Chapter 5 were unable to determine the radius of the PMMA rich endblock aggregates. It proved difficult to extract this parameter from SAXS data, because of the difficulty in acquiring appropriate backgrounds. Also, it was not possible to directly compare the scattering intensities between different samples as SAXS measurements. Improvement in either of these aspects of scattering experiments would allow additional checks on the accuracy of SCFT predictions and improved determination of the temperature dependence of endblock aggregate dissolution.

With careful experimental planning it may be possible to prepare temperature dependant absolute intensity SAXS experiments. The technical challenges involved in implementing the required temperature controlled polymer solution flow systems at a synchrotron x-ray facility are considerable. However, static temperature, absolute intensity measurements could be used to determine the PMMA aggregate size and density. Alternative methods, such as light and neutron scattering may also be able to provide more accurate results. Small angle neutron scatting, in conjunction with the selective deuteration of polymer blocks and solvent, could be particularly fruitful. The advantage of SANS in conjunction with deuteration methods is direct control of the scattering length density contrast mechanism. This should allow absolute intensity measurements and improved the contrast of small angle scattering data.

Long range objectives for this research are the continued exploration of the phase space offered by variations in polymer architecture with SCFT, the simulation of systems with mixed triblock architectures, and expansion of simulation capabilities to a wider selection of chemical species. The exploration of the effects of variation of polymer architecture with SCFT is a useful exercise. It would be particularly interesting to examine the effect of changing endblock length on the calculated polymer volume fraction profile. It should be possible through the study of the polymer architecture phase space to design gels with particular aggregate sizes, nearest neighbor spacing, and equilibrium volume fractions. This information could allow the improvement of acrylic triblock based materials for the known application of pressure sensitive adhesives. More exciting still, is the possibility of using SCFT to design systems with more complex polymer architectures and additional chemical components. A topic of research that is currently receiving a high degree of interest is high mechanical strength double network hydrogel gels, which were first developed by the Gong research group [101]. It is conceivable that the SCFT theory presented in this work could be built upon to design double network gels that use endblock aggregation to physically crosslink one or both of its polymer networks. Expanding the catalogue of chemical constituents that could be simulated with SCFT also opens up the possibility of applying the lessons learned in predicting acrylic triblock copolyers to hydrogel systems. In tissue engineering and drug delivery applications the careful control of osmotic and temperature dependant mechanical property is critical for success.

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