Block Copolymer Self-Assembly in Solution:
Structure and Dynamics

A DISSERTATION
SUBMITTED TO THE FACULTY OF THE GRADUATE SCHOOL
OF THE UNIVERSITY OF MINNESOTA
BY

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IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

Frank S. Bates and Timothy P. Lodge

August 2010
Acknowledgements

I feel this thesis would have not been completed without help and support from many people to whom I owe thank. First and foremost, I would like to thank my advisors Dr. Frank S. Bates and Dr. Timothy P. Lodge for their invaluable guidance and encouragement throughout the entire period of my Ph. D. Without their advices from distinguished insight and experience, the project presented here would not be possible. I also would like to point out that I’ve learned how to survive as an independent scientist and engineer from their formal teaching and informal discussion. This sentence will last in my mind: “Writing and presentation will determine your future.”

I am very proud of being a part of polymer group at the University of Minnesota. Particularly, I thank to Kwanho Chang, Sangwoo Lee, Sangeon Han, and Jaewook Nam for fruitful discussion and many supports for my research. Kwanho helped me to settle down in Minneapolis and to develop my work through his theoretical knowledge. Sangwoo taught me anionic polymerization and TEM with his patience. Sangeon and Jaewook assisted me to set up scientific problems based on experimental data. Dr. Steve Weigand at Argonne National Lab and Dr. Paul Butler, Dr. Steve Kline, and Dr. Yun Liu at NIST helped me with much advice and support for the small-angle x-ray/neutron scattering measurements and data analyses. Rajiv Taribagil and Brad Jones assisted me to collect the key data in my research at the neutron beam line, and I enjoyed casual conversations and discussions with them. I am grateful to those who were involved in my project; Dr. Maria Torija at CharFac, and Dr. Isabella Goldmints, Dr. Dean Clarke, and Dr. Stuart Briggs at Infineum. I also have benefited a lot from scholarly and casual conversation with current and former group members: Adam Meuler, Kevin Davis, Ning Zhou, Jian Qin, Sudeep Maheshwari, Sayeed Abbas, Ilan Zeroni, Zach Thomson, Michael Blumle, Sehban Ozir, Peter Simone, Ashshi Gaikwad, Todd Pangburn,

I believe that refreshment is as important as research in my life. Without friends around me in Minneapolis as well as in Korea I could not make any good progress in my research and refresh my mind. In addition, I thank very much Linda Hinderscheit, a clinical specialist in the department of speech-language-hearing sciences at the University of Minnesota, and John Corlett for assisting me with improving my speaking issue. And Moon Sung and Brad were good partners for many sports and gave me joyful time.

Finally, I can never thank my parents and sister’s family enough for their endless love and support.
To My Family
Abstract

Block copolymers can self-assemble into micelles or vesicles when dispersed in a selective solvent. In this study, spherical micelles were formed by poly(styrene-\textit{b}-ethylene-\textit{alt}-propylene) (PS-PEP) in squalane, highly selective to PEP blocks, leading to PS cores and swollen PEP coronas. The micelle structure was characterized by dynamic light scattering (DLS) and small-angle x-ray scattering (SAXS). The experimental results provide a detailed picture of micelle structure and intermicelle interaction as a function of block copolymer molecular weight and composition, concentration, and temperature. Based on this structural information, the single molecular exchange kinetics between the spherical micelles in dilute solution was examined by time-resolved small-angle neutron scattering (TR-SANS). Two pairs of structurally matched partially protonated and deuterated micelles were prepared and each pair was blended to provide an initially isotopically segregated state in solution. The SANS intensity is directly related to the concentration of protonated chains in the micelle cores. Therefore, a reduction in the measured scattering intensity can be quantitatively correlated with the exchange of chains. This measurement was aimed at probing the dependence of molecular exchange kinetics on temperature, molecular weight, and concentration. The temperature dependence of the chain exchange rate $R(t)$ can be explained based on the core block dynamics, while the documented quasi-logarithmic decay of $R(t)$ is shown to be consistent with single chain exchange that is hypersensitive to the core degree of polymerization and therefore polydispersity. Complementary measurements were also conducted with concentrated solutions where the micelles pack onto a body-centered cubic lattice. Based on a first-principles model, the exchange kinetics are expected to be independent of micelle concentration. However, slower dynamics in ordered micelles
were observed. These results suggest that contributions from factors other than core block
dynamics can come into play in the exchange kinetics for ordered micelles.
Table of Contents

List of Tables x
List of Figures xii

Chapter 1 Introduction
1.1 Block Copolymer Micelles 1
1.2 Thesis Outline 3
1.3 References 5

Chapter 2 Background
2.1 Introduction 7
2.2 Structure of Diblock Copolymer Micelles 9
   2.2.1 Theoretical Approaches 9
   2.2.2 Spherical Diblock Copolymer Micelles 12
   2.2.3 Nonspherical Diblock Copolymer Micelles 15
2.3 Dynamics of Block Copolymer Micelles 17
   2.3.1 Theoretical Approaches 18
   2.3.2 Experimental Results 20
      - Dynamic Equilibrium Exchange Kinetics 21
      - Micellization Kinetics 24
2.4 References 30

Chapter 3 Experimental Section
3.1 Synthesis of Block Copolymers 38
   3.1.1 Anionic Polymerization 39
   3.1.2 Selective Saturation 41
3.2 Characterization of Block Copolymers 42
   3.2.1 Size Exclusion Chromatography (SEC) 42
3.2.2 Nuclear Magnetic Resonance (NMR) 43
3.3 Rheology 46
3.4 Dynamic Light Scattering (DLS) 48
3.5 Small-Angle Scattering 51
3.6 References 60

Chapter 4 Structure of Diblock Copolymer Micelles
4.1 Introduction 63
4.2 Experimental Section 65
   4.2.1 Materials 65
   4.2.2 Dynamic Light Scattering (DLS) 67
   4.2.3 Rheology 68
   4.2.4 Small-Angle X-ray Scattering (SAXS) 69
4.3 Fitting Model 69
4.4 Results and Discussion 73
   4.4.1 DLS 73
   4.4.2 SAXS 76
   4.4.3 Rheology 90
4.5 Summary 94
4.6 Acknowledgement 95
4.7 References and Notes 96

Chapter 5 Mechanism of Molecular Exchange in Diblock Copolymer Micelles
5.1 Introduction 100
5.2 Experimental Section 103
   5.2.1 Materials 103
   5.2.2 Sample Preparation 106
   5.2.3 Time-Resolved Small-Angle Neutron Scattering 107
5.3 Results and Analysis 111
5.3.1 Micelle Structure 111
5.3.2 Chain Exchange Kinetics 113
5.4 Discussion 118
  5.4.1 Logarithmic Decay 118
  5.4.2 Core Block Length Dependence 119
  5.4.3 Molecular Exchange Kinetic Model 121
5.5 Conclusion 128
5.6 References and Notes 129

Chapter 6 Molecular Exchange in Ordered Diblock Copolymer Micelles
  6.1 Introduction 133
  6.2 Experimental Section 134
    6.2.1 Materials 134
    6.2.2 Sample Preparation 134
    6.2.3 Time-Resolved Small-Angle Neutron Scattering 135
    6.2.4 Small-Angle X-ray Scattering (SAXS) 136
  6.3 Background of SANS 136
  6.4 Results and Analysis 139
    6.4.1 SAXS 139
    6.4.2 SANS 144
    6.4.3 TR-SANS 148
  6.5 Discussion 153
    6.5.1 Sensitivity of Fitting Parameters 153
    6.5.2 Postulated Reasons for Slower Dynamics 157
  6.6 Summary 159
  6.7 References and Notes 160

Chapter 7 Summary and Outlook
  7.1 Summary 164
7.2 Outlook 165
7.3 References 169

Chapter 8 Supporting Information
8.1 Phase Diagram of SEP(42-60) 170
   8.1.1 Lamellae (LAM) 170
   8.1.2 Hexagonally Packed Cylinders (HEX) 175
   8.1.3 Body-Centered Cubic Spheres (BCC) 178
   8.1.4 Summary 182
8.2 Model Fitting to Data Obtained by Lund et al. 184
8.3 References 187

Bibliography 188
List of Tables

Table 2.1 Scaling relationships of block copolymer micelles for two limiting cases

Table 2.2 Summary of studies on the equilibrium exchange kinetics measured by the fluorescent quenching method

Table 2.3 Summary of Studies on the micellization kinetics measured by light scattering

Table 2.4 Abbreviations for all of the polymers discussed in Chapter 2

Table 3.1 Allowed reflections for known morphologies in diblock copolymers

Table 4.1 Polymer Characteristics
Table 4.2 Fit results upon heating
Table 4.3 Fit results upon cooling

Table 5.1 Diblock copolymer and micelle characteristics
Table 5.2 Scattering length densities
Table 5.3 Fitting results a at \( T = 125 \, ^\circ \text{C} \)

Table 6.1 Diblock copolymer characteristics
Table 6.2 Micelle characteristics
Table 6.3 Fitting results for relaxation kinetics

Table 8.1 Calculated volume fraction of PS domain where peaks are disappear for lamellae
Table 8.2 Characteristics of 2D hexagonal-packed cylinder
Table 8.3 Characteristics of body-centered cubic spheres 181
Table 8.4 Fitting Results 185
List of Figures

Figure 2.1 Phase behavior of block copolymer micelles as a function of temperature and polymer concentration. 8

Figure 2.2 Schematic figures of micelle morphologies (e.g., sphere, cylinder, and bilayerd vesicle) as a function of (a) the core block ratio (block copolymer composition) and (b) interfacial tension between core block segments and solvents. Reproduced from Reference 76 and 81. 16

Figure 2.3 Two primary mechanisms of molecular exchange kinetics: (a) single chain insertion/expulsion, and (b) micelle fusion/fission. 18

Figure 2.4 Representative time-resolved intensity from a T-jump experiment. Reproduced from Reference 114. 26

Figure 3.1 Synthetic scheme of poly(styrene-b-ethylene-alt-propylene). 39

Figure 3.2 SEC traces of SI(42-60) and SEP(42-60). 44

Figure 3.3 Molecular structure and ¹H-NMR spectra of SI(42-60) and SEP(42-60). 44

Figure 3.4 Schematic frequency-dependent behavior of the storage modulus ($G'$) for disordered and other ordered structures. Reproduced from Reference 16. 47

Figure 3.5 Schematic geometry of small angle scattering by two particles and path difference. 52

Figure 4.1 Schematic drawing of diblock copolymer micelle 71

Figure 4.2 Temperature dependence of the hydrodynamic radius $R_h$ of (a) SEP(42-60) in squalane at 0.5 wt% (Rh measured upon heating and cooling twice), (b) all four polymers in squalane at 0.5 wt%, upon heating and cooling, and (c) SEP(42-60) in squalane at 0.02 wt% and 0.5 wt% upon heating. 75
Figure 4.3 SAXS data upon heating for SEP diblock copolymers in squalane at 1 wt%: (a) SEP(42-60), (b) SEP(36-69), (c) SEP(26-66), and (d) SEP(17-73). For clarity, data are multiplied by powers of 3 as temperature increases. The symbols are the SAXS data and the solid lines are the model fit.

Figure 4.4 SAXS data upon cooling for SEP diblock copolymers in squalane at 1wt% : (a) SEP(42-60), (b) SEP(36-69), (c) SEP(26-66), and (d) SEP(17-73). For clarity, data are multiplied by $3^n$ as temperature increases. The symbols are the SAXS data and the solid lines are the model fit.

Figure 4.5 Temperature dependence of (a) core radius ($R_c$) and (b) corona layer thickness ($L_{\text{corona}}$) for the four polymers in squalane at 1 wt%.

Figure 4.6 The relationship between the core radius and the number of repeat units in the core block.

Figure 4.7 Temperature dependence of the solvent fraction in the core ($f$).

Figure 4.8 The temperature dependence of (a) corona chain stretching and (b) brush density for four PS-PEP diblock copolymers in squalane at 1 wt%.

Figure 4.9 SAXS data of SEP(42-60) in squalane at various concentrations including 1 wt%, 3 wt%, 6 wt% and 10 wt%.

Figure 4.10 SAXS data of ordered 10 wt% PS-PEP solutions in squalane upon heating: (a) SEP(42-60), (b) SEP(36-69), (c) SEP(26-66), and (d) SEP(17-73).

Figure 4.11 Temperature dependence of (a) peak position $q^*$ and (b) the nearest neighbor radius corrected for thermal expansion, for the four SEP polymers in squalane.

Figure 4.12 Concentration dependence of the solution viscosity for SEP(42-60) block copolymers in squalane at 30 °C. The solution viscosities below 2 wt% are zoomed in inset for convenience.
**Figure 4.13** Frequency sweeps for dilute solutions of SEP(42-60) diblock copolymers in squalane at 30 ºC: (a) elastic modulus ($G'$) and (b) viscous modulus ($G''$) at 2 wt% (square), 3 wt% (circle), 5 wt% (triangle), and 6 wt% (up-side-down triangle).

**Figure 4.14** Superimposed frequency dependence of $G'$ and $G''$ for SEP(42-60) in squalane at (a) 7 wt%, (b) 8 wt%, and (c) 10 wt% using (d) shift factors (aT) at the reference temperature of 30 ºC. Data were collected at multiple temperatures shown in legends. In (d), Solid line is the best fit to WLF equation and dashed line denotes $\frac{\eta}{\eta(T=30 ºC)}$ for squalane.

**Figure 5.1** SEC traces of (a) PS-PEP-1 and (b) PS-PEP-2: dPS (dash) and hPS (solid)

**Figure 5.2** Experimental scheme of time-resolved small-angle neutron scattering (TR-SANS). The different degree of brightness represents the neutron scattering length density of each part. Protonated micelle cores (white) and deuterated micelle cores (black) are prepared separately in an isotopic solvent mixture (grey). The micelles are mixed at room temperature, where the glassy cores inhibit diblock copolymer exchange. Heating above $T_g$ of the cores makes possible diblock exchange between micelles. Molecular exchange leads to contrast matching between the solvent and cores.

**Figure 5.3** Scattering curves for spherical micelles of (a) PS-PEP-1 and (b) PS-PEP-2 in squalane with different levels of contrast: dPS cores (square), hPS cores (circle), premixed cores (triangle), and postmixed cores (star) micelles. Background (incoherent) scattering was measured using the squalane solvent (diamond).

**Figure 5.4** Scattering curves for postmixed specimen after mixing (square) and after 18 h annealing at 30 ºC (circle).
Figure 5.5 Time dependence of SANS patterns obtained from postmixed specimens (a) PS-PEP-1 at 100 °C and (b) PS-PEP-2 at 135 °C. Initial measurements were made at 30 °C (filled circles) and followed by the acquisition of SANS data every 5 min (shown in the legend) at 100 °C for PS-PEP-1 and 135 °C for PS-PEP-2. Premixed specimens were also measured at 100 °C and 135 °C (filled stars).

Figure 5.6 Decay of reduced SANS intensity as a function of time for (a) dPS-PEP-1/hPS-PEP-1 at 100 °C (circle), 110 °C (square), and 115 °C (triangle) and (b) dPS-PEP-2/hPS-PEP-2 at 135 °C (circle), 140 °C (square), and 145 °C (triangle). These results are linear on logarithmic time scale over the measurement range.

Figure 5.7 Concentration dependence of chain exchange kinetics for (a) PS-PEP-1 at 101 °C and (b) PS-PEP-2 at 140 °C: 0.5 vol% (triangle), 1 vol% (square), and 2 vol% (circle).

Figure 5.8 Time-temperature superposed TR-SANS results with $T_{\text{ref}} = 125$ °C. $\alpha_T$ shift factors conform to a single equation as shown in the inset. Master curves for chain exchange kinetics for PS-PEP-1 (circles, originally measured at 100 °C (blue), 110 °C (green), and 115 °C (red)) and PS-PEP-2 (squares, originally measured at 135 °C (blue), 140 °C (green), and 145 °C (red). Solid curves are best fit to Eq. (3) with $\alpha_T = 0.041$ (circles) and 0.042 (squares). Dotted and dashed curves were calculated with $\alpha_T = 0.03$ and 0.06 and $N_{\text{core}} = 255$ and $N_{w}/N_n = 1.08$.

Figure 5.9 Schematic drawing for the single molecule exchange between micelles involving three steps: extraction of a core block, transportation of block copolymer through a solvent medium, and insertion into another micelle. Extraction of the core block carries the unfavorable interaction between the core block segments and solvent at the interface, thus is rate-limiting.
Figure 5.10 Sensitivity of calculated $R(t)$ to variations in core block polydispersity. Data are superimposed PS-PEP-2 ($T_{ref} = 125$ °C) results from Figure 3. Polydispersity of core block length: 1 (dash), 1.02 (dash-dot), 1.04 (solid), and 1.20 (dot).

Figure 6.1 SAXS patterns obtained from 15 vol% of (a) PS-PEP-1 and (b) PS-PEP-2 in squalane at room temperature: dPS-PEP, hPS-PEP, premixed, postmixed as shown in the legend. The representative data for both polymers are indexed to bcc morphologies. Solid curves in (b) are the fits to a form factor of polydisperse PS spheres in the squalane matrix. Data are vertically shifted for convenience.

Figure 6.2 SAXS patterns obtained from 15 vol% of (a) PS-PEP-1 at 120 °C and (b) PS-PEP-2 at 150 °C in squalane: dPS-PEP, hPS-PEP, premixed, postmixed as shown in the legend. The representative data for both polymers are indexed to bcc morphologies. Data are vertically shifted for convenience.

Figure 6.3 SANS patterns obtained from 15 vol% of (a) PS-PEP-1 and (b) PS-PEP-2 in squalane at 30 °C: dPS-PEP (square), hPS-PEP (circle), postmixed (star), premixed (triangle), and solvent (diamond) as shown in legend. Solid curves are best fit to eq (6.9). Arrows indicate the position of $q^*$ observed in SAXS.

Figure 6.4 Schematic figure of the cup-rotor mixer (MiniMAX). Reproduced from Reference 20.

Figure 6.5 Time evolution of SANS patterns collected from a 15 vol% (a) dPS-PEP-1/hPS-PEP-1 50/50 mixture at 119.5 °C and (b) dPS-PEP-2/hPS-PEP-2 50/50 mixture at 156.5 °C. Initial measurements were obtained at 30 °C (filled circle), followed by the acquisition of SANS data every 5 min (shown in legend) at the target temperature. The statistically mixed core data were obtained from premixed specimens at the target temperature.
Figure 6.6 Relaxation function of (a) dPS-PEP-1/hPS-PEP-1 at 110 °C (square), 119.5 °C (circle), and 130.3 °C (triangle) and (b) dPS-PEP-2/hPS-PEP-2 at 144.5 °C (square), 156.5 °C (circle), and 164.5 °C (triangle). The straight lines are guides to the eye indicating logarithmic time dependence of relaxation decay.

Figure 6.7 Comparison of time-temperature superposed $R(t)$ between dilute solution (open, regenerated from Chapter 5) and the bcc ordered state (filled) for (a) PS-PEP-1 at $T_{ref} = 110$ °C [originally measured at 110 °C (filled circle), 119.5 °C (filled square) and 130.3 °C (filled triangle)] and (b) PS-PEP-2 at $T_{ref} = 145$ °C [originally measured at 144.5 °C (filled square), 156.5 °C (filled circle), and 164.5 °C (filled triangle)]. Solid curves are best fit to eq (5.6). The shift factors $a_T$ are shown in the inset.

Figure 6.8 Sensitivity of calculated $R(t)$ to variation in interfacial tension $\alpha \chi$. Data are superimposed PS-PEP-1 ($T_{ref} = 110$ °C) results for dilute solutions (unfilled) and bcc ordered state (filled) from Figure 6. Lines are estimated $R(t)$ by eq (9) as a function of the values of $\alpha \chi$: 0.045 (solid), 0.0495 (dash), 0.054 (dash-dot), and 0.57 (dot) with fixed PDI (1.07) and $\zeta (= 1.18 \times 10^{-7}$ N s m$^{-1}$).

Figure 7.1 (a) Temperature dependence of hydrodynamic radius ($R_h$) in the mixed solvents at 0.5 wt%: 75% squalane (open), 50% squalane (half filled), and 25% squalane (solid). Upper triangles are measure upon increasing temperature and down upon decreasing temperature. (b) The critical micelle temperature (CMT) as a function of the squalane fraction in the binary mixtures.

Figure 8.1 SAXS patterns of SEP(42-60) in squalane at (a) 100 wt%, (b) 88 wt%, and (c) 80 wt% upon heating. The sequence of peak ratio $q/q^*$ indicates a lamellar morphology for the three specimens. Data are vertically shifted for convenience.
Figure 8.2 SAXS patterns of SEP(42-60) in squalane at (a) 67 wt%, (b) 59 wt%, (c) 49 wt%, and (d) 40 wt% upon heating. The sequence of peak ratio \( q/q^* \), indicated by arrows, shows that four specimens are ordered into hexagonally packed cylinder, and solid lines are best fit to cylindrical form factor. Data are vertically shifted for convenience.

Figure 8.3 SAXS patterns of SEP(42-60) in squalane at (a) 30 wt%, (b) 20 wt%, (c) 10 wt%, (d) 7 wt%, and (e) 6.5 wt% upon heating. The sequence of peak ratio \( q/q^* \) indicates body-centered cubic morphology, and solid line is best fit to spherical form factor.

Figure 8.4 Phase diagram of SEP(42-60) in squalane as a function of the weight fraction of polymer and the volume fraction of PS. Shaded area denotes disordered micelle. The lines are drawn as guidance to eye indicating the estimated locus between two morphologies.

Figure 8.5 (a) Primary \( q^* \) and domain spacing, and (b) \( q \) of first minimum and core radius as a function of weight fraction of SEP(42-60) in squalane at 100 °C.

Figure 8.6 Left: Master curves of chain exchange kinetics at reference temperature of 55 °C for PEP-PEO in water/DMF at \( X_{\text{DMF}} = 0.25 \) (circle) and \( X_{\text{DMF}} = 0.30 \) (square) measured at several temperature (42, 47, 55, 60, 65 °C). Solid lines are best fit to Eq (5.7). Right: shift factor for \( X_{\text{DMF}} = 0.25 \) (red) and \( X_{\text{DMF}} = 0.30 \) (blue).

Figure 8.7 Temperature dependence of the monomeric friction factor of PEP block. Square: experimental data using neutron spin echo, Solid line: simulation prediction by J. Luettmer-Strathmann.
Chapter 1

Introduction

1.1 Block Copolymer Micelles

Block copolymers are macromolecules composed of chemically distinct polymers linked by covalent bonds. Polymer blends typically experience macrophase separation that is theoretically estimated by entropic and enthalpic contributions as described in the Gibbs free energy of mixing. However, the chemical linkage between the polymers in a block copolymer suppresses macrophase separation, and therefore provides widely tunable mechanical properties by choosing polymers having desired characteristics. Instead of macrophase separation, the incompatibility (i.e., immiscibility) between blocks results in self-assembly into various ordered microstructures such as body-centered cubic spheres, hexagonally packed cylinders, bicontinuous cubic gyroid, and alternating lamellae.\textsuperscript{1-3} For A-B diblock copolymers, the relevant parameters of the onset of order-order transitions between these structures and order-disorder transitions are the product of the Flory-Huggins interaction parameter ($\chi_{AB}$) and the degree of polymerization ($N$), and the block copolymer composition ($f_A$).

The chemical linkage of block copolymers also imparts amphiphilic properties analogous to low molecular weight surfactants in solution. The addition of a solvent (S) to a neat A-B diblock copolymer creates two additional interactions between the solvent and both A and B blocks, described by $\chi_{AS}$ and $\chi_{BS}$, respectively. This elevated
complexity expands the range of accessible self-assembled morphologies. The distribution of solvent molecules in a block copolymer solution is determined by the solvent selectivity. When a solvent equally favors both blocks (i.e., $\chi_{AS} = \chi_{BS}$), the “neutral” solvent is equally distributed, and therefore dilutes the incompatibility between two blocks. This behavior typically reduces the temperature where order-order transitions and order-disorder transitions occur. Contrary to neutral solvents, the partial distribution of “selective” solvents (i.e., $\chi_{AS} \neq \chi_{BS}$) induces a renormalization of the block copolymer composition. If a solvent is selective for block A, the volume fraction of the block ($f_A$) effectively increases with the addition of the solvent, potentially inducing a variation of morphologies.

In dilute solutions, it is of particular interest that diblock copolymers dispersed in a selective solvent (e.g., $\chi_{AS} > \chi_{BS}$) can self-assemble into micelles or vesicles with cores of an insoluble A block and coronas of a soluble B block. Block copolymer micelles are highly attractive as superior alternatives to low molecular weight surfactant micelles because of increased stability, increased flexibility to targeting media, and widely tunable molecular structure. For technological and industrial applications, this class of materials can be employed as detergents in aqueous and organic media, segregated storage containers, drug delivery vehicles, nano-reactors, and viscosity modifiers.

The majority of investigations dealing with block copolymer micelles have studied the micelle structure as a function of block copolymer composition and architecture, molecular weight, solvent selectivity, and temperature. For example, the transition of micelle structure from spherical to cylindrical to bilayer has been well documented, and more complicated micelle structures (e.g., multicompartmen micelles) have been reported recently with appropriately-designed block copolymers. In comparison with the micelle structure, significantly less is known about the micelle dynamics. While
previous investigations have attempted to attain the equilibrated structures, kinetically frozen micelles have been observed almost ubiquitously due to the high incompatibility between the core blocks and solvents (i.e., a low critical micelle concentration), and the glassy nature of the cores.\textsuperscript{18-21} It is anticipated that the fundamental understanding of molecular exchange kinetics in block copolymer micelles will provide better insights into the micelle structure and future applications. This thesis, therefore, focuses on dynamic equilibrium exchange kinetics - one particular class of micelle kinetics - in conjunction with the micelle structure.

1.2 Thesis Outline

This thesis comprises 8 chapters. Chapter 2 provides a literature review regarding the structure and kinetics of block copolymer micelles. This discussion gives the readers some prerequisite background to understand the remaining chapters. Experimental techniques that were frequently performed in this research are described in Chapter 3. This chapter gives a general overview of the block copolymer synthesis performed and the characterization of block copolymer micelles using dynamic light scattering (DLS), rheology, and small-angle x-ray/neutron scattering (SAXS/SANS). More specific details of each measurement are described in the appropriate chapter.

The investigation of micelles formed by poly(styrene-\textit{b}-ethylene-\textit{alt}-propylene) (PS-PEP) in squalane, highly selective to PEP, is provided in Chapter 4. The micelle structures were characterized by DLS, rheology, and SAXS with a detailed fitting model. The experimental results provide a detailed picture of micelle structure and intermicelle interaction as a function of block copolymer molecular weight and composition, concentration, and temperature. Based on the structural information obtained, molecular
exchange between spherical micelles in dilute solution was investigated using time-resolved small-angle neutron scattering (TR-SANS), as described in Chapter 5. The goal of these experiments was to probe the dependence of molecular exchange between block copolymer micelles on temperature, molecular weight, and concentration. Based on our observations, we proposed that molecular exchange kinetics are governed by a single chain insertion/expulsion mechanism which is significantly affected by the unfavorable interaction between the core block segments and the solvent. Then, the molecular exchange between ordered block copolymer micelles in concentrated solutions are provided in Chapter 6. As the concentration of spherical micelles increases, the micelles are packed onto a body-centered cubic lattice. The exchange kinetics were expected to be independent of micelle concentration according to our assumption described in Chapter 5; however, slower dynamics were observed in ordered micelles. Chapter 6 discusses several postulated reasons to account for the slower dynamics. Chapter 7 contains a brief summary and potential future research related to this thesis.
1.3 References


Chapter 2

Background

2.1 Introduction

Block copolymer micelles are self-assembled aggregates of amphiphilic macromolecules in an excess of selective solvent, composed of a compact core containing the insoluble blocks and a swollen corona containing the soluble blocks.\textsuperscript{1–4} This implies that the block copolymer micelles behave in a similar manner to classical low molecular weight surfactant micelles. However, the relatively longer block length provides a greater stability and rigidity, which are desirable when the micelles are used for drug delivery or segregated storage.\textsuperscript{5–7}

The structure of block copolymer micelles in both aqueous and organic solvents has been widely investigated. As the simplest example, the general phase behavior of sphere-forming diblock copolymer micelles in organic solvents is described in Figure 2.1 as a function of temperature and concentration. The behavior depicted is that of an upper critical solution temperature (UCST) system. In contrast, block copolymers dispersed in aqueous media typically exhibit lower critical solution temperature (LCST) behavior, wherein the temperature dependence of Figure 2.1 is reversed. When dispersed in a selective organic solvent, block copolymers can self-assemble into micelles above a critical micelle concentration (CMC) and below a critical micelle temperature (CMT) to avoid the unfavorable interaction between the core block segments and solvent. In other
words, the block copolymers are molecularly dissolved as unimers below the CMC and above the CMT. The unfavorable interaction is dominated by the enthalpic contribution for organic solutions and entropic contribution for aqueous solutions. These contributions are temperature dependent, therefore the micelle structure is also a function of temperature. As the concentration of spherical micelles increases, the micelles begin to overlap and eventually pack onto either a body-centered cubic (bcc) or face-centered cubic (fcc) lattice, depending on the detailed form of the intermicellar potential.\textsuperscript{8–14} Other micelle morphologies than spheres, including cylinders and vesicles, have been also well documented.\textsuperscript{15–19} The structure of such block copolymer micelles will be briefly reviewed in the first part of this chapter.

**Figure 2.1** Phase behavior of block copolymer micelles as a function of temperature and polymer concentration.
In comparison to thermodynamics, significantly less is known about the kinetics of block copolymer micelles underlying the attainment of thermodynamically equilibrium structures. Block copolymer micelles must undergo exchange of individual chains with one another to reach thermodynamic equilibrium. Contrary to classical surfactant micelles, kinetically frozen micelles, also known as path dependent micelle structures, or nonergodic micelles, have been commonly observed for block copolymer micelle systems. Intuitively, block copolymer micelles with a glassy or semicrystalline core (e.g., PS or PMMA) must experience nonergodicity due to the frozen chain mobility. However, such non-equilibrium structures have been observed even with a rubbery core (e.g., PB, PI or PEP), and this is attributable to the high incompatibility between the core block segments and solvent. This implies that kinetics play an important role in micelle formation, yet this issue has not been well resolved due to experimental difficulties. Hence, the second part of this chapter will extensively review the micelle kinetics.

2.2 Structure of Diblock Copolymer Micelles

In this section, a concise overview is provided of theoretical predictions and experimental results towards understanding the structure of block copolymer micelles and their behavior. Extensive reviews of this subject, including multiblock copolymer micelles, are available elsewhere.

2.2.1 Theoretical Approaches

Several theoretical descriptions for predicting the structure of diblock copolymer micelles in a selective solvent have been developed using scaling, self-consistent mean-field theory (SCFT), or computation / simulation. In general, the micelle properties,
including the aggregation number \((N_{\text{agg}})\), core radius \((R_c)\), corona thickness \((L_{\text{corona}})\), and hydrodynamic radius \((R_h)\), are characterized by three energy contributions: the interfacial tension between the core block segments and the solvent \((F_{\text{int}})\), chain stretching of core blocks \((F_{\text{core}})\), and excluded volume interactions between solvated corona blocks \((F_{\text{corona}})\). The mathematical expression of these energy terms is model dependent. The total Gibbs free energy of the micelle \((F_{\text{tot}})\) is the sum of the three contributions:

\[
F_{\text{tot}} = F_{\text{int}} + F_{\text{core}} + F_{\text{corona}}.
\] (2.1)

Minimization of \(F_{\text{tot}}\) in terms of the characteristic parameters (e.g., \(N_{\text{agg}}\) or \(R_c\)) results in scaling correlations between the micelle properties and the employed block copolymer characteristics.

A simple scaling model of block copolymers forming spherical micelles was developed by de Gennes, when corona blocks are relatively shorter than core blocks (i.e., \(N_{\text{core}} \gg N_{\text{corona}}\), where \(N_x\) is the degree of polymerization of \(x\)), which have been designated as “crew-cut” micelles.\(^{29,30}\) In this theory, the radial density profile of the corona block was assumed to be a step function, analogous to tethered polymer brushes on a flat surface. As the length of the corona blocks, however, becomes comparable to or longer than that of the core blocks, a curved core/corona interface should be considered, and accordingly the radial density profile becomes a function of distance from the core. Daoud and Cotton developed a scaling correlation for star-shaped micelles (i.e., \(N_{\text{core}} \ll N_{\text{corona}}\)), also known as “hairy” micelles, by employing the radial variation of the monomer concentration for the corona region, the so-called blob.\(^{31}\) As an extension of these previous works, Zhulina and Birshtein indentified four available micelle structures for relative values of \(N_{\text{core}}\) and \(N_{\text{corona}}\) by extending the concept of tethered layers on
Table 2.1 Scaling relationships of block copolymer micelles for two limiting cases

<table>
<thead>
<tr>
<th></th>
<th>( N_{\text{core}} \gg N_{\text{corona}} )</th>
<th>( N_{\text{core}} \ll N_{\text{corona}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N_{\text{agg}} )</td>
<td>( \gamma N_{\text{core}} )</td>
<td>( \gamma^{6/5} N_{\text{core}}^{4/5} )</td>
</tr>
<tr>
<td>( R_c )</td>
<td>( N_{\text{core}}^{2/3} )</td>
<td>( N_{\text{core}}^{3/5} )</td>
</tr>
<tr>
<td>( L_{\text{corona}} )</td>
<td>( N_{\text{corona}} )</td>
<td>( N_{\text{agg}}^{1/5} N_{\text{corona}}^{3/5} )</td>
</tr>
<tr>
<td>Radius of the micelle (~( R_h ))</td>
<td>( N_{\text{core}}^{2/3} )</td>
<td>( N_{\text{corona}}^{4/25} N_{\text{core}}^{3/5} )</td>
</tr>
</tbody>
</table>

curved surfaces.\(^{32}\) Later, Halperin et al. summarized the scaling models for tethered or grafted polymer chains on both flat and curved surfaces of several accessible geometries.\(^{33,34}\) Table 2.1 summarizes the scaling predictions for the two limiting cases – crew-cut and hairy micelles – in terms of \( N_{\text{core}} \) and \( N_{\text{corona}} \), and the interfacial tension between the core block segments and the solvent (\( \gamma \)). Recently, a theoretical description for block copolymer micelles of nonspherical morphologies (e.g., cylinder and bilayers) has been developed by Zhulina et al. as an extension of scaling expressions for spherical micelles.\(^{35}\) The transition of micelle structure is predicted to occur with block copolymers having \( N_{\text{core}} \gg N_{\text{corona}} \), where the contribution from the chain stretching of core blocks is relatively large.

Since scaling models predict only the relationship between micelle properties and corresponding block copolymers, these methods are somewhat limited to estimate detailed values of \( R_c \), \( L_{\text{corona}} \), and \( N_{\text{agg}} \), for a particular micelle. SCFT\(^{36-39}\) computation/simulation\(^{40,41}\) have been widely employed as complementary techniques to the scaling models, for predicting the behavior of block copolymer micelles.
2.2.2 Spherical Diblock Copolymer Micelle

The thermodynamic properties, such as CMT, CMC, the standard Gibbs free energy of micellization, and micelle dimensions, are of fundamental importance to understand principles that govern the self-assembly of block copolymers. Static and dynamic light scattering (SLS and DLS) have been widely employed to determine these values as a function of concentration, temperature, and solvent selectivity. For example, Quintana et al. studied the micellar properties of PS-PEP in \( n \)-alkane solvents using SLS and DLS, and reported the molecular weight of micelles, radius of gyration, and the standard enthalpy and entropy of micellization by measuring CMT and CMC.\(^{42,43}\) These last two values were calculated to be negative, implying that the micellization of PS-PEP in alkane is mainly enthalpy-driven, in contrast to the behavior of classical surfactant micelles, where entropy is largely responsible, the so-called hydrophobic effect. The authors also investigated several the systems of PS-PEP in various solvent mixtures of dodecane/1,4-dioxane,\(^{44,45}\) and 5-methyl-2-hexanone/2-pentanol\(^{46,47}\) to understand the effect of solvent selectivity. Less selective solvents typically induced smaller micelle size, lower CMT, and higher CMC for the UCST system.

In comparison with the light scattering measurements, small-angle x-ray scattering (SAXS) and small-angle neutron scattering (SANS) provide more detailed structural properties including the shape and radius of the core and the radial density profile of corona blocks.\(^{48,49}\) The advantages of SAXS are easy access to the instruments and short exposure time, while the advantages of SANS stem from the contrast matching technique to measure a particular part selectively via deuterium labeling and isotopic solvent mixtures. For these techniques, detailed fitting models are required to extract the micelle structure, including \( R_c \), \( N_{agg} \), \( L_{corona} \), and the radial density profile in particular. In general,
spherical micelles have been modeled as corona blocks tethered on spherical cores, and the radial distribution of corona blocks have been described in several different ways. Examples include a uniform corona shell, a power law density profile, a Gaussian profile, a Fermi-Dirac type density profile, a power law profile with a Fermi-Dirac type cutoff, and the combination of analytical expressions (e.g., spline function) supported by computer simulations.

Early work on the spherical micelle structure in aqueous solutions was performed by Mortensen et al. by investigating PEO-PPO-PEO triblock copolymers in deuterated water, i.e., LCST system. The authors modeled the SANS patterns with the assumption of compact cores without solvent molecules and no coronas, and observed that $R_c$ increases with increasing temperature and with decreasing soluble PEO block length. Later, Goldmints et al. studied the internal structure of similar triblock copolymers in water in more detail using contrast variation method and model fitting. The model assumed homogeneous cores and coronas swollen by solvent molecules and suggested solvent penetration into the micelle cores. It was found that the water content in the cores decreases and $N_{agg}$ increases with increasing temperature, while $R_c$ is constant. The properties of micelles formed by PEO-PPO-PEO triblock copolymers in formamide or in the mixture of water and polar cosolvents, such as formamide, ethanol, and glycerol were investigated by Alexandridis et al. The authors observed that the micellar structure follows the similar trend to that in water, but the specific micelle structure can be tuned by mixing solvents. In addition, the radial density profile for corona blocks for PEO-PPO-PEO micelles in water was described with a detailed model by Lobry et al. Recently, Castelletto et al. studied highly swollen PBO-PEO diblock copolymers dispersed in water and showed the similar behavior with PEO-PPO-PEO micelles. Most authors above also reported that PEO-PPO-PEO micelles in
aqueous solutions are independent of polymer concentration up to the onset of order-disorder transitions.

Similar to classical surfactants, polyalkanes, including PE, \(^{67}\) PB, \(^{57}\) and PEP, \(^{54,58-60,70}\) as a hydrophobic part instead of oxide group (e.g., PPO or PBO), also have been well documented. For example, Willner et al. observed a coronal shape crossover from crew-cut micelles to hairy micelles with a series of PEP-PEO in water, characterized by different block composition between PEP and PEO.\(^{58}\) Lund et al. investigated the influence of the interfacial tension (\(\gamma\)) on hairy micelle structures formed by PEP-PEO in several mixtures of water and \(N,N\)-dimethylformamide (DMF).\(^{59}\) The combined results of SANS and pendant drop tensiometry in measuring \(\gamma\) provided the correlation of \(N_{agg} \sim \gamma^{6/5}\), consistent with the scaling prediction. Later, they also studied the evolution of hairy micelles from unimers with PEP-PEO in the water/DMF mixture using time-resolved small-angle x-ray scattering (TR-SAXS).\(^{70}\) Based on the evolution of the SAXS patterns, the scaling relation \(L_{corona} \sim N_{agg}^{1/5}\) was reported, which is in good agreement with the scaling prediction.

As a counterpart of micelles in aqueous solutions, early work on the micelle structure in organic solvents was performed by McConnell et al. using PS-PI in \(n\)-decane.\(^{8,71}\) The micelle cores were characterized by contrast matching between the corona blocks and isotopic solvent mixture, and they examined the relationship between the behavior of order-disorder transitions of micelles in concentrated solutions and the corresponding micelle structure in dilute solutions. With highly asymmetric PS-P4VP diblock copolymers in toluene, Förster et al. investigated the radial density profile of corona blocks.\(^{55}\) The SANS data with the detailed model confirmed that the radial density profile of corona blocks follows the hyperbolic form \(r^{-\alpha}\) (1.05 < \(\alpha\) < 1.35), which is in good agreement with the scaling prediction by Daoud and Cotton. Recently, Bang et al.
systematically studied the temperature-dependent micellar structures of PS-PI dispersed either in diethyl phthalate or in tetradecane with contrast matching method. The authors reported that $N_{\text{agg}}$ and $R_c$ decrease and the solvent content in the core region increases with increasing temperature (i.e., decreasing solvent selectivity), which is similar temperature-dependent behavior to micelles in aqueous solvents. These results also provided quantitative information to understand the thermoreversible fcc to bcc transition observed in concentrated solutions.\textsuperscript{13}

2.2.3 Nonspherical Diblock Copolymer Micelles

As far as thermodynamic properties are concerned, one of the interesting features in block copolymer micelles is the transition between micelle morphologies (e.g., spheres, cylinders, bilayers, and etc.), which also has been observed with low molecular weight surfactant micelles. As the length of hydrophobic tails (i.e., core blocks) increases, the micelle morphologies of the surfactant micelles tend to have the smaller interfacial area per chain, resulting in transitions from spheres to cylinders to bilayers. In a simple description this trend is correlated with a packing parameter ($P$), defined by $P=\frac{v}{l_c a_0}$, where $v$ is the volume of the hydrophobic tails, $l_c$ is the maximum hydrophobic length, and $a_0$ is the interfacial area.\textsuperscript{72}

For diblock copolymer micelles most investigations dealing with the micelle polymorphism have considered two parameters as shown in Figure 2.2: the block ratio and solvent selectivity. Similar to low molecular weight surfactant micelles, the lower-curvature structure is preferred with the larger core block ratio. Systematic investigations of the micelle morphologies as a function of the block ratio were performed using PEO based diblock copolymers (e.g., PEO-PB, PEO-PEE, and PEO-POMCL) or PS-PAA
**Figure 2.2** Schematic figures of micelle morphologies (e.g., sphere, cylinder, and bilayerd vesicle) as a function of (a) the core block ratio (block copolymer composition) and (b) interfacial tension between core block segments and solvents. Reproduced from References 76 and 81, respectively.
dispersed in aqueous media, characterized by TEM.\textsuperscript{73–75} Recently, the systematic transition of micelle morphologies in an ionic liquid was reported using a series of PB-PEO and PS-PMMA copolymers.\textsuperscript{76,77} Notwithstanding that nonergodicity such as coexistence and metastability has been observed due to strong amphiphilicity of core blocks against aqueous or ionic media, the evolution of micelle morphologies is well consistent with the thermodynamic expectation.

In addition, the increase of the solvent selectivity increases the interfacial tension, resulting in the change of the micelle morphologies. The solvent selectivity can be typically tuned by the solvent mixture\textsuperscript{78–82} or temperature\textsuperscript{35,82,83} for nonionic diblock copolymer micelles. For example, Bang et al. studied PS-PI dispersed in a series of solvent mixtures with varying solvent selectivity for PS, and reported the expected sequence of micelle morphologies characterized by the combination of small-angle x-ray scattering (SAXS) and TEM.\textsuperscript{81} LaRue et al. changed temperature to adjust the solvent selectivity, and accordingly to induce the transition between spheres and cylinders formed by PS-PI in heptane,\textsuperscript{83} which was supported by the theoretical prediction.\textsuperscript{35}

\section*{2.3 Dynamics of Block Copolymer Micelles}

In this section, the kinetics of block copolymer micelles are discussed with regard to theoretical predictions and experimental results. Here, it is necessary to introduce two standard mechanisms of molecular exchange kinetics as shown in Figure 2.3: single chain insertion/expulsion, and micelle fusion/fission. For the former mechanism, a single chain is extracted from a micelle, transported through the solvent medium, and inserted into another micelle. For the latter, a micelle can break into two distinct micelles or two small micelles merge to form a large micelle. Most arguments dealing with micelle kinetics have been formulated based on these two mechanisms.
Figure 2.3 Two primary mechanisms of molecular exchange: (a) single chain insertion/expulsion, and (b) micelle fusion/fission.

2.3.1 Theoretical Approaches

The first analytical description of kinetics in low molecular weight surfactant micelles was developed by Aniansson and Wall. The description was based on the experimental results that dilute micelle kinetics are characterized by two well-separated relaxation processes. A fast process was assigned to the single chain exchange between micelles and free chains and a slow process was assigned to the micelle formation/breakdown through step-wise chain insertion/expulsion. Under a small perturbation, the micelles achieve a pseudo-equilibrium via the fast process, followed by attainment of a final equilibrium state via the slow process. The micelle fusion/fission mechanism was excluded in the original theory, but later was considered by Kahlweit et al. Based on these theories, the estimated characteristic times for the proposed processes
are qualitatively in good agreement with experimental data.\(^{87}\)

Compared to low molecular weight surfactant micelles, the relative length and the nature (e.g., entanglement, semicrystalline and glassy state, and etc.) of polymers result in slower dynamics for block copolymer micelles. With the assumption of a small perturbation to the equilibrium state, Halperin and Alexander proposed a theoretical description that polymeric micelles assemble and disassemble by single chain exchange, analogous to the prediction by Aniansson and Wall.\(^{88}\) The authors argued that the micelle fusion/fission mechanism was excluded due to steric hindrance with the presence of sizable coronas. In the theoretical description, the expulsion of a block copolymer from a micelle was described as a two-step process: (i) the block junction leaves the core/corona interface by forming a spherically collapsed state of the core block, and (ii) the copolymer escapes from the corona area. Accordingly, the expulsion rate constant \(k^--\) of this process was expressed as a single exponential decay:

\[
k^- \sim f(N_{\text{core}}, N_{\text{corona}})\exp[-N_{\text{core}}^{2/3} \gamma a^2 / kT], \tag{2.2}
\]

where \(\gamma\) is the interfacial tension between the core block segments and matrix (i.e., the corona block and solvent), \(a\) is a monomer size, and \(f(N_{\text{core}}, N_{\text{corona}})\) is dependent on the micelle characteristics (e.g., hairy micelle, crew-cut micelle). In eq (2.2), the surface area of the collapsed core block is proportional to \((N_{\text{core}}^{1/3} a)^2\), thus \(N_{\text{core}}^{2/3} \gamma a^2\) reflects the enthalpic penalty of exposing the collapsed core block to the matrix at the core/corona interface.

As an extension of the previous prediction, Dormidontova described the micelle kinetics with a large perturbation – micelle formation from unimers in a selective solvent – based on the two aforementioned mechanisms.\(^{89,90}\) According to obtained expressions
for the rate constants of the two mechanisms, micelle fusion/fission, in conjunction with chain insertion/expulsion, plays an important role at the initial stage of micellization to increase the aggregation number. As equilibrium is approached, chain insertion/expulsion becomes gradually dominant over micelle fusion/fission.

Computer simulations have the potential to show the dependence of system variables, such as the block composition, polymer concentration, and interfacial tension, on the micelle kinetics. Wang et al. observed that micelle formation from unimers under weak segregation occurs in two steps with different time scales. The faster step is the formation of micelles with a wide range of sizes, while the second, slower step involves the redistribution of micelle size. This simulation method was extended by Haliloğlu et al. for relatively short block copolymers ($6 < N_{\text{core}} < 12$ and $N_{\text{corona}} = 10$) in a selective solvent under dynamic equilibrium. They considered the two primary mechanisms (i.e., the chain insertion/expulsion and micelle fusion/fission), and their relative contributions to overall dynamics as a function of the copolymer concentration, core block length, and interfacial tension between core block segments and matrix. Relative to chain insertion/expulsion, the micelle fusion/fission mechanism was observed to be negligible at low copolymer concentrations, and dominant at high concentrations.

### 2.3.2 Experimental Results

The earliest experimental studies of the kinetics of block copolymer micelles employed size exclusion chromatography (SEC) as the primary characterization tool. These studies provided the presence of two separate peaks associated with free chains and micelles in block copolymer micellar solutions. However, SEC does not provide quantitative data due to the limitation of this methodology. After these early attempts, several experimental techniques have been exploited for revealing the micelle kinetics.
The results can be categorized into two groups depending on the experimental methodologies employed: dynamic equilibrium exchange kinetics and micellization kinetics. The latter requires either large or small perturbations from the equilibrium state, while the former does not.

- Dynamic Equilibrium Exchange Kinetics

The rate of chain exchange between micelles at equilibrium has been investigated using time-resolved measurements including fluorescence quenching method,\textsuperscript{24,97–103} sedimentation,\textsuperscript{22} and SANS.\textsuperscript{26,28,104–106} For these experiments a pair of block copolymers tagged with different fluorescent or deuterium labels is typically prepared. Micelles from the pair are developed under the same condition, but in separate containers, and the two micelles solutions are then blended. The exchange between differently labeled copolymers results in the change of particular properties measured at a detector, for example, the intensity in the fluorescent quenching and SANS, or the elution time in the sedimentation. The rate of change in the intensity or elution time provides both quantitative and qualitative information about the equilibrium exchange kinetics.

The fluorescence quenching method has been widely applied to measure the micelle kinetics in their equilibrium state, as listed in Table 2.2. Some quantitative results have been reported, but they are inconsistent with each other and controversial. For example, the number of relaxation times ($n$), expressed via exponential functions in the fitting of the data, should suggest the number of dominant mechanisms. In the theoretical descriptions, $n = 1$, associated with single chain insertion/expulsion, was expected in the equilibrium state due to the presence of sizable coronas. The fact that more than two relaxation times ($n \geq 2$) have been observed by the fluorescent quenching method suggests mechanisms other than single chain insertion/expulsion are active. These were
proposed to be either attributable to the presence of the bulky label\textsuperscript{97,102} or to competing micelle fusion/fission,\textsuperscript{100} the latter being supported by computer simulations.\textsuperscript{92}

Sedimentation velocity measurements with PS-PMMA diblock copolymers dissolved in mixtures of water and 1,4-dioxane provided indirect and qualitative information about the chain exchange kinetics.\textsuperscript{22} For this experiment, two different micellar solutions were blended, and their hybridization was identified by sedimentation velocity. They argued that the driving force for the micelle hybridization is the increase of entropy when the two types of block copolymers are mixed within the micelles. However, it should be noted that different thermodynamic properties of two micelle solutions formed by different block copolymers affect the exchange kinetics.

In most cases listed in Table 2.2, the core blocks are glassy (i.e., PS and PMMA) in solid state, and plasticized by non-selective cosolvents to facilitate the chain exchange between micelles at an experimental temperature. Naturally, the presence of frozen or slow kinetics was assumed to be a consequence of kinetic hindrance by a high $T_g$ or entanglement. However, frozen or slow kinetics were reported with rubbery cores such as PI and plasticized PMMA.\textsuperscript{25,103} Rager et al. proposed that this behavior is due to the strong incompatibility between the core blocks and the matrix rather than the kinetic hindrance by glassy cores. Later, Won et al. reported that the micelle structures initially formed by PB-PEO in water are completely frozen, as measured by small-angle neutron scattering.\textsuperscript{26} This work was extended to characterize morphologies of blended micelles formed by a series of PB-PEO block copolymers dissolved in water, measured by TEM.\textsuperscript{27} The authors concluded that the frozen micelles are attributable to the relatively high incompatibility between the core block segments and solvent.
Table 2.2 Summary of studies on the equilibrium exchange kinetics measured by the fluorescent quenching method.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvent</th>
<th>Fluorescence</th>
<th>(n^b)</th>
<th>Variables</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(F)-PS-PEP</td>
<td>heptane/1,4-dioxane</td>
<td>carbazole/anthracene</td>
<td>2</td>
<td>solvent composition, (T = 25 , ^\circ\C)</td>
<td>97</td>
</tr>
<tr>
<td>(F)-PS-PMAA</td>
<td>water/1,4-dioxane</td>
<td>oligovinyl-2-naphthalene</td>
<td>(\sim 4)</td>
<td>solvent composition, (T = 25 , ^\circ\C)</td>
<td>98</td>
</tr>
<tr>
<td>(F)-PS-PtBMA</td>
<td>water/1,4-dioxane</td>
<td>naphthalene/pyrene</td>
<td>2</td>
<td>solvent composition, temperature (23 (, ^\circ\C &lt; T &lt; 40 , ^\circ\C))</td>
<td>100</td>
</tr>
<tr>
<td>PS-(F)-PEO</td>
<td>water/methanol</td>
<td>pyrene</td>
<td>2</td>
<td>solvent composition, temperature (23 (, ^\circ\C &lt; T &lt; 40 , ^\circ\C))</td>
<td>101c</td>
</tr>
<tr>
<td>(F1)-PMAA-PtBMA-(F2)</td>
<td>ethyl acetate/methanol</td>
<td>pyrene (F1), fluorine (F2)</td>
<td>3</td>
<td>solvent composition, copolymer concentration</td>
<td>102</td>
</tr>
<tr>
<td>(F)-PCEMA-PS</td>
<td>THF/Cyclopentane</td>
<td>Pyrene</td>
<td>2</td>
<td>solvent composition, temperature (22 (, ^\circ\C &lt; T &lt; 50 , ^\circ\C)), copolymer concentration, length of two blocks</td>
<td>103</td>
</tr>
<tr>
<td>(F)-PMMA-PAA</td>
<td>water/organic solvent</td>
<td>naphthalene/pyrene</td>
<td>–</td>
<td>solvent composition, organic solvent</td>
<td>103</td>
</tr>
<tr>
<td>(F)-PS-PMA(^{+})Na(^{-})</td>
<td>Water</td>
<td>naphthalene</td>
<td>1(^d)</td>
<td>temperature (22 (, ^\circ\C &lt; T &lt; 60 , ^\circ\C)), cosolvents (dioxane, toluene), cosurfactants</td>
<td>24</td>
</tr>
<tr>
<td>(F)-PtBS-PMA(^{+})Na(^{-})</td>
<td>Water</td>
<td>naphthalene</td>
<td>1(^d)</td>
<td>temperature (22 (, ^\circ\C &lt; T &lt; 60 , ^\circ\C)), cosolvents (dioxane, toluene), cosurfactants</td>
<td>24</td>
</tr>
</tbody>
</table>

\(^a\) (F) denotes the location of the fluorescence.

\(^b\) The number of exponentials used in fitting experimental data.

\(^c\) This experiment was designed to measure the expulsion rate of a single polymer chain under equilibrium, supported by the theoretical expression.\(^{107}\)

\(^d\) The data were fitted with a detailed model.
Richter and coworkers investigated micelle kinetics in the equilibrium state using time-resolved small-angle neutron scattering (TR-SANS) conducted with PEP-PEO diblock copolymers in mixtures of water and DMF; the water/DMF ratio controls the interfacial tension, hence the segregation strength. This technique requires only deuterium labeling and accordingly minimizes experimental artifacts, such as those due to bulky labels or interactions between the different block copolymers. They proposed only the single chain exchange mechanism to explain an observed logarithmic relaxation, and suggested that this behavior reflects a coupling between the core (PEP) block molecular dynamics and the geometric constraints imposed by the spherical core. They also investigated a hydrocarbon system of PS-PB diblocks and PB-PS-PB triblocks dispersed in $n$-alkane solvents, and observed the logarithmic relaxation decay. This implies that the logarithmic relaxation is the universal behavior for chain exchange kinetics.

- **Micellization Kinetics**

Typically, studies of micellization kinetics have monitored the time-resolved response of micelles after an abrupt change in solution micelle condition. As with the equilibrium exchange kinetics, this time-resolved response provides both quantitative and qualitative information. In general, the large difference in scattered intensity before and after the adjustment makes the light scattering (due to the large difference in molecular weight between micelles and unimers) and fluorescence methods promising measurement techniques for investigations of micellization kinetics. In contrast to the equilibrium exchange kinetics, a perturbation is required to change the condition from one state of micelle or unimer equilibrium to another. Experimentally, fast reaction techniques have been selected such as the stop-flow method, where the solvent composition is
altered, temperature jump, and pH jump.

Table 2.3 summarizes some experimental results obtained by light scattering measurements. Most authors agree that two distinct processes are involved in micellization: (i) the fast process ($\tau_1 \sim 0.1-10$ ms) corresponds to the single chain insertion/expulsion to achieve a pseudo equilibrium micelle state, followed by (ii) the slow process ($\tau_2 \sim 1-100$ ms) corresponds to the redistribution of micelle size. In the earliest report, Bednář et al. modeled the obtained time-resolved intensity with a double exponential function, but reported the average value to acquire a sense of the relaxation time in polymeric micelles. The majority of micellization kinetic studies employing light scattering measurements have utilized PEO-PPO-PEO triblock copolymers due to their commercial availability and biocompatibility and because it is not necessary to label such polymers in this measurement. Typical time-resolved intensity data are shown in Figure 2.4, where the fast process, characterized by an increase in the scattered intensity, is attributable to single chain insertion into micelles, and the slow process, characterized by a decrease in scattered intensity, is associated with the micelle size redistribution. Later, Kositza et al. proposed a third relaxation process in micellization – micelle clustering into large aggregates. However Waton et al. suggested that both the second and third processes have the same origin, supported by their theoretical description which reproduces the experimental results of Kositza et al.

Regarding the mechanisms responsible for the two aforementioned processes, most authors agree that the fast process follows the single chain insertion/expulsion. However, the mechanism of the redistribution of micelle size, the second process, has been explained by either the step-wise micelle formation/breakdown via the single chain insertion/expulsion (analogous to the prediction by Aniansson and Wall) or by the micelle fusion/fission. As discussed previously, Dormidontova
argued that the predictions by Aniansson and Wall and Halperin and Alexander considers a small perturbation and accordingly may not be applicable to the experiments described above.

Recently, Lund et al. proposed that the formation and growth of micelles can be described by a nucleation and growth process governed by only the single chain insertion/expulsion mechanism. They investigated the self-assembly process of PEP-PEO in mixtures of water and DMF, characterized by TR-SAXS with stop-flow equipment. This measurement can probe the evolution of structural parameters during micellization, such as $R_{\text{core}}$, $L_{\text{corona}}$, and $N_{\text{agg}}$. The authors observed a time-dependent $N_{\text{agg}}$ by fitting the SAXS pattern with a detailed kinetic model.

Meli et al. studied spherical micelles formed by PB-PEO in ionic liquids, and observed that the micelle dimension is highly dependent on sample preparation procedure. $R_n$ of the micelles at high temperature showed the relaxation behavior
from ~ 60 nm to ~ 30 nm for samples developed by direct dissolution (DD) method, but the constant $R_h$ (~ 10 nm) for samples by cosolvent-assisted (CS), measured by DLS. The fact that single chain exchange is highly restricted, observed by TR-SANS, resulted in that micelle fusion/fission is main mechanism for DD samples.
Table 2.3 Summary of Studies on the micellization kinetics measured by light scattering.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvent</th>
<th>Pert.</th>
<th>n&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Measurement</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-PEP</td>
<td>1,4-dioxane/</td>
<td>S</td>
<td>1</td>
<td>unimer-micelle transition (τ ~ 10 ms)</td>
<td>109</td>
</tr>
<tr>
<td></td>
<td>heptane</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>αMS-PVPA</td>
<td>benzyl alcohol</td>
<td>T</td>
<td>2</td>
<td>unimer-micelle transition</td>
<td>111,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>micelle-micelle transition (τ&lt;sub&gt;1&lt;/sub&gt; ~ 0.1 hr, τ&lt;sub&gt;2&lt;/sub&gt; ~ 10 hr)</td>
<td>112</td>
</tr>
<tr>
<td>PEO-PPO-PEO</td>
<td>water</td>
<td>T</td>
<td>1</td>
<td>unimer-micelle transition (τ ~ 1 ms)</td>
<td>113</td>
</tr>
<tr>
<td>PEO-PPO-PEO</td>
<td>water</td>
<td>T</td>
<td>2</td>
<td>micelle-micelle transition (τ&lt;sub&gt;1&lt;/sub&gt; ~ 0.1–10 ms, τ&lt;sub&gt;2&lt;/sub&gt; ~ 1–100 ms)</td>
<td>114</td>
</tr>
<tr>
<td>PEO-PPO-PEO</td>
<td>water</td>
<td>T, S</td>
<td>3</td>
<td>unimer-micelle transition (τ&lt;sub&gt;1&lt;/sub&gt; ~ 0.01–1 ms, τ&lt;sub&gt;2&lt;/sub&gt;, τ&lt;sub&gt;3&lt;/sub&gt; ~ 1–100 ms)</td>
<td>110,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>115</td>
</tr>
<tr>
<td>PEO-PPO-PEO</td>
<td>water</td>
<td>T</td>
<td>2</td>
<td>unimer-micelle transition (τ&lt;sub&gt;1&lt;/sub&gt; ~ 0.1–10 ms, τ&lt;sub&gt;2&lt;/sub&gt; ~ 1–100 ms)</td>
<td>116,</td>
</tr>
<tr>
<td>PDEA-PDMA</td>
<td>water</td>
<td>pH</td>
<td>3</td>
<td>unimer-micelle transition (τ&lt;sub&gt;1&lt;/sub&gt; ~ 4 ms, τ&lt;sub&gt;2&lt;/sub&gt; ~ 200 ms, τ&lt;sub&gt;3&lt;/sub&gt; ~ 10 s)</td>
<td>118</td>
</tr>
</tbody>
</table>

<sup>a</sup> The perturbation was induced by changing solvent composition (S), temperature (T), or pH.

<sup>b</sup> The number of the relaxation process proposed by the authors.
### Table 2.4 Abbreviations for all of the polymers discussed in Chapter 2

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>polystyrene</td>
<td>PS</td>
</tr>
<tr>
<td>Polyisoprene</td>
<td>PI</td>
</tr>
<tr>
<td>polybutadiene</td>
<td>PB</td>
</tr>
<tr>
<td>polyethylene</td>
<td>PEE</td>
</tr>
<tr>
<td>poly(ethylene-\textit{alt}-propylene)</td>
<td>PEP</td>
</tr>
<tr>
<td>poly(4-vinylpyridine)</td>
<td>P4VP</td>
</tr>
<tr>
<td>poly(2-cinnamoyl ethyl methacrylate)</td>
<td>PCEMA</td>
</tr>
<tr>
<td>poly(ethylene oxide)</td>
<td>PEO</td>
</tr>
<tr>
<td>poly(propylene oxide)</td>
<td>PPO</td>
</tr>
<tr>
<td>poly(methyl methacrylate)</td>
<td>PMMA</td>
</tr>
<tr>
<td>poly(γ-methyl-ε-caprolactone)</td>
<td>POMCL</td>
</tr>
<tr>
<td>polydimethylsiloxane</td>
<td>PDMS</td>
</tr>
<tr>
<td>poly(acrylic acid)</td>
<td>PAA</td>
</tr>
<tr>
<td>poly(methacrylic acid)</td>
<td>PMAA</td>
</tr>
<tr>
<td>poly(\textit{tert}-butyl methacrylate)</td>
<td>PtBMA</td>
</tr>
<tr>
<td>poly(\textit{tert}-butyl styrene)</td>
<td>PtBS</td>
</tr>
<tr>
<td>poly(sodium methacrylate)</td>
<td>PMA\textsuperscript{Na\textsuperscript{+}}</td>
</tr>
<tr>
<td>poly(\textit{α}-methyl styrene)</td>
<td>PaMS</td>
</tr>
<tr>
<td>poly(vinylphenethyl alcohol)</td>
<td>PVPA</td>
</tr>
<tr>
<td>poly(2-(diethylamino)ethyl methacrylate)</td>
<td>PDEA</td>
</tr>
<tr>
<td>poly(2-(dimethylamino)ethyl methacrylate)</td>
<td>PDMA</td>
</tr>
</tbody>
</table>
2.4 References


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Chapter 3

Experimental Section

In this study, a model block copolymer should meet four criteria to make experiments feasible and reasonable: (i) a core block should be glassy in a model solvent at room temperature to lock the micelle structure during blending process, (ii) the glass transition temperature \((T_g)\) of the core block should be within the experimentally available temperatures, (iii) the critical micelle temperature (CMT) should be higher than \(T_g\) of the core block to distinguish core block dynamics from the change of micelle structure, and (iv) the block copolymer should be stable at experimental temperatures. Considering the above four criteria, poly(styrene-\(b\)-ethylene-\(alt\)-propylene) (PS-PEP) diblock copolymer and squalane were selected as the model polymer and solvent, respectively. In this chapter, the synthesis and characterization of block copolymers will be discussed, followed by experimental techniques to characterize block copolymer solutions.

3.1 Synthesis of Block Copolymers

PS-PEP diblock copolymers were prepared by an anionic polymerization of poly(styrene-\(b\)-isoprene) (PS-PI), followed by a selective saturation of the polyisoprene using Ni/Al catalyst. General scheme is illustrated in Figure 3.1.
3.1.1 Anionic Polymerization

Living anionic polymerization is a useful method to synthesize well-defined block copolymers. Under the ideal condition where any impurities (i.e., protic and basic compounds) do not exist, active sites (i.e., carbanions) are living for a sufficiently long time. Lack of termination makes it possible to control the molecular weight with a narrow distribution, a specified block composition and a predetermined molecular architecture. Following initiation with an appropriate initiator (i.e., sec-butyl lithium), monomers are added to the active sites ideally until complete consumption of the monomers. Thus, the sequential addition of different monomers to the reactor results in a block copolymer with narrow molecular weight distribution and a predictable molecular weight. Termination of the active sites is simply done by injection of suitable acidic-proton sources (i.e., water or alcohol). The concept of anionic polymerization is so simple that the molecular weight can be easily estimated by the ratio of the initial monomer concentration to the injected initiator concentration. The polydispersity index (PDI = $M_n/M_w$, where $M_n$ and $M_w$ is the
number-averaged molecular weight and weight-averaged molecular weight, respectively) can be approximated by the Poisson distribution.

The anionic polymerization of PS-PI begins with the purification of monomers. The first step was degassing of monomers three times to remove oxygen and carbon dioxide by the freeze/pump/thaw technique. This step was performed by pulling vacuum when the monomers were frozen in a liquid nitrogen bath. Degassing was followed by mixing with a suitable purification agent (i.e., weak anionic initiator) to remove any acidic impurities. An inappropriate match between the purification agent and the monomer may cause significant polymerization of the monomer during the purification step. In this study, \( n \)-butyl lithium and di-butyl magnesium were selected for isoprene and styrene, respectively. This step was accompanied by mixing the degassed isoprene monomer and the \( n \)-butyl lithium in a flask at 0 °C (with an ice bath) for 30 min. Then, the isoprene monomer was transferred to another flask containing the dried agent via vacuum transfer. After two successive treatments with the purification agent, a designated amount of the isoprene monomer was collected in a burette. In a similar way, styrene monomer was purified and collected in a burette, but using di-butyl magnesium as the purification agent at 40 °C.

Cyclohexane solvent was purified by passing it through two purification columns, packed with copper-alumina redox catalyst to remove oxygen and activated alumina to remove polar impurities such as water.\(^4\)

A Pyrex glass reactor (c.a. 1–2 L) was assembled by attaching two monomer burettes and the solvent flask, followed by the removal of any impurities through several heating, vacuum, and purging argon cycles. A water bath was placed under the reactor to maintain the reactor temperature of 40 °C. After charging the reactor with argon, cyclohexane was added, followed by the addition of initiator using a syringe. In this study \( sec \)-butyl lithium
was used as the initiator due to good solubility in hydrocarbon (non-polar) solvents and strong nucleophilicity. A measured amount of isoprene was polymerized for at least 8 h, then an aliquot (~3 ml of solution) was extracted from the reactor and terminated in degassed methanol. The PI block was analyzed using size exclusion chromatography (SEC) calibrated with ten PS standards to provide molecular weight and PDI of the PI block. Styrene monomer was then added to the reactor and allowed to react for at least 8 hours. As soon as the styrene monomer was added, the solution turned orange indicating the existence of living polystyryl anions. Degassed methanol was injected into the reactor to terminate the living sites. The polymer was recovered by precipitation in methanol, which is a poor solvent for the polymer, but can dissolve impurities such as lithium ions or small molecules. Then the block copolymer was dried under vacuum. Because the reactivity ratios for addition of styrene to isoprenyllithium, and vice versa, are similar, either sequence of reactions can be used to prepare PS-PI diblock copolymers.

### 3.1.2 Selective Saturation

According to the four criteria, the PI block needs to be saturated to achieve thermal and oxidative stability while the phenyl group in the PS block is retained to keep $T_g$ of around 100 °C ($T_g$ of its saturated equivalent is around 145 °C). Homogeneous and heterogeneous catalytic and non-catalytic methods to achieve this product are well documented.\(^5\)\(^{-7}\) Homogeneous catalysts show high activity, reproducibility, and selectivity for PI because of higher solubility and less possibility of catalyst poisoning. Nickel-Aluminum coordination catalysts have been employed in this study to saturate polyisoprene selectively in the PS-PI diblock copolymers.\(^8\)\(^,\)\(^9\)

The reactions were performed in a 1 L stainless steel reactor described elsewhere.\(^7\) After the reactor was assembled, argon was purged into the reactor to remove air (i.e.,
oxygen and water molecules). A polymer solution was prepared with about 10 g of a dried polymer in 500 mL purified cyclohexane and injected into the reactor using a cannula. The Ni/Al catalyst solution was prepared by slowly injecting 6 mL of triethylaluminum (TEA) into 20 mL of 0.1 M nickel 2-ethylhexanoate dissolved in a purified cyclohexane using a syringe. Since the reaction is exothermic, this reaction was performed in an ice bath. During addition of TEA, the solution turned from pale green to dark brown. The catalyst solution was transferred into the reactor with a wide bore needle and a syringe. Then the reactor was charged with high purity hydrogen (300–400 psi) and heated to and held at 77 °C for at least 24 h. After the reaction was done, the catalyst was extracted by stirring with 1000 mL aqueous citric acid (8 wt%) until the mixture turned white. The upper organic phase (in cyclohexane) was separated from aqueous phase and filtered with basic alumina (Sigma Aldrich) to remove residual water and citric acid. The PS-PEP diblock copolymers were recovered by precipitation in methanol.

3.2 Characterization of Block Copolymers

3.2.1 Size Exclusion Chromatography (SEC)

Size exclusion chromatography (SEC), also known as gel permeation chromatography (GPC) is a method typically used for the characterization of molecular weight and molecular weight distribution. Macromolecules with different hydrodynamic radii in a mobile phase are separated by passing through the SEC column packed with cross-linked gel particles or glass beads of various pore sizes. Smaller molecules experience more permeation to the porous stationary phase than larger ones. Thus, the largest molecules elute first through the column, followed by elution of sequentially smaller polymer molecules. A detector (i.e., RI and UV) is placed at the end of the
column and measures the polymer concentration as a function of time. The molecular
weight was calculated according to the universal calibration with the assumption that the
retention volume depends only on hydrodynamic volume regardless of the detailed
structure or shape. Representative SEC traces are illustrated in Figure 3.2 in which SI(42-
60) with molecular weight 42,000 g/mol of PS and 60,000 g/mol of PI elutes later than its
saturated equivalent SEP(42-60).

In this study, the molecular weight of first PI block was characterized by the universal
calibration of ten PS standards using SEC. Then combination of the block volume
fraction measured by $^1$H-NMR and the molecular weigh of the first PI block was used
to determine the total molecular weight of the diblock copolymers. The polydispersity
index (PDI) of all the diblock copolymers was determined using this method.

### 3.2.2 Nuclear Magnetic Resonance (NMR)

Nuclear magnetic resonance (NMR) spectroscopy was used to determine the block
mole fractions and microstructure. The various chemical shifts evidenced by NMR
spectra arise because the local magnetic fields experienced by protons is dependent on
the molecular structure near the protons.$^{10}$ Figure 3.3 illustrates representative NMR
spectra of SI(42-60) and SEP(42-60) dissolved in deuterated chloroform at room
temperature. Broad chemical shifts at 6.6 and 7.2 ppm are associated with hydrogens
attached to the phenyl group. PI is comprised of three isomers: 1,4 unit including cis and
trans, 3,4 unit and 1,2 unit, which correspond to chemical shifts at 5.1 ppm, 4.7 ppm, and
4.8 ppm, respectively. The amount of saturated PI was determined by reduction of PI
peaks near chemical shift of 4.7 – 5.1 ppm and appearance of peaks near 0.9 ppm. A
sharp peak near 7.26 ppm is attributed to a solvent (i.e., chloroform).
Figure 3.2 SEC traces of SI(42-60) and SEP(42-60).

Figure 3.3 Molecular structure and $^1$H-NMR spectra of SI(42-60) and SEP(42-60).
Since the integrated area ($A$) below a peak corresponds to the relative number of hydrogen atoms belonging to a particular structure, the percentage of 1,4 units in PI in SI(42-60) can be calculated as:

$$\text{Mol\% of 1,4 unit} = \frac{A(5.1)}{A(5.1) + \frac{A(4.7)}{2}} = \frac{41.05}{41.05 + \frac{5.73}{2}} = 93.5\%$$

The mole percentage of styrene is calculated from

$$\text{Mol\% PS} = \frac{\left[A(7.02) + A(6.6)\right]}{5} + \frac{\left[A(5.1) + \frac{A(4.7)}{2}\right]}{5} = \frac{100}{5 + \frac{41.05 + \frac{5.73}{2}}{5}} = 31.3\%$$

The corresponding volume fraction of PS ($f_{PS}$) is computed, based on published densities for PS (= 1.047 g/cm$^3$) and PI (= 0.913 g/cm$^3$) at room temperature,$^{11}$

$$f_{PS} = \frac{(0.313\text{mol\%})(104.15 \text{ g/mmol})}{1.047 \text{ g/cm}^3} = \frac{(0.687\text{mol\%})(68.12 \text{ g/mmol})}{0.913 \text{ g/cm}^3} = 0.38$$

where the monomer molecular weight of PS and PI are 104.15 g/mol and 68.12 g/mol, respectively.
3.3 Rheology

Polymer melts and solutions are viscoelastic materials that have properties intermediate to solids (elastic) and liquids (viscous)\textsuperscript{3,12}. The frequency-dependent response to an applied deformation depends on the material characteristics such as microstructure if ordered. Therefore, rheology is a powerful tool to investigate phase transitions such as order-order transitions (OOT) or order-disorder transitions (ODT) by measuring the dynamic storage modulus $G'$ and the dynamic loss modulus $G''$ using a sinusoidal oscillation.

Two types of mechanical spectroscopy measurements are commonly applied to investigate block copolymer materials. The isochronal temperature ramping test measures $G'$ and $G''$ with increasing or decreasing temperature at fixed frequency and strain. $T_{\text{ODT}}$ and $T_{\text{OOT}}$ are assigned where $G'$ increase or decrease abruptly. The frequency should be kept at a sufficiently low level (e.g., $\omega = 0.5 – 1$ rad/s), and the strain should also be maintained within the linear viscoelastic regime (e.g., 0.1 – 1 %). A temperature ramping rate of 0.5 – 1 °C/min is usually applied to allow the sample to equilibrate during heating or cooling. The second type of measurement is the isothermal frequency sweep test where $G'$ and $G''$ are measured as a function of frequency at a fixed temperature. The frequency sweep data measured at multiple temperatures are often superimposed to a single reference temperature using the time-temperature superposition principle. This is not rigorously valid for microphase separated block copolymer materials since each domain is characterized by different $T_g$s and shift factors\textsuperscript{13,14}. Nevertheless, it provides a useful way to reduce data to a single form. Both $G'$ and $G''$ are sensitive to microdomain structure at lower frequencies ($\omega < \omega_c$ where $\omega_c$ is a critical frequency for the material). A homogeneous (disordered) block copolymer follows $G' \sim \omega^2$ and $G'' \sim \omega$ below $\omega_c$, which is the characteristic behavior of liquids. Triply periodic morphologies such as bcc
Figure 3.4 Schematic frequency-dependent behavior of the storage modulus ($G'$) for disordered and other ordered structures. Reproduced from Reference 16.

and gyroid produce an elastic plateau ($G' \sim \omega^0$) for $\omega < \omega_c$. Lamellae follow the scaling relationship of $G' \sim \omega^{1/2}$, and the two-dimensional hexagonally packed cylinders often yield $G' \sim \omega^{1/3}$. Thus, phase transitions between ordered states leads to failure of time-temperature superposition at low frequencies ($\omega < \omega_c$). Rheological responses from various microstructures of block copolymers are summarized in Figure 3.4. Although the rheological response with frequency is a good indicator to provide identification of microstructure, conclusive evidences should be achieved by complimentary experiments such as small-angle scattering (SAXS and SANS) and transmission electron microscopy (TEM).

In this study, rheological measurements were performed with a Rheometric Scientific ARES strain-controlled instrument equipped with a parallel plate (typically 25 mm in
diameter and 0.5–1.5 mm in gap) for ordered (concentrated) samples and a Rheometrics RFS II rheometer with a cup-and-bob geometry (34 mm cup and 32 mm bob) for disordered (dilute) samples. The ARES rheometer has the lowest level for detectable torque of 0.2 g/cm. If the torque is smaller than the lowest limit, the plate should be replaced with larger diameter plate for more reliable measurement. Since temperature was controlled by a convection oven with nitrogen ranging from –50 °C to 300 °C, the solvent evaporation should be considered when polymer solutions are measured at higher temperature. For the Rheometrics RFS II rheometer, temperature was controlled by a circulating water system between room temperature and 100 °C. In all measurements, the samples were equilibrated at target temperatures for at least 5 min.

3.4 Dynamic Light Scattering (DLS)

Static and dynamic light scattering (SLS and DLS) are widely used to characterize polymer solutions. SLS provides an absolute measurement of weight-averaged molecular weight (\(M_w\)) of particles (single chain or micelle), and the second virial coefficient (\(A_2\)), if the refractive index increment (\(\partial n/\partial c\)) is known. The radius of gyration (\(R_g\)) of isolated particles also can be estimated using a Guinier plot at low angle (\(qR_g < 1\), where \(q\) is wavevector defined as \(q = 4\pi\lambda^{-1}\sin(\theta/2)\)) if the solution is sufficiently dilute to ignore inter-particle contributions. DLS, also known as quasi-elastic light scattering, provides dynamic properties (e.g., diffusion coefficient) of polymers in the dilute and semi-dilute solution regime. The fluctuations in scattered intensity against the background detected by DLS are related to changes in the spatial distribution of the particles (thus, fluctuations in composition).

The amplitude of the scattered light wave \(E_s(q,t)\) emanating from \(N\) particles at time \(t\)
in a solution can be defined as

\[ E_s(q,t) = \sum_{i=1}^{N} b_i \exp[-i q \cdot r_i(t)], \quad (3.1) \]

in which \( b_i \) is the contrast factor of particle \( i \) (refractive index difference against background for light scattering), and \( r_i(t) \) is the relative position of particle \( i \) to the origin at time \( t \). The time autocorrelation of the scattered wave can be expressed by the degree of correlation at time \( \tau \) and \( t+\tau \), \( \langle E_s(\tau)E_s^*(t+\tau) \rangle \). Particularly, the normalized autocorrelation function of the scattered electric amplitude \( g^{(1)}(q,t) \) is defined as

\[ g^{(1)}(q,t) = \frac{\langle E_s(\tau)E_s^*(t+\tau) \rangle}{\langle |E_s(\tau)|^2 \rangle} = \frac{1}{\langle |E_s(t)|^2 \rangle} \lim_{T \to \infty} \int_0^T E_s(\tau)E_s^*(t+\tau) d\tau, \quad (3.2) \]

in which the bracket indicates an ensemble average over time. For the sake of convenience, a dynamic structure factor \( S(q,t) \) is defined as

\[ S(q,t) = \frac{1}{N^2} \sum_{i=1}^{N} \sum_{j=1}^{N} \langle b_i b_j \exp[-i q \cdot (r_i(t) - r_j(0))] \rangle, \quad (3.3) \]

then \( g^{(1)}(q,t) \) is expressed as \( S(q,t)/S(q,0) \). However DLS measures not amplitude fluctuations, but intensity fluctuations. Therefore, the normalized autocorrelation function of the scattered intensities \( g^{(2)}(q,t) \) were converted into \( g^{(1)}(q,t) \) by the Siegert relation expressed as\(^2\)

49
\[ g^{(2)}(q,t) = \frac{\langle I_s(\tau)I'_s(\tau + \tau) \rangle}{\langle I'_s(\tau) \rangle^2} = 1 + \beta |g^{(1)}(q,t)|^2, \tag{3.4} \]

where \( \beta \) is the coherence factor which ranges from 0 to 1.

For a monodisperse particle in dilute solution, the \( g^{(1)}(q,t) \) is expressed by a single exponential function as

\[ g^{(1)}(q,t) = \exp[-\Gamma t] = \exp[-q^2D_m t], \tag{3.5} \]

where \( \Gamma \) is a decay rate and \( D_m \) is a mutual diffusion coefficient. As the concentration of solution goes to zero, the mutual diffusion coefficient becomes the translational diffusion coefficient \( D_0 \). Combination of the diffusion coefficient and the solvent viscosity \( (\eta_s) \) yields the hydrodynamic radius \( (R_h) \) based on the Stokes-Einstein equation,

\[ R_h = \frac{kT}{6\pi\eta_D}. \tag{3.6} \]

For a polydisperse system, \( g^{(1)}(q,t) \) can be expressed as the weighted sum of the individual contributions.

\[ g^{(1)}(q,t) = \int_0^\infty G(\Gamma) \exp[-\Gamma t] d\Gamma, \tag{3.7} \]

where \( G(\Gamma) \) is a distribution function of the decay rates. Several procedures have been developed to interpret data obtained from polydisperse samples. A cumulant method
provides an averaged decay rate and distribution using a power series expressed as

\[ g^{(1)}(q,t) = \exp \left( -\Gamma t \left( 1 + \frac{\mu_2}{2!} \left( \frac{\Gamma t}{\overline{\Gamma}} \right)^2 - \frac{\mu_3}{3!} \left( \frac{\Gamma t}{\overline{\Gamma}} \right)^3 \right) \right), \]  

(3.8)

where \( \overline{\Gamma} \) is a mean of \( \Gamma \) in terms of the distribution \( G(\Gamma) \), and \( \mu_2 \) and \( \mu_3 \) are combinations of moments about the mean. The cumulant analysis is one of the useful methods to measure particle sizes and distribution (= \( \mu_2/\Gamma^2 \)) when the particle sizes are narrowly distributed.

Another procedure is to perform inverse Laplace transform of eq (3.7). Although this is ill-conditioned due to noise and rounding errors, the inverse Laplace transform with limited time scale can provide a reasonable particle size distribution as used in CONTIN and REPES.\(^{26}\)

The polymer solutions were filtered through 0.2 µm filters to remove dust, and sealed in 0.25 in. tubes under vacuum. The solutions were investigated using home-built goniometer equipped with a silicon oil index-matching bath, an electric heater (25 – 200 °C), a Brookhaven BI-DS photomultiplier, a Lexel 95-2 Ar+ laser operating at 488 nm and a Brookhaven BI-9000 correlator. At a target temperature, samples were annealed for more than 10 minutes and measured for at least 5 min.

### 3.5 Small-Angle Scattering

Small angle x-ray scattering (SAXS) and small angle neutron scattering (SANS) are powerful tools to investigate block copolymer solutions and melts (characteristic length
scale of 10–1000 Å) because the wavelength ($\lambda$) is of order 1 Å.\textsuperscript{27,28} For polymer solution, DLS is easier to perform and gives valuable characteristics of the materials as discussed in the previous section. SAXS and SANS, however, give more detailed information about shorter length scale from 5 to 500 Å such as core radius, the distribution of core radius, and the shape of corona. SAXS and SANS also provides dimension and symmetry for microstructured polymer materials.

Most theoretical descriptions developed for the interpretation of small angle scattering can be equally employed to both types of radiation (i.e., x-ray and neutron). Figure 3.5 illustrates a general scheme of scattering by two particles separated by a distance $r_{jk}$. The amplitude of the incident traveling wave in the direction $k_i$ at a position $r$ and a time $t$ is expressed by

![Diagram of small angle scattering](image)

**Figure 3.5** Schematic geometry of small angle scattering by two particles and path difference.
\[ A(r, t) = A_0 \exp[i(\omega t - k \cdot r)], \]  

(3.9)

where \( A_0 \) is the amplitude, and \( \omega \) is the angular frequency \((= 2\pi v)\). \( k_i \) and \( k_s \) are the wavevectors of the incident and scattered beam, respectively and their magnitudes are expressed as \( 2\pi/\lambda \).

In this study, we consider only coherent elastic scattering. Elastic scattering involves no energy transfer between the beam and particles, hence the wavelength before and after the scattering remains unchanged (i.e., \( \lambda_i = \lambda_s \)). The phase difference \( (\delta_{jk}) \) between two scattered waves is dependent on the path length difference expressed as \( d_k - d_j \), each of which are the projection of \( r_{jk} \) on a unit vector of \( k_i \) and \( k_s \), respectively, as shown in Figure 3.5:

\[ \delta_{jk} = \frac{2\pi |d_k - d_j|}{\lambda} = q \cdot r_{jk}, \]  

(3.10)

where \( q \) is the wavevector defined as \( q = 4\pi \lambda^{-1} \sin(\theta/2) \). In Figure 3.5, the superimposed wave that reaches the detector is the sum of two scattered waves from particle \( j \) and \( k \). In general, the amplitude of scattered beam from a sample containing \( N \) identical particles placed at position \( r_i \) \((i = 1, 2, \ldots, N)\) is given by

\[ A(q) = b \sum_{i=1}^{N} \exp[-iq \cdot r_i], \]  

(3.11)

in which \( A(q) \) is the normalized amplitude by \( A_0 \), and \( b \) is the scattering length. The
intensity \((I(q))\) is given by \(A(q)A^*(q)\), where \(A^*(q)\) is the complex conjugate of \(A(q)\), and accordingly expressed as

\[
I(q) = \sum_{i=1}^{N} \sum_{j=1}^{N} b_i b_j \exp[-iq \cdot (r_i - r_j)].
\]

Eq (3.12) indicates that the intensity is independent of the choice of the origin because only the difference, \(r_i - r_j\), appears in the final expression. The intensity actually measured by the detector is averaged over time due to the thermal motion of the scattering center during a scattering measurement.

In general a polymer molecule includes several scattering centers. Therefore, the intensity of \(N\) identical macromolecules composed of \(z\) scattering centers in solution can be defined as

\[
I(q) = (\Delta\rho)^2 v^2 \sum_{p=1}^{N} \sum_{q=1}^{N} \sum_{i=1}^{z} \sum_{j=1}^{z} \langle \exp[-iq \cdot (r_{p,i} - r_{q,j})] \rangle,
\]

where \(v\) is the volume of the scattering center, and \(\Delta\rho\) is the excess scattering length density of the particle against background (i.e., \(\Delta\rho = (b/v)_{\text{particle}} - (b/v)_{\text{background}}\)). The angular bracket \(< >\) indicates an ensemble average over the values. The quadruple summation includes \(N\) terms of intra-particle contribution \((p = q)\) corresponding to the interferences of two scattering centers on the same macromolecule, and \(N(N-1)\) terms of inter-particle contribution associated with the interferences of two scattering centers on different macromolecules. When \(N\) is large, \(N(N-1)\) can be replaced with \(N^2\). Therefore, the intensity can be rewritten as
\[ I(q) = (\Delta \rho)^2 \nu^2 \left\{ N \sum_{i=1}^{\tilde{z}} \sum_{j=1}^{\tilde{z}} \exp[-iq \cdot \tilde{r}_{n_i,j}] \right\} + N^2 \sum_{i=1}^{\tilde{z}} \sum_{j=1}^{\tilde{z}} \exp[-iq \cdot \tilde{r}_{n_i,j}] \right\}. \quad (3.14) \]

The first term in right-hand side depends on the shape and size of the macromolecule, while the second term relates with inter-particle interaction. For the sake of convenience, \( P(q) \) and \( Q(q) \) are defined as

\[ P(q) = \frac{1}{\tilde{z}^2} \sum_{i=1}^{\tilde{z}} \sum_{j=1}^{\tilde{z}} \exp[-iq \cdot \tilde{r}_{n_i,j}] \quad (3.15) \]
\[ Q(q) = \frac{1}{\tilde{z}^2} \sum_{i=1}^{\tilde{z}} \sum_{j=1}^{\tilde{z}} \exp[-iq \cdot \tilde{r}_{n_i,j}] \quad (3.16) \]

Therefore,

\[ I(q) = (\Delta \rho)^2 \nu^2 \left\{ Nz^2 P(q) + N^2 z^2 Q(q) \right\} \quad (3.17) \]

\( Q(q) \) is related to the radial distribution function by introducing a form factor amplitude \( F(q) \) and a static structure factor \( S(q) \).

\[ F(q) = \frac{1}{z} \sum_{i=1}^{\tilde{z}} \exp[-i\tilde{q} \cdot \tilde{r}_{0i,n}] \quad (3.18) \]
\[ S(q) = \frac{1}{N} \sum_{a=1}^{N} \sum_{\beta=1}^{N} \exp[-i\tilde{q} \cdot \tilde{r}_{0\beta,0\beta}] \quad (3.19) \]

where \( \tilde{r}_{0i} \) denotes the center of a particular macromolecule 1. In eq (3.16), \( \tilde{r}_{n_i,j} \) can be
expressed as the sum of three vectors such as \( \vec{r}_{i,1} = \vec{r}_{i,01} + \vec{r}_{01,02} + \vec{r}_{02,j} \). Therefore, eq (3.17) can be rewritten as

\[
I(q) = (\Delta \rho)^2 v^2 z^2 N P(q) \left[ 1 + \frac{|F(q)|^2}{P(q)} (S(q) - 1) \right]
\]

(3.20)

For the uniform density particles, \( P(q) = |F(q)|^2 \), resulting in the well-known result,

\[
I(q) = (\Delta \rho)^2 v^2 z^2 NP(q) S(q).
\]

(3.21)

Eq (3.21) will be modified to fit small-angle scattering (SANS and SAXS) data obtained from dilute micelle solutions in Chapter 4 and Chapter 5, and from ordered micelle solutions in Chapter 6. Micelle properties such as a core radius, aggregation number, and hard-sphere radius can be extracted with a detailed model.\(^{29-32}\) More detailed expressions will be provided in Chapter 4 and Chapter 6.

With SAXS and SANS, morphologies formed by block copolymers in concentrated solutions can be identified based on \( S(q) \) in eq (3.19) or \( Q(q) \) in eq (3.16). In a simple description the Bragg’s law gives a good starting point to provide the reason that the constructive interference occurs at a certain angle. Consider two incident plane waves: one reflects at the top plane and the other at nearest neighbor plane with interplanar spacing \( D \). The reflected wave at the top plane interferes with that at the other plane, which must travel an additional distance \( = 2D \sin(\theta/2) \), where \( (\theta/2) \) is an incident angle. Constructive interference occurs when the path difference between two incident waves of \( 2D \sin(\theta/2) \) is equal to \( n\lambda \) where \( n \) is an integer, resulting in sharp peaks in scattering patterns. Here Bragg’s law can be expressed as
where hkl is the Miller index of the plane for a given symmetry.\textsuperscript{33,34} The morphology of ordered structure can be determined by the sequence of peak ratio to primary $q^*$ (i.e., $q/q^*$). The 230 space groups and the associated allowed reflections are tabulated in the International Tables for Crystallography.\textsuperscript{35} The allowed reflections for the known morphologies in diblock copolymers are listed in Table 3.1 and SAXS data obtained from ordered diblock copolymer in solution will be provided in the Chapter 8.

Although x-ray and neutron scattering show similar behavior in many ways, some important differences make the two methods complementary to each other. One of the major differences is the energy of the sources. The energy of hard x-rays is an order of 10 keV, while for similar wavelength neutrons it is 10 meV. Considering the average energy associated with the atomic motion (~20 meV at room temperature), x-ray photons are hardly affected by the atoms, leading to negligible energy transfer when scattered. The energy of neutrons, however, can be modified considerably, resulting in significant inelastic scattering. Therefore, the atomic motion, related to dynamics of the atoms, can be measured by neutron scattering with instruments such as neutron spin-echo or backscattering spectrometers. Here, at low scattering angles where $q (= k_s - k_i)$ approaches zero, simultaneous conservation of momentum and energy dictates nearly elastic (quasielastic) scattering.

X-rays and neutrons scatter from condensed matter by different mechanisms: x-rays scatter from electrons and neutrons scatter from nuclei. The strength of the interaction is characterized by a property called as a scattering length. The scattering length for SAXS
Table 3.1 Allowed reflections for known morphologies in diblock copolymers

<table>
<thead>
<tr>
<th>Morphology</th>
<th>Allowed reflections</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lamellar</td>
<td>1 : 2 : 3 : 4 : 5 : 6 ⋯</td>
</tr>
<tr>
<td>Gyroid (Ia3d)</td>
<td>( \sqrt{3} : \sqrt{4} : \sqrt{7} : \sqrt{8} : \sqrt{10} : \sqrt{11} : \sqrt{12} : \sqrt{13} : \sqrt{15} \cdots )</td>
</tr>
<tr>
<td>Hexagonal-packed cylinder</td>
<td>1 : ( \sqrt{3} : \sqrt{4} : \sqrt{7} : \sqrt{9} : \sqrt{12} : \sqrt{13} \cdots )</td>
</tr>
<tr>
<td>Body-centered cubic</td>
<td>1 : ( \sqrt{2} : \sqrt{3} : \sqrt{4} : \sqrt{5} : \sqrt{6} : \sqrt{7} : \sqrt{8} : \sqrt{9} \cdots )</td>
</tr>
<tr>
<td>Face-centered cubic</td>
<td>( \sqrt{3} : \sqrt{4} : \sqrt{8} : \sqrt{11} : \sqrt{12} : \sqrt{16} : \sqrt{19} : \sqrt{20} : \sqrt{24} \cdots )</td>
</tr>
</tbody>
</table>

depends on the electron density of the material, thus is a function of atomic number. However, the scattering length for SANS is determined by neutron-nuclear interaction, thus is not simply a function of atomic number. For example, the scattering length of hydrogen and deuterium are remarkably different for SANS, but the physical properties of the two are nearly identical. As a consequence deuterium labeling provides a simple, but powerful method to investigate polymer materials with neutron scattering.

Another difference is the nature of incoherence in scattering. If scattered radiation does not contain information about the structural arrangement within a sample, it is called incoherent scattering. For SAXS, the incoherent scattering is introduced by the inelastic Compton-modified scattering due to the particle nature of x-rays. However, the random variability in the spin state (i.e., parallel and antiparallel neutron and nuclear spins) gives rise to the incoherent scattering for SANS. This incoherent scattering is \( q \)-independent and contributes only to the noise level of the measurements, therefore can be subtracted using scattering from background (e.g., solvent).
SAXS was performed using beam line 5ID-D, at the DuPont-Northwestern-Dow (DND-CAT) station at the Advanced Photon Source, Argonne National Laboratory. A tunable radiation energy between 9 keV and 17 keV, corresponding to a wavelength $\lambda = 0.73 - 1.54$ Å, was selected from an undulated beam using a double-crystal monochromator, and the sample to detector distance was adjusted to access the necessary $q$ range. Two-dimensional SAXS patterns were collected using a MAR-CCD detector that has a maximum resolution of $2048 \times 2048$ pixels (78.75 × 78.75 $\mu$m$^2$ pixel size) with a 16-bit intensity scale, and a circular active area of 133 mm diameter. Temperature was controlled by an electric heater under a slightly positive pressure of helium. Dilute solutions and concentrated solutions were loaded in sealed capillary tubes and DSC pans, respectively. Experiments were performed by annealing samples at a target temperature for at least four minutes, followed by x-ray exposure for 2 – 20 s. The images were azimuthally averaged to the one-dimensional form of intensity $I(q)$ versus wavevector $q$ using the data reduction software FIT2D. The solvent background was also collected and subtracted from the solution data. The resulting data were not adjusted to an absolute scale.

SANS experiments were performed with the NG7 30 m instrument at the Center for Neutron Research located at the National Institute of Standards and Technology, Gaithersburg, MD. Scattering data were acquired with a neutron wavelength $\lambda$ of 7 Å and a wavelength spread $\Delta\lambda/\lambda$ of 0.11. Sample to detector distances between 1 m and 13 m were selected to provide a necessary $q$ range. A temperature-controlled electric heating block was used to maintain the sample temperature to within ±1 °C. Polymer solutions were loaded in quartz cells with ca. 1–1.5 mm thickness. Two-dimensional scattering data were corrected for detector sensitivity, sample transmission, empty cell scattering and sample thickness, then azimuthally averaged and reduced to absolute intensity by the
direct beam flux method. Data reduction was performed using the Igor package provided by NIST.\textsuperscript{37}

3.6 References


Chapter 4

Structure of Diblock Copolymer Micelles

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4.1 Introduction

Block copolymers can self-assemble into micelles when dispersed in selective solvents. Typically, micelles consist of a compact core of insoluble blocks and a swollen corona of soluble blocks. Three free energy terms contribute to determining the micelle structure: the interfacial tension between the core block and the solvent, chain stretching of the core block, and excluded volume interactions between the solvated corona blocks. Extensive reviews of theories and experimental results describing these systems are available elsewhere.1–3 Micelle structure in both aqueous and organic solvents has been investigated using small angle neutron or x-ray scattering (SANS or SAXS), in combination with detailed fitting models.4–20 In most of these studies, temperature was a key parameter to change solvent selectivity, which leads to changes in micellar properties. Most of the authors cited above have used a low glass transition temperature ($T_g$) material as the core block, such as poly(isoprene) (PI), poly(ethylene-alt-propylene) (PEP), poly(propylene oxide) (PPO), and poly(butylene oxide) (PBO), to avoid complications resulting from kinetically frozen dispersed micelles. However, even glassy
polymers such as polystyrene (PS) will experience a reduction in \(T_g\) when immersed in a neutral or less selective solvent; for example, \(T_g\) of the PS blocks in PS-PI micelles in tetradecane is reported to be less than 40 °C because of solvent penetration into the core.\(^{21}\)

While most investigations dealing with block copolymers dispersed in a selective solvent have attempted to focus on an equilibrated structure of molecular assembly, non-equilibrium effects are ubiquitous and have been attributed either to a glassy core, a low critical micelle concentration (CMC), or both. Well-studied examples of the latter phenomenon can be found in the class of amphiphilic diblocks comprised of poly(ethylene oxide) (PEO) and any of a variety of hydrocarbon polymers including poly(butadiene) (PB) and PEP.\(^{22–24}\) When dispersed in water at concentrations up to about 10% by weight, PB-PEO and PEP-PEO diblocks produce nonergodic dispersions that exhibit no measurable chain exchange, notwithstanding a core \(T_g\) well below the experimental temperature. This result can be traced to the extreme thermodynamic incompatibility between the organic core blocks and the aqueous medium. Further details of kinetics in the block copolymer micelles are described in Chapter 5.

Increasing the core \(T_g\) introduces a second type of complication. In this situation the micelle shape and dimensions reflect a state of assembly established at a higher temperature and subsequently frozen upon cooling. A glassy core resists both block copolymer exchange and micelle fusion/fission. Non-equilibrium structures, prepared at low temperatures, may transform through full or partial equilibration upon heating above \(T_g\), leading to a new state of organization that is locked in place with cooling. The shape and dimensions of the micelle core and corona can be characterized by SAXS, SANS, dynamic light scattering (DLS), rheological measurements, and cryogenic transmission electron microscopy (cryo-TEM). In general several of these techniques are required to
establish the structural and dynamical features that govern a particular micelle dispersion.

This chapter focuses on the structure of sphere-forming poly(styrene-\textit{b}-ethylene-\textit{alt}-propylene) (PS-PEP or SEP) diblock copolymers in squalane, a highly selective solvent for the PEP blocks. DLS, rheology, and synchrotron SAXS, conducted between 35 °C and 190 °C, have cataloged the structure of four PS-PEP solutions characterized by differing molecular weights and compositions, both above and below the PS core glass transition temperature. Previously, Quintana et al. deduced based on light scattering that the micellar properties of PS-PEP in \textit{n}-alkane solvents ($n \leq 16$) become less dependent on temperature (up to 85 °C) with increasing $n$.\textsuperscript{25,26} This was attributed to the associated increase in $T_g$ with $n$, which results from a decrease in the solvent quality. Our choice of squalane ($n = 30$) as a model solvent avoids this complication while affording access to a wide range of experimental temperatures. In this way, we have been able to investigate the transition from nonequilibrium to equilibrium behavior in SEP micelles over the aforementioned range of temperatures. Our findings shed new light on the fascinating and technologically important topic of block copolymer micellization in selective solvents.

4.2 Experimental Section

4.2.1 Materials

Four poly(styrene-\textit{b}-ethylene-\textit{alt}-propylene) (PS-PEP) diblock copolymers were prepared via anionic polymerization of poly(styrene-\textit{b}-isoprene) (PS-PI), followed by selective saturation of the PI block. Isoprene and styrene were polymerized sequentially by standard anionic polymerization procedures.\textsuperscript{27} Isoprene and styrene were purified with \textit{n}-butyl lithium and dibutyl magnesium for 4 h, respectively. Cyclohexane was used as the solvent and purified by passing through a purification column. Using \textit{sec}-butyl
lithium as an initiator, the isoprene was polymerized for 8 h at 40 °C, followed by the addition of styrene and polymerization for 8 h at the same temperature.

PS-PI diblock copolymers were selectively saturated with hydrogen using a homogeneous Ni-Al catalyst. A polymer solution was prepared by dissolving 10 g of PS-PI polymer in 500 mL of purified cyclohexane, which was added to a 1 L stainless steel reactor. A catalyst solution was prepared by injecting 6 mL of triethylaluminum (Sigma-Aldrich) into stirred 20 mL of 0.1M nickel 2-ethylhexanoate (Sigma-Aldrich) in cyclohexane under argon. After addition of the catalyst solution, the reactor was charged with high purity hydrogen (300 ~ 400 psi) at the temperature of 77 °C for at least 24 h. PS-PEP polymer was recovered by stirring with 1000 mL of 8 wt% aqueous citric acid until the catalyst color disappeared, followed by filtration with activated alumina and precipitation from methanol.

The polymers were characterized by size exclusion chromatography (SEC, Waters) using a refractive index detector, and by 1H nuclear magnetic resonance spectroscopy (1H NMR, Varian Inova 300). Number average molecular weights (Mn) were determined using a combination of SEC and 1H NMR. A small aliquot of PI was removed from the reactor prior to addition of styrene, and characterized by SEC (calibrated with PS standards). 1H NMR was used to determine the mole fraction of 4,1-addition in the PI block (94 ± 1%), and the volume fraction of each block, assuming densities of 1.047 and 0.913 g/cm³ for PS and PI, respectively. Based on these two quantities we calculated the overall Mn. Overall polydispersities were estimated by SEC curves on the PS-PEP. 1H NMR also was employed to establish the extent of PI saturation, which in all cases was greater than 99%. The characteristics of the four PS-PEP polymers in this study are shown in Table 4.1. The polymer name refers to SEP diblock copolymers with the PS and unsaturated PI molecular weight (kg/mol).
### Table 4.1 Polymer Characteristics

<table>
<thead>
<tr>
<th>Reference</th>
<th>PS block $M_n$[kg/mol]</th>
<th>PI block $M_n$[kg/mol]</th>
<th>$N_{PS}$</th>
<th>$N_{PEP}$</th>
<th>$M_w/M_n$</th>
<th>$f_{PS}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEP(42-60)</td>
<td>42</td>
<td>60</td>
<td>400</td>
<td>880</td>
<td>1.04</td>
<td>0.38</td>
</tr>
<tr>
<td>SEP(36-69)</td>
<td>36</td>
<td>69</td>
<td>350</td>
<td>1020</td>
<td>1.03</td>
<td>0.31</td>
</tr>
<tr>
<td>SEP(26-66)</td>
<td>26</td>
<td>66</td>
<td>250</td>
<td>970</td>
<td>1.04</td>
<td>0.26</td>
</tr>
<tr>
<td>SEP(17-73)</td>
<td>17</td>
<td>73</td>
<td>170</td>
<td>1070</td>
<td>1.04</td>
<td>0.17</td>
</tr>
</tbody>
</table>

- a Number-average molecular weight of PS block is based on $M_n,PI$ and the composition determined by $^1$H-NMR.
- b Number-average molecular weight of PI block before hydrogenation determined by SEC based on ten PS standards.
- c Number of monomer repeat units in PS block.
- d Number of monomer repeat units in PEP block.
- e Volume fraction of PS block in diblock copolymers.

Polymer solutions in squalane (Sigma-Aldrich) were prepared gravimetrically using dichloromethane as a cosolvent, followed by removal of the cosolvent at room temperature until constant weight was achieved.

#### 4.2.2 Dynamic Light Scattering (DLS)

DLS was utilized to determine the micelle hydrodynamic radius ($R_h$) as a function of temperature. The polymer solutions were filtered through 0.2 µm filters to remove dust, and sealed in 0.25 in. tubes under vacuum. The solutions were investigated using home-
built goniometer equipped with a silicon oil index-matching bath, an electric heater, a Brookhaven BI-DS photomultiplier, a Lexel 95-2 Ar$^+$ laser operating at 488 nm and a Brookhaven BI-9000 correlator. The intensity autocorrelation function ($g^{(2)}(q,t)$) was typically measured at an angle of 90º. The cumulant method was used to obtain an average decay rate ($\bar{\Gamma}$) and the second cumulant ($\mu_2$) which, when appropriately normalized, is a measure of the relative width of the distribution ($\mu_2 / \bar{\Gamma}^2$). The corresponding $R_h$ is then calculated via the Stokes-Einstein equation

$$R_h = \frac{kT}{6\pi \eta_s D_0}$$

(4.1)

where $k$, $T$, $\eta_s$, and $D_0$ ($= \bar{\Gamma}/q^2$, where $q$ is the scattering wave vector) are the Boltzmann constant, absolute temperature, solvent viscosity, and diffusion coefficient, respectively.

4.2.3 Rheology

Dynamic and steady rheological measurements were performed with a Rheometric Scientific ARES strain-controlled instrument equipped with a parallel plate (typically 25 mm in diameter and 0.5–1.5 mm in gap) for ordered (concentrated) samples and a Rheometrics RFS II rheometer with a cup-and-bob geometry (34 mm cup and 32 mm bob) for disordered (dilute) samples. The ARES rheometer has the lowest level for detectable torque of 0.2 g/cm. Temperature was controlled by a nitrogen convection oven between −50 ºC and 300 ºC, and accordingly the solvent evaporation should be considered when polymer solutions are measured at higher temperature. For the Rheometrics RFS II rheometer, temperature was controlled by a fluid circulating system between room temperature and 100 ºC with water. In all measurements, the samples were
equilibrated at target temperatures for at least 5 min.

### 4.2.4 Small-Angle X-ray Scattering (SAXS)

SAXS was performed using beam line 5ID-D, in the DuPont-Northwestern-Dow (DND-CAT) station at the Advanced Photon Source, Argonne National Laboratory. Radiation of 14 keV, corresponding to a wavelength $\lambda = 0.8856 \, \text{Å}$, was selected from an undulated beam using a double-crystal monochromator, and the sample to detector distance was 5.47 m. Two-dimensional SAXS patterns were collected using a MAR-CCD detector. Temperature was controlled by an electric heater under a slightly positive pressure of helium. Dilute solutions loaded in sealed capillary tubes were pre-annealed at 190 °C for at least five hours. Experiments were performed by annealing samples at a target temperature for at least four minutes, followed by x-ray exposure for 2 – 20 s. The sample temperature was increased from room temperature to 190 °C, and then decreased to room temperature, by 15 – 20 degree intervals. The images were azimuthally averaged to the one-dimensional form of intensity versus wavevector using the data reduction software FIT2D. The solvent background was also collected and subtracted from the solution data. The resulting data were not adjusted to an absolute scale. The data of 1 wt% samples were analyzed with a fitting model described below, using IGOR Pro.

### 4.3 Fitting Model

The scattering form factor ($P_{\text{mic}}(q)$) for a micelle composed of a spherical core and swollen corona chains attached to the core surface was applied to fit the SAXS data from dilute solutions.\textsuperscript{11,12,18} In the form factor, four terms are considered: the self-correlation of
the core, the self-correlation of the corona chains, the cross term between the spherical cores and the corona chains, and the cross term between different corona chains:

\[
P_{\text{mic}}(q) = N_{\text{agg}}^2 \beta_{\text{core}}^2 A_{\text{core}}^2(q) + N_{\text{agg}}^2 \beta_{\text{corona}}^2 P_{\text{chain}}(q) + 2N_{\text{agg}}^2 \beta_{\text{core}} \beta_{\text{corona}} A_{\text{core}}(q) A_{\text{corona}}(q) + N_{\text{agg}}(N_{\text{agg}} - 1) \beta_{\text{corona}}^2 A_{\text{corona}}^2
\]  

(4.2)

in which \(q\) is the scattering wavevector, \(N_{\text{agg}}\) is the aggregation number, and \(\beta_{\text{core}}\) and \(\beta_{\text{corona}}\) are the excess scattering lengths of core and corona blocks, respectively, defined as 

\[\beta_{\text{core}} = \nu_{\text{core-block}} (\rho_{\text{core-block}} - \rho_{\text{solvent}}) \quad \text{and} \quad \beta_{\text{corona}} = \nu_{\text{corona-block}} (\rho_{\text{corona-block}} - \rho_{\text{solvent}}),\]

where \(\nu_{\text{core-block}}\) and \(\nu_{\text{corona-block}}\) are the volume of the core and corona chains, calculated by densities of 1.047 and 0.856 g/cm\(^3\) for PS and PEP, respectively. In addition \(\rho_{\text{core-block}}, \rho_{\text{corona-block}}, \) and \(\rho_{\text{solvent}}\) are the scattering length densities of the core block, corona block and solvent, respectively.

The first term in eq (4.2) is the self-correlation of the spherical homogeneous core with radius \(R_c\) and a smoothly decaying scattering length density at the core-corona surface:

\[
A_{\text{core}}^2(q) = \Phi^2(qR_c) \exp(-q^2 \sigma_{\text{int}}^2)
\]  

(4.3)

where \(\Phi(x) = 3[\sin x - x \cos x]/x^3\) is the hard-sphere form factor. The exponential term reflects smooth transition of the scattering density at the core-corona surface, and \(\sigma_{\text{int}}\) takes into account the width of the interface.
The second term in eq (4.2) is the self-correlation of the corona chains, which is approximated by the Debye function where the chains are considered as Gaussian chains with radius of gyration $R_g$:

$$P_{\text{chain}}(q) = \frac{2[\exp(-q^2 R_g^2) - 1 + q^2 R_g^2]}{q^4 R_g^4}$$  \hspace{1cm} (4.4)$$

The last two terms in eq (4.2) are the cross terms between cores and coronas and between corona chains, respectively. Both terms include the form factor of the corona chains which is given as the normalized Fourier transform of the radial density distribution function of the corona chains ($\phi_{\text{corona}}(r)$) as follows:

Figure 4.1 Schematic drawing of diblock copolymer micelle
A corona \( \phi_{	ext{corona}}(r) \) = \( 4 \pi \int \frac{\sin(qr) \sin^2(r \sigma_{	ext{core}} / 2)}{q r^2} dr \) \[ (4.5) \]

A linear combination of two cubic b spline functions was assumed for \( \phi_{	ext{corona}}(r) \), as has been successfully applied previously.\(^{11,18}\) The explicit form of \( \phi_{	ext{corona}}(r) \) is given by Bang and coworkers,\(^{19}\) following the function originally developed by Pedersen and coworkers.\(^{18}\) The last exponential term in eq (4.5) provides a smooth variation of scattering length density at the core-corona interface.

Assuming a hard-sphere structure factor, the total coherent scattering intensity is

\[ I(q) = P_{\text{mic}}(q) + A_{\text{mic}}(q)^2 [S(q) - 1] \] \[ (4.6) \]

where \( S(q) \) is the monodisperse hard-sphere structure factor (which depends on the hard sphere radius \( R_{\text{hs}} \) and the hard sphere volume fraction \( \eta_{\text{hs}} \)), and \( A_{\text{mic}}(q) \) is the form factor amplitude of the radial scattering length distribution of the micelle given by

\[ A_{\text{mic}}(q) = N_{\text{agg}} (\beta_{\text{core}} A_{\text{core}}(q) + \beta_{\text{corona}} A_{\text{corona}}(q)) \] \[ (4.7) \]

A Gaussian distribution for the core radii was employed to account for polydispersity in the micelle cores:

\[ D(R_c) = \frac{1}{\sqrt{2\pi\sigma_R}} \exp \left[ -\frac{(R_c - \langle R_c \rangle)^2}{2\sigma_R^2} \right] \text{ for } R_c > 0. \] \[ (4.8) \]
In this expression, \( <R_e> \) is the average radius and \( \sigma_R \) is the width of the distribution, which is truncated at \( R_c = 0 \). Consequently, the coherent scattering intensity for the polydisperse micelles is given as

\[
I(q) = \int D(R_c)( P_{mic}(q) + A_{mic}(q)^2[S(q) - 1])dR_c. \tag{4.9}
\]

This expression is known as the local monodisperse approximation, as derived by Pedersen.\textsuperscript{30}

In all, nine parameters could be adjusted in the fits: the core radius (\( R_c \)), the radius of gyration of the corona chains (\( R_g \)), the width of the core-corona interface (\( \sigma_{int} \)), the width of the distribution for the core radius (\( \sigma_R \)), two terms (\( a_1, s \)) in the cubic \( b \) spline function for the corona term, the hard sphere radius (\( R_{hs} \)), the hard sphere volume fraction (\( \eta_{hs} \)), and the aggregation number (\( N_{agg} \)). Since the SAXS data were not converted into an absolute scale, an arbitrary prefactor was introduced. The fitting range was \( 0.008 \text{ Å}^{-1} < q < 0.11 \text{ Å}^{-1} \).

### 4.4 Results and Discussion

#### 4.4.1 DLS

The hydrodynamic radii (\( R_h \)) of the four block copolymer micelles are shown as a function of temperature in Figure 4.2, during both heating and cooling ramps. A test sample of 0.5 wt\% SEP(42-60) in squalane was prepared by dissolving the copolymers in squalane with dichloromethane as a cosolvent, but without annealing at high temperature. As shown in Figure 4.2(a), \( R_h \) at the initial room temperature was around 650 Å, but after
heating to 190 °C and cooling, the value was closer to 400 Å. Subsequent heating and cooling cycles for this polymer gave more reproducible results, with much less temperature dependence to the micelle dimensions. This initial metastable state has been reported previously with SEP in PEP selective solvents\textsuperscript{31,32} and interpreted in terms of kinetically frozen micelles, due to the low critical micelle concentration and high glass transition temperature ($T_g$) of the core block. Thereafter, all micelle solutions were annealed at high temperature ($\sim 190$ °C) for at least 15 min before measurement to achieve thermal reproducibility. The resulting $R_h$ of the four SEP polymer solutions as a function of temperature are shown in Figure 4.2(b). All four polymers have similar and constant radii up to about 60 °C. Then, $R_h$ begins to increase slightly, before leveling off at higher temperature. The apparent increase in $R_h$ is due at least in part to intermicellar interactions;\textsuperscript{25} the temperature dependence of $R_h$ is attenuated when a more dilute solution (0.02 wt%) SEP(42-60) is examined as illustrated in Figure 4.2(c). A critical micelle temperature (CMT) near 140 °C is evident for SEP(17-73), and a suggestion of a CMT appears for SEP(26-66) near 200 °C. The two polymers with longer polystyrene blocks do not show evidence of a CMT, because of the high incompatibility between squalane and polystyrene block. Quintana and coworkers characterized PS-PEP micelles in $n$-alkane solvents ($n \leq 16$), and found the aggregation numbers to be constant far below the CMT, but to decrease sharply near the CMT.\textsuperscript{25,26} This is consistent with our DLS results, and the more detailed small angle x-ray scattering results to be described next.
Figure 4.2 Temperature dependence of the hydrodynamic radius $R_h$ of (a) SEP(42-60) in squalane at 0.5 wt% ($R_h$ measured upon heating and cooling twice), (b) all four polymers in squalane at 0.5 wt%, upon heating and cooling, and (c) SEP(42-60) in squalane at 0.02 wt% and 0.5 wt% upon heating.
4.4.2 SAXS

Figure 4.3 and Figure 4.4 display the SAXS patterns for 1 wt% PS-PEP polymer solutions measured upon heating and cooling, respectively. Each solution shows a distinct first minimum and maximum in the form factor at low temperature, which becomes progressively smeared out as temperature increases. Also, the position of the first minimum shifts to higher $q$ as the molecular weight of the PS block decreases. All of the smooth curves in Figure 4.3 and Figure 4.4 represent the best fits to the model given in the previous section, as will be discussed subsequently. The electron density difference between PS and squalane (0.101 mol e$^{-}$ cm$^{-3}$) is four times as large as that between PEP and squalane (0.025 mol e$^{-}$ cm$^{-3}$), thus most of the scattering comes from the core contribution. Consequently, the calculated scattering intensity is insensitive to variations in the three terms in eq (4.2) associated with the corona contribution, $R_g$, $a_1$, and $s$, and accordingly these parameters are not reported here. The temperature dependence of the core radius and the corona layer thickness, which is taken as the difference between the core radius and the hard sphere radius in the structure factor, are shown in Figure 4.5(a) and (b), respectively. Within the uncertainty, both quantities do not show any appreciable temperature dependence prior to falling off rapidly near the CMT. All of the fitting parameters are listed in Table 4.2 and Table 4.3.

Because of the strong core scattering, the position of the first minimum in the form factor can be used directly to extract a core size. Applying the characteristic equation of the hard-sphere form factor, $\sin(qR_c) - qR_c \cos(qR_c) = 0$, the core radius $R_c$ at 70 °C can be estimated as 110 Å, 102 Å, 86 Å, and 75 Å for SEP(42-60), SEP(36-69), SEP(26-66), and SEP(17-73), respectively, with $qR_c = 4.493$ at the first minimum. These estimated values agree well with the fitting results.
Figure 4.3 SAXS data upon heating for SEP diblock copolymers in squalane at 1 wt%: (a) SEP(42-60), (b) SEP(36-69), (c) SEP(26-66), and (d) SEP(17-73). For clarity, data are multiplied by powers of 3 as temperature increases. The symbols are the SAXS data and the solid lines are the model fit.
Figure 4.4 SAXS data upon cooling for SEP diblock copolymers in squalane at 1wt% : 
(a) SEP(42-60), (b) SEP(36-69), (c) SEP(26-66), and (d) SEP(17-73). For clarity, data 
are multiplied by $3^n$ as temperature increases. The symbols are the SAXS data and the 
solid lines are the model fit.
Table 4.2 Fit results upon heating

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### Table 4.3 Fit results upon cooling

**SEP(42-60) in squalane at 1 wt%**

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**SEP(36-69) in squalane at 1 wt%**

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**SEP(26-66) in squalane at 1 wt%**

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**SEP(17-73) in squalane at 1 wt%**

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Figure 4.5 Temperature dependence of (a) core radius ($R_c$) and (b) corona layer thickness ($L_{corona}$) for the four polymers in squalane at 1 wt%.
**Figure 4.6** The relationship between the core radius and the number of repeat units in the core block.

**Figure 4.7** Temperature dependence of the solvent fraction in the core ($f$).
We can compare the unperturbed radius of gyration $<R_g>_0$ of the core block to the core radius. Since the value of $6<R_g^2>_0/MW$ is equal to 0.434 for PS at 413 K, $<R_g>_0$ of PS with 41,800, 36,300, 26,100, and 17,300 g/mol is 55, 51, 44, and 35 Å for SEP(42-60), SEP(36-69), SEP(26-66), and SEP(17-73), respectively. The fact that the core radius is only about twice $<R_g>_0$ shows that core chains are not significantly stretched. As shown in Figure 4.6, $R_c$ is roughly proportional to $N_{PS}^{0.5}$, where $N_{PS}$ is the degree of polymerization of the core block. This is somewhat surprising, because theory anticipates significant stretching of the core blocks. For example, $R_c$ is expected to be proportional to $N_{core}^{3/5}$ or $N_{core}^{2/3}$ for $N_{core} << N_{corona}$ (so called, hairy micelles) or $N_{core} >> N_{corona}$ (so called, crew-cut micelles), respectively, where $N_{core}$ and $N_{corona}$ are the degrees of polymerization of the core block and corona block.

Figure 4.7 shows the solvent fraction in the core ($f$), calculated by $(4/3)\pi R_c^3 = N_{agg^{core-block}}/(1-f)$. Roughly, solvent molecules begin to penetrate into the core above 100 °C, i.e., near the glass transition of the core block. Lai et al. have reported that the glass transition temperature ($T_g$) of 19 kg/mol PS block in a PS-PI diblock copolymer is approximately 70 °C and 40 °C in squalane and tetradecane, respectively, in dilute solution. Bang et al. also determined that the solvent fraction in the core of 30 kg/mol symmetric PS-PI in $n$-tetradecane is almost zero below 40 °C. Therefore, it is reasonable that virtually no squalane penetration in the PS core domain is observed below 70 °C. Above 100 °C, the fraction of solvent in the core increases with temperature, attributable to a decrease of the solvent selectivity for the core blocks. Nevertheless, the core size is only weakly dependent on temperature in the system, and penetration of solvent is accompanied by only small changes in aggregation number except near the CMT where the width of the core size distribution ($\alpha_R$) also increases.
Figure 4.8 The temperature dependence of (a) corona chain stretching and (b) brush density for four PS-PEP diblock copolymers in squalane at 1 wt%.
As noted previously, the radius of gyration ($R_g$) of the corona chains cannot be extracted reliably from the fits, due to the small electron density difference between the corona and the solvent. In place of $R_g$, a corona thickness, $L_{\text{corona}} = R_{\text{hs}} - R_c$, can be used to describe the corona profile, where $R_{\text{hs}}$ is the effective hard sphere radius in the structure factor. Roughly, $R_g$ can be estimated as half of the corona thickness, with the assumption of non-penetration of the corona chains into the core region. The corona layer thickness is independent of temperature between 30 °C and 190 °C for SEP(42-60) and SEP(36-69), where the CMT is far above the experimental range, and decreases near the CMT for SEP(26-66) and SEP(17-73) as shown in Figure 4.5(b). Here, we can compare $R_g$ of the corona chains to the unperturbed $<R_g>_0$ of the corona block. Since the value of $6< R_g^2>_0/MW$ is equal to 0.924 for alt-PEP at 298 K, $< R_g>_0$ of PEP with 61,800, 71,200, 68,000, and 75,200 g/mol is 98, 105, 102, and 108 Å, respectively. A dimensionless
parameter $s_{\text{corona}} = R_g/\langle R_g \rangle_0$ provides a measure of corona chain stretching: $s_{\text{corona}}$ is 1.5, 1.6, 1.4 and 1.5 for SEP(42-60), SEP(36-69), SEP(26-66), and SEP(17-73), respectively at 70 °C. As temperature approaches the CMT, the interfacial tension decreases and both core and corona chains can relax, therefore $R_g$ approaches $\langle R_g \rangle_0$ near the CMT for SEP(17-73) as shown in Figure 4.8(a). The corona chains can also be characterized by the dimensionless brush density ($\equiv N_{\text{agg}} \pi \langle R_g \rangle_0^2 / 4 \pi R_c^2$). The brush density relates the projected surface area per chain ($\pi \langle R_g \rangle_0^2$) to that available per chain on the surface of the core ($4 \pi R_c^2 / N_{\text{agg}}$), which is a two-dimensional analog of the reduced concentration $c/c^*$, where $c^*$ is the overlap concentration. The brush density is 16, 20, 23, and 33 for SEP(42-60), SEP(36-69), SEP(26-66), and SEP(17-73), respectively at 70 °C. Due to the relatively high brush density, the corona chains are expected to be tightly packed and stretched out in order to reduce the number of monomer-monomer interactions. More detailed corona profiles could be acquired using small angle neutron scattering with appropriate contrast. 

Representative SAXS data for more concentrated solutions of SEP(42-60) at 70 °C are shown in Figure 4.9. At 1 wt% copolymer, clear structure factor peaks emerge at low $q$, which evolve into well-defined Bragg reflections from a body-centered cubic (bcc) lattice by 10 wt%. The solution at 6 wt% is right on the edge of forming an ordered state. The first minimum of the form factor is found at similar $q$ values ($\approx 0.041 \text{ Å}^{-1}$) for the four different concentration samples, but the position of the first structure factor peak moves toward higher $q$. This suggests that the core size and aggregation number do not depend much upon polymer concentration, but the mean distance between two neighboring cores decreases with concentration. Since the corona chains are well solvated at the periphery of the corona layer, PEP blocks should be able to interpenetrate somewhat as the concentration is raised to the point of ordering, resulting in relatively
“soft” intermicelle interactions.

Figure 4.10 shows SAXS data for 10 wt% solutions, which clearly adopt well-defined BCC lattices with peak ratios \( q/q^* \), where \( q^* \) is the primary peak) of \( 1 : \sqrt{2} : \sqrt{3} : \sqrt{4} : \sqrt{5} : \sqrt{6} : \sqrt{7} \). Since the four PS-PEP polymers have very long corona blocks relative to the core, and the micelles interact through a “soft” potential, it is reasonable that they pack on a BCC lattice.\(^{21,36-40} \)
The distance between two micelles leads to a nearest neighbor radius \( (R_{nn}) \) that can be computed through the bcc lattice parameter \( (a_{bcc}) \) as

\[
R_{nn} = \frac{\sqrt{6}}{4} \frac{2\pi}{q^*} = \frac{\sqrt{3}}{4} a_{bcc}.
\]

(4.10)

As expected, \( R_{nn} \) is smaller than both \( R_h \) and \( R_{hs} \), i.e., \( R_{nn} = 320 \) Å relative to \( R_{hs} = 405 \) Å (at 1 wt%) and \( R_h = 450 \) Å (at 0.5 wt%) for SEP(42-60) at 70 °C, due to corona interpenetration at higher concentration. The temperature dependence of the primary peak position \( q^* \) is shown in Figure 4.11(a); \( q^* \) decreases smoothly with increasing temperature, except that an abrupt decrease near the CMT is observed for SEP(17-73). The corresponding \( R_{nn} \) is presented in Figure 4.11(b), after correcting for the temperature dependence of the (solvent) density.\(^{41} \) The adjusted lattice parameter is essentially independent of temperature. This is consistent with the work of Liu et al., who found that the primary peak of the BCC lattice is independent of temperature for poly(styrene-\( b \)-ethylene-\( a l t \)-propylene) in squalane.\(^{42} \) Note that the magnitude of \( R_{nn} \) at a given temperature varies in the sequence SEP(17-73) \( \leq \) SEP(26-66) \( < \) SEP(42-60) \( < \) SEP(36-69), although the overall range of \( R_{nn} \) is small (< 10% variation). This sequence follows the size of the core block, except for the latter two, where the longer corona block in SEP(36-69) dominates. This work contrasts with the position of the primary peak of the
Figure 4.10 SAXS data of ordered 10 wt% PS-PEP solutions in squalane upon heating:
(a) SEP(42-60), (b) SEP(36-69), (c) SEP(26-66), and (d) SEP(17-73).
Figure 4.11 Temperature dependence of (a) peak position $q^*$ and (b) the nearest neighbor radius corrected for thermal expansion, for the four SEP polymers in squalane.
BCC lattice for PS-PI in selective solvents, in which $q^*$ increases with increasing temperature.\textsuperscript{43,44} This behavior has been attributed to the decreasing solvent selectivity with increasing temperature.

4.4.3 Rheology

Figure 4.12 illustrates the solution viscosities ($\eta$) as a function of the concentration of SEP(42-60) polymers in squalane, measured under the steady shear of 1 s\textsuperscript{-1} at 30 °C using cup-and-bob geometry for dilute solutions and parallel plate for concentrated solutions. It is observed that the solution viscosity increases with increasing polymer concentration. Consistent with SAXS results described in Figure 4.9, there is a large increase between 5 wt% and 6 wt% polymer solutions where micelles begin to pack onto bcc lattice. However, solutions below 6 wt% are still disordered as evidenced by frequency dependence of $G'$ and $G''$ illustrated in Figure 4.13. The solutions below 6 wt% follow a relationship of $G' \sim \omega^2$ and $G'' \sim \omega$, which is characteristic response of a disordered liquid solution. Here, the solution viscosity can be also calculated at low frequency by the relationship that the solution viscosity is equal to $G''/\omega$, and accordingly the calculated solution viscosities are 0.055 Pa s, 0.13 Pa s, 0.52 Pa s, and 2.7 Pa s at 2 wt%, 3 wt%, 5 wt% and 6 wt% of SEP(42-60) polymers in squalane, respectively, consistent with those measured by steady shear experiment.

Above the 7 wt% polymer solutions, frequency sweeps were performed at multiple temperatures below $T_{ODT}$, and the data were shifted to the reference temperature of 30 °C by exploiting time-temperature superposition. Figure 4.14 illustrates superimposed frequency dependence of $G'$ and $G''$ for (a) 7 wt%, (b) 8 wt%, and (c) 10 wt% of SEP(42-60) in squalane using shift factors illustrated in Figure 4.14(d). A crossover of $G'$ and $G''$
Figure 4.12 Concentration dependence of the solution viscosity for SEP(42-60) block copolymers in squalane at 30 °C. The solution viscosities below 2 wt% are zoomed in inset for convenience.

Figure 4.13 Frequency sweeps for dilute solutions of SEP(42-60) diblock copolymers in squalane at 30 °C: (a) elastic modulus ($G'$) and (b) viscous modulus ($G''$) at 2 wt% (square), 3 wt% (circle), 5 wt% (triangle), and 6 wt% (up-side-down triangle).
Figure 4.14 Superimposed frequency dependence of $G'$ and $G''$ for SEP(42-60) in squalane at (a) 7 wt%, (b) 8 wt%, and (c) 10 wt% using (d) shift factors ($\alpha_T$) at the reference temperature of 30 °C. Data were collected at multiple temperatures shown in legends. In (d), Solid line is the best fit to WLF equation and dashed line denotes $\eta/\eta(T=30 \degree C)$ for squalane.
is observed at around $4 \times 10^{-4}$ rad/s only for the 7 wt% solution at 30 ºC. Below the crossover frequency, the solution behaves like a liquid in that $G''$ is greater than $G'$. This crossover frequency is not observed for the 8 wt% and 10 wt% solutions; both mixtures maintain solid behavior for wider ranges of frequency and temperature.

Clearly, a large plateau of elastic modulus (denoted $G_{\text{cubic}}^0$) exists over several decades in frequency consistent with the three-dimensional order consistent with the assignment of a bcc phase,\textsuperscript{45} based on SAXS results. $G_{\text{cubic}}^0$ values increase with increasing copolymer concentration. For a perfect cubic lattice $G_{\text{cubic}}^0$ can be calculated by considering how the free energy of the periodic structure varies in response to an affine deformation of the unit cell. Kossuth et al. estimated that the dimensionless modulus $G_{\text{cubic}}^0 V_c/RT$ ($V_c$ is the molar volume of the copolymer and $R$ is the gas constant) is constant for all bcc-forming diblock copolymers with equal values of the block copolymer composition, asymmetric parameter, and Flory-Huggins parameter.\textsuperscript{45} They observed, however, that $G_{\text{cubic}}^0 V_c/RT$ is a weak function of $V_c$. Watanabe et al. suggested that $G_{\text{cubic}}^0$ is related to the entropic elasticity of corona chains grafted on micelle cores, showing $G_{\text{cubic}}^0 = \nu kT (= kT q^* N_{\text{agg}}/(8\sqrt{2}\pi^3)$ for a bcc lattice) in which $\nu$ is the number density of the corona chains.\textsuperscript{46,47} Following the analogy of Watanabe et al., $G_{\text{cubic}}^0$ for 7 wt% and 10 wt% solutions at 30 ºC can be calculated as 1300 Pa and 1800 Pa, respectively, based on $q^*$ of each solution (0.01096 Å\textsuperscript{-1} and 0.01221 Å\textsuperscript{-1} for 7 wt% and 10 wt% solutions, respectively) and $N_{\text{agg}} = 84$. The calculated $G_{\text{cubic}}^0$ values are approximately 4–5 times higher than those obtained experimentally (290 Pa and 520 Pa for 7 wt% and 10 wt% solutions, respectively), consistent with the observations of Watanabe et al. They suggested the discrepancy is attributable to the reduced number of effective corona chains due to the osmotic constraint for the corona blocks.\textsuperscript{47} Another possibility, suggested by Liu et al., is coexistence of disordered and ordered micelles at
low concentrations of polymers.\textsuperscript{42} In other words, a fraction of the spherical micelles are not contained in the bcc lattice, and accordingly the theoretical description, based on 100\% ordering of all micelles, would fail.

The shift factors ($a_T$), shown in Figure 4.14(d), obtained from three different solutions (7, 8, and 10 wt\% of polymer) are described by a single WLF function; $c_1 = 5.17$ and $c_2 = 159 \, ^\circ C$. Comparing to the temperature dependence of the squalane viscosity (dashed line in Figure 4.14(d)), $a_T$ follows a much stronger temperature dependence, implying that relaxation times are governed by other factors than the squalane viscosity, such as interactions between corona chains.

\section*{4.5 Summary}

In this chapter, the structure of PS-PEP diblock copolymers in squalane was investigated. Due to the elevated glass transition temperature of the PS cores, the micelles can be trapped in non-equilibrium assemblies following low temperature dispersion. Such metastable configurations were largely eliminated by using a volatile cosolvent followed by heating to well above $T_g$ of the polystyrene cores. DLS, rheology and SAXS measurements of the resulting micellar dispersions, augmented by quantitative modeling of the latter, provides a detailed picture of micelle structure and intermicelle association as a function of block copolymer molecular weight and composition, concentration, and temperature. Selectivity of squalane for the PEP corona blocks diminishes with increasing temperature, ultimately resulting in dissolution at the highest measurement temperatures for the lowest molecular weight diblocks. This decrease in solvent selectivity leads to solvent penetration into the core resulting in a reduction in core diameter as the critical micelle temperature (CMT) is approached. An interesting
conclusion drawn from our analysis is that the core blocks appear to be unstretched and that the core radius is only weakly dependent on temperature. Increasing the block copolymer concentration causes the corona chains from opposing micelles to interpenetrate. Between 6 and 10 wt%, all four SEP copolymers order on a BCC lattice. The intermicellar spacing, corrected for thermal expansion of the solution, is essentially independent of temperature. For the lowest molecular weight studied, an order-to-disorder transition occurs below 190 °C, consistent with the dilute solution CMT. Overall, these results will aid in designing complex fluids based on dispersions of diblock copolymers in hydrocarbon solvents.

4.6 Acknowledgement

This work was supported by Infineum USA L.P. The works were performed at the DuPont-Northwestern-Dow Collaborative Access Team (DND-CAT) Synchrotron Research Center located at Sector 5 of the Advanced Photon Source. DND-CAT is supported by the E.I. DuPont de Nemours & Co., the Dow Chemical Company, the U.S. National Science Foundation through Grant DMR-9304725, and the State of Illinois through the Department of Commerce and the Board of Higher Education Grant IBHE HECA NWU 96. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Basic Energy Sciences, Office of Science, under Contract No. W-31-109-Eng-38. Lastly, I thank Carrie Stephani, an undergraduate student in Chemistry, for assistance with the Rheological measurements.
4.7 References and Notes


(31) Higgins, J. S.; Blake, S.; Tomlins, P. E.; Ross-Murphy, S. B.; Staples, E.; Penfold,


98
Chapter 5

Mechanism of Molecular Exchange in Diblock Copolymer Micelles

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5.1 Introduction

Diblock copolymers can self-assemble into micelles or vesicles when dispersed in a medium that solvates one block selectively. Diblock copolymer micelles show similarities with low molecular weight surfactants in their amphiphilic nature, but advantages including widely accessible structures, enhanced mechanical properties and versatility to targeting media.\textsuperscript{1,2} As potential alternatives to surfactants, block copolymer micelles have been largely used as delivery vehicles or viscosity modifiers. The majority of investigations have studied variations in the micelle structure as a function of block copolymer composition and architecture, molecular weight, solvent selectivity, and concentration.\textsuperscript{1,2,3}

Much less attention has been paid to the kinetics of chain exchange between block copolymer micelles, which is significantly harder to characterize, yet this is the fundamental process that must underlie the attainment of thermodynamic equilibrium. With very strongly segregated block copolymer dispersions, such as poly(butadiene-\textit{b}-
ethylene oxide) (PB-PEO) in water, spherical and worm-like micelles have been shown to be nonergodic based on time-resolved small-angle neutron scattering (TR-SANS) and transmission electron microscopy (TEM). There is virtually no chain exchange between micelles due to a combination of an extremely low critical micelle concentration (CMC) and a repulsive corona that inhibits micelle fusion. As the degree of incompatibility between the core block segments and the solvent decreases, the rate of exchange increases up to the point of micelle dissolution.

For low molecular weight surfactant micelles, a chemical relaxation model developed by Aniansson and Wall (AW mechanism) accounts for the relatively fast chain exchange kinetics that control micelle dynamics, a subject that has been thoroughly reviewed. For block copolymer micelles, the strong thermodynamic incompatibility between the core block segments and the solvent, coupled with the relative length of the core blocks, leads to highly retarded exchange rates and challenging experiments. Several techniques have been applied to investigate chain exchange kinetics for block copolymer micelles, including sedimentation, temperature jump (T-jump) experiments, nonradiative energy transfer and fluorescence quenching methods, transmission electron microscopy (TEM), and small-angle neutron scattering (SANS). In spite of extensive experimentation, chain exchange mechanisms in block copolymer micelles have not been fully resolved due in large part to experimental complications, e.g., large system perturbations (T-jump method) and the use of bulky chemical labels (fluorescence quenching method). In addition to experiments, Halperin and Alexander proposed a theoretical description whereby polymeric micelles assemble and disassemble only via unimer exchange analogous to the AW mechanism; merging (fusion) and splitting (fission) of micelles was excluded based on the scaling calculation indicating unimer insertion/expulsion is more favorable. Nevertheless, the possibility of micellar fusion
and/or fission processes has been suggested based on dynamic Monte Carlo simulation\textsuperscript{26} and scaling analysis,\textsuperscript{27} and invoked to explain relaxation data that fail to conform to multiple exponential functions.\textsuperscript{15,16}

Recently, a unimer exchange mechanism was proposed to explain a logarithmic relaxation obtained using TR-SANS experiments conducted with PEP-PEO diblock copolymers in mixtures of water and \textit{N,N}-dimethylformamide (DMF),\textsuperscript{23,24} the water/DMF ratio controls the interfacial tension, and hence the segregation strength.\textsuperscript{28} These authors suggested that their findings reflect a coupling between the core (PEP) block molecular dynamics and the geometric constraints imposed by the spherical core. Lund et al. also investigated a hydrocarbon system, poly(styrene-\textit{b}-butadiene) (PS-PB) diblocks and PB-PS-PB triblocks dispersed in \textit{n}-alkane solvents, a relatively weakly segregated system in which the PS cores are plasticized with 30 to 60\% solvent.\textsuperscript{29} They reported that the relaxation kinetics approach to the single exponential decay when the micellar cores are highly swollen, and thus chains are less coupled in the spherical core.

In Chapter 4, we characterized the dispersion of poly(styrene-\textit{b}-ethylene-\textit{alt}-propylene) (PS-PEP) in excess squalane. This solvent selectively dissolves PEP but is a non-solvent for PS, resulting in the formation of micelles that contain a glassy PS core and a solvated PEP corona at temperatures up to about 70 °C. Micelle structure, including the aggregation number and core radius, is dependent on solvent selectivity, which is often related to temperature. In Chapter 4, we reported the structure of PS-PEP micelles in squalane as a function of temperature during heating and cooling cycles. Based on SAXS and DLS measurements the structure was found to be only weakly dependent on temperature up to 200 °C for core PS block molecular weights $M_{n,PS} \geq 26$ kDa. This nearly temperature independent behavior may reflect thermodynamic equilibrium, or may be a consequence of slow chain exchange kinetics.
In this chapter, molecular exchange between spherical micelles formed from isotopically labeled PS-PEP diblock copolymers in squalane was investigated using TR-SANS. Temperature is found to affect the micelle exchange rate $R(t)$ consistent with melt dynamics for the core polymer. Varying the core block length ($N_{\text{core}}$) produces gigantic changes in $R(t)$ due to the thermodynamic penalty associated with ejecting a core block into the solvent. This hypersensitivity to $N_{\text{core}}$, combined with modest polydisperse core block length, leads to an approximately logarithmic $R(t)$.

5.2 Experimental Section

5.2.1 Materials
Two pairs of poly(styrene-$b$-ethylene-$alt$-propylene) (PS-PEP) diblock copolymers were synthesized using anionic polymerization of poly(styrene-$b$-isoprene) (PS-PI), followed by selective saturation of the PI block with deuterium, as described in Chapter 4. Each matched pair includes perdeuterated styrene (dPS-PEP) and protonated styrene (hPS-PEP). Isoprene and both perdeuterated (Polymer Source, Inc.) and protonated styrene were purified with $n$-butyl lithium and di-butyl magnesium for 4 h, respectively. Isoprene monomer was initiated by sec-butyl lithium and polymerized in cyclohexane for 8 h at 40 °C. An aliquot (~3 mL of solution) was then extracted from the reactor and terminated in degassed methanol. The PI block was characterized by size exclusion chromatography using a refractive index detector, with molecular weight determined by the universal calibration of ten PS standards. Subsequently, styrene monomer was added and polymerized for at least 8 h at 40 °C. Degassed methanol was injected into the reactor to terminate the polymerization. The PS-PI diblock copolymer was then recovered by precipitation in methanol.
The PS-PI diblock copolymers were selectively saturated using a homogeneous Ni/Al catalyst. A catalyst solution was prepared by adding 6 mL of triethylaluminum (Sigma-Aldrich) to 20 mL of 0.1 M nickel 2-ethylhexanoate (Sigma-Aldrich) stirred in cyclohexane under argon. A polymer solution in cyclohexane and the catalyst solution were injected into a stainless steel reactor at room temperature. Then, the reactor was charged with deuterium (400 psi, Cambridge Isotope Laboratories) and heated to 77 °C for at least 24 h. The PS-PEP diblock copolymer was recovered by stirring with 8 wt% citric acid in water until the catalyst color disappeared, followed by filtration with activated alumina and precipitation in methanol.

The polymers were characterized by SEC and $^1$H nuclear magnetic resonance spectroscopy (NMR, Varian Inova 300). SEC was used to give the molecular weight of the PI aliquot by universal calibration based on ten PS standards, and the overall polydispersity ($M_w/M_n$) of all diblock copolymers. Molecular weights of the PS-PI diblocks were computed by the molecular weights of the initiated PI block determined by SEC, and the masses of isoprene and styrene subsequently added to the reactor. The actual block copolymer compositions were verified by the $^1$H NMR spectroscopy indicating that complete addition of monomers was achieved. SEC traces of four copolymers are shown in Figure 5.1. The extent of PI saturation was characterized by $^1$H NMR spectroscopy (> 99%). Molecular characteristics of the four polymers are given in Table 5.1. The number of deuterons per repeat unit in the PEP block was estimated to be 2.3 using $^1$H NMR, which indicates a slight isotopic exchange during saturation. An isotopic solvent mixture of 42 vol% protonated squalane (h-squalane, Sigma-Aldrich) and 58 vol% perdeuterated squalane (d-squalane, C/D/N Isotopes) was used to contrast match a 50/50 mixture of dPS and hPS in the micelle cores, as will be discussed in more detail later. The densities of each compound are specified in Table 5.2.
**Figure 5.1** SEC traces of (a) PS-PEP-1 and (b) PS-PEP-2: dPS (dash) and hPS (solid)
<table>
<thead>
<tr>
<th>Polymer</th>
<th>(N_{PS}) (^{a})</th>
<th>(N_{PEP}) (^{b})</th>
<th>(M_w/M_n)</th>
<th>(R_c) [Å]</th>
<th>(N_{agg}) (^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hPS-PEP-1</td>
<td>250</td>
<td>970</td>
<td>1.04</td>
<td>87</td>
<td>67</td>
</tr>
<tr>
<td>dPS-PEP-1</td>
<td>260</td>
<td>985</td>
<td>1.10</td>
<td>89</td>
<td>72</td>
</tr>
<tr>
<td>hPS-PEP-2</td>
<td>400</td>
<td>880</td>
<td>1.05</td>
<td>105</td>
<td>77</td>
</tr>
<tr>
<td>dPS-PEP-2</td>
<td>423</td>
<td>926</td>
<td>1.10</td>
<td>102</td>
<td>78</td>
</tr>
</tbody>
</table>

\(^{a}\) number of PS repeat units, \(^{b}\) number of PEP repeat units, \(^{c}\) core radius, \(^{d}\) aggregation number

### 5.2.2 Sample Preparation

1 vol% polymer solutions with either hPS-PEP or dPS-PEP were prepared by dissolving the polymers in the isotopic squalane mixture with dichloromethane as a cosolvent, followed by removal of the dichloromethane at room temperature. Since the hydrodynamic radius \((R_h)\) measured by dynamic light scattering in Chapter 4 was thermally reproducible after 5 min annealing at \(\sim 190 \, ^\circ C\), the polymer solutions were annealed accordingly. The polymer solutions were then cooled down to room temperature where the PS cores become glassy. Subsequently, hPS-PEP and dPS-PEP polymer solutions were blended (50/50 by volume) and stored at room temperature to produce “postmixed” specimens: molecular exchange is completely suppressed at this temperature. “Premixed” specimens were prepared by codissolving hPS-PEP and dPS-PEP (50/50 by volume) in squalane with dichloromethane as a cosolvent, followed by removal of the latter.
5.2.3 Time-Resolved Small-Angle Neutron Scattering (TR-SANS)

TR-SANS experiments were performed with the NG7 30 m instrument at the Center for Neutron Research located at the National Institute of Standards and Technology, Gaithersburg, MD.\textsuperscript{32} Scattering data were acquired with a neutron wavelength $\lambda$ of 7 Å and a wavelength spread $\Delta \lambda / \lambda$ of 0.11. A sample to detector distance of 11 m or 13 m was used to provide a $q$ range of $0.005 \, \text{Å}^{-1} < q < 0.03 \, \text{Å}^{-1}$, where $q$ is the scattering wave vector defined as $q = 4\pi \lambda^{-1} \sin(\theta/2)$. A temperature-controlled electric heating block was used to maintain the sample temperature to within $\pm 1$ °C. 1 vol\% polymer solutions (hPS-PEP, dPS-PEP, postmixed, and premixed specimens) were loaded in quartz cells with ca. 1–1.5 mm thickness and exposed for 5–10 min at room temperature. Then, postmixed specimens were heated to a target temperature, and monitored by SANS every 5 min. Two-dimensional scattering data were corrected for detector sensitivity, sample transmission, empty cell scattering and sample thickness, then azimuthally averaged and reduced to absolute intensity by the direct beam flux method. Data reduction was performed using the Igor package provided by NIST.\textsuperscript{33}

Table 5.2 lists the calculated neutron scattering length density ($\rho$) of each material. The $\rho_{\text{sol}}$ for the isotopic solvent mixture was estimated by $\rho_{\text{sol}} = \phi_{\text{h-squalane}}\rho_{\text{h-squalane}} + (1- \phi_{\text{h-squalane}})\rho_{\text{d-squalane}}$, where $\phi_{\text{h-squalane}}$ is the volume fraction of h-squalane in the solvent mixture. $\phi_{\text{h-squalane}} = 0.42$ was used to match the scattering length density of a completely mixed 50/50 hPS/dPS micelle core ($= 3.93 \times 10^{10} \, \text{cm}^{-2}$) in this study.

Figure 5.2 illustrates the strategy behind the TR-SANS experiment. The overall goal is to determine the time required to exchange a specific fraction of hPS-PEP and dPS-PEP block copolymers in an initially completely segregated mixture of deuterated and protonated micelles. Following mixing of hPS-PEP and dPS-PEP dispersions at room temperature (well below the core glass transition temperature), the mixture is heated to a
Table 5.2 Scattering length densities

<table>
<thead>
<tr>
<th>Material</th>
<th>Formula</th>
<th>Molecular Weight of Repeat Unit (g/mol)</th>
<th>Density&lt;sup&gt;a&lt;/sup&gt; (g/cm&lt;sup&gt;3&lt;/sup&gt;)</th>
<th>V&lt;sup&gt;b&lt;/sup&gt; (10&lt;sup&gt;-22&lt;/sup&gt; cm&lt;sup&gt;3&lt;/sup&gt;)</th>
<th>b&lt;sup&gt;c&lt;/sup&gt; (10&lt;sup&gt;-12&lt;/sup&gt; cm)</th>
<th>ρ (=b/v) (10&lt;sup&gt;10&lt;/sup&gt; cm&lt;sup&gt;-2&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>d-squalane</td>
<td>C&lt;sub&gt;30&lt;/sub&gt;D&lt;sub&gt;62&lt;/sub&gt;</td>
<td>484</td>
<td>0.929</td>
<td>8.65</td>
<td>61.30</td>
<td>7.08</td>
</tr>
<tr>
<td>dPS</td>
<td>C&lt;sub&gt;8&lt;/sub&gt;D&lt;sub&gt;8&lt;/sub&gt;</td>
<td>112</td>
<td>1.128</td>
<td>1.65</td>
<td>10.66</td>
<td>6.46</td>
</tr>
<tr>
<td>hPS</td>
<td>C&lt;sub&gt;8&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;</td>
<td>104</td>
<td>1.047</td>
<td>1.65</td>
<td>2.33</td>
<td>1.41</td>
</tr>
<tr>
<td>PEP</td>
<td>C&lt;sub&gt;5&lt;/sub&gt;D&lt;sub&gt;2.3&lt;/sub&gt;H&lt;sub&gt;7.7&lt;/sub&gt;</td>
<td>72.3</td>
<td>0.884</td>
<td>1.36</td>
<td>1.98</td>
<td>1.46</td>
</tr>
<tr>
<td>h-squalane</td>
<td>C&lt;sub&gt;30&lt;/sub&gt;H&lt;sub&gt;62&lt;/sub&gt;</td>
<td>422</td>
<td>0.810</td>
<td>8.65</td>
<td>−3.24</td>
<td>−0.374</td>
</tr>
</tbody>
</table>

<sup>a</sup>density of deuterated material was calculated with the assumption that the volume per repeat unit is identical to that of protonated material, <sup>b</sup>volume per repeat unit, <sup>c</sup>coherent scattering length.

target temperature and then monitored by SANS over time. As the hPS-PEP and dPS-PEP chains exchange, the contrast between the core and matrix evolves towards the final matched state. Scattering intensity is related to the difference in the scattering length density between the background (i.e., solvent) and particle (i.e., micelle core and corona) such that \( I(t) = (\rho_{\text{core}}(t) - \rho_{\text{sol}}) \). Qualitatively, a high intensity characterizes the scattering associated with the unmixed micelle cores, due to a large difference in \( \rho \) with respect to the solvent, while the difference in \( \rho \) between the completely mixed cores and the solvent is negligible, resulting in little or no coherent intensity. The corona scattering remains virtually constant during chain exchange. Quantitatively, \( \rho_{\text{core}} \) is proportional to the
Figure 5.2 Experimental scheme of time-resolved small-angle neutron scattering (TR-SANS). The different degree of brightness represents the neutron scattering length density of each part. Protonated micelle cores (white) and deuterated micelle cores (black) are prepared separately in an isotopic solvent mixture (grey). The micelles are mixed at room temperature, where the glassy cores inhibit diblock copolymer exchange. Heating above $T_g$ of the cores makes possible diblock exchange between micelles. Molecular exchange leads to contrast matching between the solvent and cores.
volume fraction of hPS and dPS chains in the core, thus \( \rho_{\text{core}} = f_{\text{hPS}}\rho_{\text{hPS}} + (1 - f_{\text{hPS}})\rho_{\text{dPS}}, \)
where \( f_{\text{hPS}} \) is the volume fraction of hPS chains in the core. Since the isotopic solvent mixture was prepared to match the \( \rho \) of the completely mixed core (i.e., \( \rho_{\text{sol}} = 1/2(\rho_{\text{hPS}} + \rho_{\text{dPS}}) \)), the square root of the scattering intensity is directly proportional to the average volume fraction of hPS in the micelle cores, \( I(t)^{1/2} \sim (f_{\text{hPS}} - 1/2)(\rho_{\text{hPS}} - \rho_{\text{dPS}}) \). Hence, a normalized relaxation function, \( R(t) \), can be given by,

\[
R(t) = \frac{(I(t) - I_{\text{incoh}})^{1/2} - (I(\infty) - I_{\text{incoh}})^{1/2}}{(I(0) - I_{\text{incoh}})^{1/2} - (I(\infty) - I_{\text{incoh}})^{1/2}},
\]

(5.1)

where \( I_{\text{incoh}} \) is the incoherent scattering intensity (primarily from the solvent), \( I(0) \) and \( I(\infty) \) are the scattering intensities at \( t = 0 \) (i.e., the postmixed specimen) and \( t = \infty \) (i.e., the premixed specimen), respectively. \( I(t) \) is the scattering intensity of the solution during the time evolution of mixing. Since \( I(\infty) \) and \( I_{\text{incoh}} \) become indistinguishable at higher \( q \), where corona scattering is negligible, \( R(t) \) can be reduced to

\[
R(t) = \left( \frac{I(t) - I(\infty)}{I(0) - I(\infty)} \right)^{1/2}.
\]

(5.2)

SANS data were obtained from the hPS-PEP solution, dPS-PEP solution, premixed specimen, and postmixed specimen at 30 °C (10 min exposure) in order to establish the asymptotic structural features of the system under conditions where the exchange dynamics were turned off. Then, a postmixed specimen was heated from 60 °C to 160 °C in 10 °C increments and held at each temperature for 10 min while a SANS pattern was acquired. This series of experiments was used to estimate the rate of exchange at each
temperature and this information guided the selection of subsequent isothermal experiments, performed by heating directly to a target temperature and recording SANS patterns in five minute intervals until the long-time asymptotic result was approached.

5.3 Results and Analysis

5.3.1 Micelle structure

All PS-PEP diblock copolymers employed in this study formed well-defined spherical micelles in squalane, which is a selective solvent for the EP blocks as discussed in Chapter 4. Figure 5.3 displays the neutron scattering curves obtained at 30 °C from eight PS-PEP solutions in the isotopic squalane mixture. The scattering intensity of the postmixed specimen of PS-PEP-1 remains unchanged even after 18 h at 30 °C as shown in Figure 5.4. Since $T_g$ of PS in squalane is nearly 70 °C, the glassy core freezes the molecular exchange. Therefore, it is safe to keep postmixed specimens at room temperature before exposure to high temperature. Due to the differences in the scattering length densities ($\rho$) of each part (i.e., the core and corona) against that of the solvent, the scattering curves are significantly different in spite of the similar micelle properties, as shown in Table 5.1. For the dPS-PEP solutions, the first minimum ($q < 0.01 \text{ Å}^{-1}$) is attributed to corona scattering and is very sensitive to the excess $\rho$ of the core ($2.52 \times 10^{10} \text{ cm}^{-2}$) and corona ($-2.47 \times 10^{10} \text{ cm}^{-2}$). For the premixed specimen (i.e., $t \rightarrow \infty$) $\rho_{\text{core}}$ is matched with the $\rho_{\text{squalane}}$, which virtually extinguishes the scattering intensity at $q > 0.01 \text{ Å}^{-1}$, leaving only incoherent scattering. Detailed variations between the PS-PEP-1 and PS-PEP-2 scattering results are attributed to the different molecular weights, i.e., different core and corona dimensions.
Figure 5.3 Scattering curves for spherical micelles of (a) PS-PEP-1 and (b) PS-PEP-2 in squalane with different levels of contrast: dPS cores (square), hPS cores (circle), premixed cores (triangle), and postmixed cores (star) micelles. Background (incoherent) scattering was measured using the squalane solvent (diamond).
Figure 5.4 Scattering curves for postmixed specimen after mixing (square) and after 18 h annealing at 30 °C (circle).

The SANS results presented in Figure 5.3 have been modeled using a single micelle form factor described in Chapter 4. Table 5.1 lists the two most relevant structural features that were extracted by fitting this model to the hPS-PEP and dPS-PEP data (solid curves in Figure 5.3): the core radius \( R_c \), and the aggregation number \( N_{agg} \). For the premixed specimens model calculations were performed using averaged values of the dPS-PEP and hPS-PEP fitting parameters. In all cases the spherical micelle model is in reasonable agreement with the SANS measurements.

5.3.2 Chain Exchange Kinetics

The primary goal of this study is to characterize the rate of PS-PEP exchange between spherical micelles in squalane as a function of temperature. Figure 5.3 shows that the
limiting scattering patterns \((t = 0 \text{ and } t \to \infty)\) are clearly delineated, making feasible the quantitative determination of \(R(t)\). Representative transient isothermal data are presented for postmixed specimens of PS-PEP-1 at 100 °C and PS-PEP-2 at 135 °C in Figure 5.5. More than 5 h were required to produce sufficient exchange of hPS-PEP-1 and dPS-PEP-1 at 100 °C to reduce the SANS intensities from the initial values to a level approaching the premixed result. Increasing the molecular weight slowed this process dramatically. Even at the significantly higher temperature of 135 °C, the PS-PEP-2 mixture required more than 30 h to approach a similar extent of chain exchange. For times greater than about 3 h, the specimens were maintained at the target temperature outside the SANS instrument and periodically reinserted for measurement.

Data in the range \(0.010 \text{ Å}^{-1} < q < 0.023 \text{ Å}^{-1}\) were used to determine \(R(t)\) for 1 vol% solutions. The data were collected at 100 °C, 110 °C, and 115 °C for PS-PEP-1, and 135 °C, 140 °C, and 145 °C for PS-PEP-2. As the temperature increases the rate of block copolymer exchange increases, as expected. Composite plots of \(R(t)\) versus logarithmic time scale for both systems are presented in Figure 5.6. Consistent with the findings of Lund et al., \(R(t)\) is nearly linear on a logarithmic time scale.\(^{23,24}\)
**Figure 5.5** Time dependence of SANS patterns obtained from postmixed specimens (a) PS-PEP-1 at 100 °C and (b) PS-PEP-2 at 135 °C. Initial measurements were made at 30 °C (filled circles) and followed by the acquisition of SANS data every 5 min (shown in the legend) at 100 °C for PS-PEP-1 and 135 °C for PS-PEP-2. Premixed specimens were also measured at 100 °C and 135 °C (filled stars).
Figure 5.6 Decay of reduced SANS intensity as a function of time for (a) dPS-PEP-1/hPS-PEP-1 at 100 °C (circle), 110 °C (square), and 115 °C (triangle) and (b) dPS-PEP-2/hPS-PEP-2 at 135 °C (circle), 140 °C (square), and 145 °C (triangle). These results are linear on logarithmic time scale over the measurement range.
Figure 5.7 Concentration dependence of chain exchange kinetics for (a) PS-PEP-1 at 101 °C and (b) PS-PEP-2 at 140 °C: 0.5 vol% (triangle), 1 vol% (square), and 2 vol% (circle).
Two additional sets of experiments were conducted with PS-PEP-1 and PS-PEP-2 in order to establish the role of micelle concentration in the chain exchange kinetics. Three concentrations, 0.5 vol%, 1.0 vol% and 2.0 vol%, were examined at 101 °C for PS-PEP-1 and at 140 °C for PS-PEP-2, and these results are plotted in Figure 5.7. Within the statistical uncertainty of the measurements these data overlap, consistent with the notion that micelle fusion/fission does not play a significant role in determining the exchange kinetics.

5.4 Discussion

5.4.1 Logarithmic Decay

Since the relaxation function is observed to be approximately linear along log (t), we consider the logarithmic relaxation mechanism proposed by Lund et al.,23 where the relaxation function is given by36,37

\[ R(t) = \frac{1}{\ln(k_{\text{max}}/k_{\text{min}})} \left[ E_1(k_{\text{min}}t) - E_1(k_{\text{max}}t) \right], \] (5.3)

in which \( E_1(x) \) is the exponential integral function.38 This form of \( R(t) \) prevents the relaxation function from diverging at short and long times, and \( k_{\text{max}} \) and \( k_{\text{min}} \) are short and long time cutoff rates, respectively. Based on these fits (not shown), the fastest decay time, \( \tau_{\text{max}} = 1/k_{\text{max}} \), was estimated to be roughly 1 min for both PS-PEP-1 and PS-PEP-2, which is not accessible due to the 5 minute SANS exposure time. The slowest decay time, \( \tau_{\text{min}} = 1/k_{\text{min}} \), also was outside the experimental range except for 115 °C data from
PS-PEP-1, which is an order of 100 min. All the data were well approximated by the logarithmic function over the experimental range.

Logarithmic decay functions have been used to describe the dynamics of complex interacting systems such as glasses,\textsuperscript{39,40} and the local dynamics\textsuperscript{36} and folding kinetics\textsuperscript{41,42} in DNA. In general, a logarithmic relaxation can be expressed by a sum of sequential exponential decays, implying that the system comprises a series of correlated processes.\textsuperscript{37} Therefore, the logarithmic functions indicate a very broad distribution of relaxation times, which is a counter-intuitive finding. We expected that the exchange dynamics involving monodisperse micelles comprised of monodisperse block copolymers would be governed by a discrete dynamical process. Lund et al. have grappled with the same issue in discussing their TR-SANS results from PEP-PEO micelles in water/DMF, and suggest that structural rearrangements within the micelle core may require many correlated steps, thereby broadening the spectrum of relaxation times. However, since the molecular weight of their PEP block was less than 1.5 kDa, which is the critical molecular weight for entanglement for PEP,\textsuperscript{43} the chain mobility of the unentangled core blocks should not be affected by the topological constraint. In addition, Yokoyama et al. showed that the configuration of the core blocks in corona media is not necessarily a collapsed sphere in the weak segregation regime.\textsuperscript{44} Therefore transition dynamics between conformations should not be a major contributor to the broad distribution. Another reason for the relaxation behavior will be discussed in the following section.

5.4.2 Core Block Length Dependence

The TR-SANS results shown in Figure 5.6 include two parameters affecting the exchange kinetics: temperature and the molecular weight of the core block. In order to investigate the core block length dependence of the exchange kinetics, we applied the
Figure 5.8 Time-temperature superposed TR-SANS results with $T_{\text{ref}} = 125$ °C. $a_T$ shift factors conform to a single equation as shown in the inset. Master curves for chain exchange kinetics for PS-PEP-1 (circles, originally measured at 100 °C (blue), 110 °C (green), and 115 °C (red)) and PS-PEP-2 (squares, originally measured at 135 °C (blue), 140 °C (green), and 145 °C (red). Solid curves are best fit to Eq. (3) with $\alpha \chi = 0.041$ (circles) and 0.042 (squares). Dotted and dashed curves were calculated with $\alpha \chi = 0.03$ and 0.06 and $N_{\text{core}} = 255$ and $N_w/N_n = 1.08$. 
time-temperature superposition principle to account for the effect of temperature. Each set of data was shifted along time axis until data points are virtually overlapped at a reference temperature (100 °C for PS-PEP-1, and 135 °C for PS-PEP-2), which provides a shift factor \( a_T = \tau(T)/\tau(T_{\text{ref}}) \) accounting for changes in the molecular relaxation time (\( \tau \)) at temperature (\( T \)) relative to a reference temperature (\( T_{\text{ref}} \)). Then, all data were shifted onto individual master curves at \( T_{\text{ref}} = 125 \) °C using \( a_T \) as illustrated in Figure 5.8. At \( R(t) = 0.5 \) the exchange kinetics of PS-PEP-2 is more than three orders of magnitude slower than that of PS-PEP-1 in spite of the fact that the ratio of the core block length is just 1.6. Therefore, we conclude that the exchange kinetics is highly sensitive to the core degree of polymerization. A deviation of the first 2–3 points for each set of data is attributed to the experimental limit that requires a finite time (less than 10 min) for samples to reach a target temperature. While approaching the target temperature, the exchange kinetics would be delayed, resulting in slower kinetics (higher \( R(t) \)) in their short time region. The \( a_T \) can be described by a single WLF function as shown in inset of Figure 5.8, implying that the exchange kinetics follow a similar temperature dependence and one dominant mechanism governs the exchange kinetics.

### 5.4.3 Molecular Exchange Kinetic Model

Two primary mechanisms of exchange kinetics in diblock copolymer micelles have been proposed: (i) single chain insertion and expulsion, and (ii) micelle fusion and fission.\(^{16,25–27}\) When the distribution of micelle size is narrow and close to equilibrium and corona brushes are relatively long (so-called star-like micelles), the micelle fusion/fission mechanism is known to be energetically unfavorable due to the repulsive interaction of micelle coronas.\(^{24–27}\) Under this condition, the exchange kinetics of dilute PEP-PEO micelles in aqueous solution\(^{24}\) and dilute PS-PEP micelles in squalane are
independent of concentration as previously discussed, which confirms suppression of the micelle fusion/fission mechanism. Therefore, the exchange kinetics are dominated by the single chain insertion/expulsion mechanism, where a single macromolecule is extracted from a micelle, transported through a solvent medium, and inserted into another micelle as shown in Figure 5.9. Since polymer diffusion in low molecular weight solvents is much greater than in a polymer matrix, the transport step is much faster than both the extraction and insertion. Furthermore, the core block must overcome unfavorable segment-solvent interactions during extraction; therefore, we assume that the extraction of the core block is rate-limiting.

With the single dominant mechanism, the relaxation kinetics for a single chain with a core degree of polymerization $N_{\text{core}}$ can be expressed as

$$K(t, N_{\text{core}}) = \exp[-t / \tau(N_{\text{core}})],$$

(5.4)

where $\tau(N_{\text{core}})$ is the characteristic exchange time. Since $M_w$ of PS core blocks examined in this study are 2 – 3 times larger than a critical molecular weight of entanglement ($M_{e,\text{PS}} \approx 13$ kDa), the PS blocks are at most weakly entangled, and therefore governed by Rouse dynamics. The longest (Rouse) relaxation time is expressed as

$$\tau_{\text{Rouse}} = \frac{N_{\text{core}}^2 b^2 \zeta}{6\pi^2 kT},$$

(5.5)

where $k$, $T$, $b$, and $\zeta$ are the Boltzmann constant, temperature, statistical segment length, and the monomeric friction factor, respectively.
Figure 5.9 Schematic drawing for the single molecule exchange between micelles involving three steps: extraction of a core block, transportation of block copolymer through a solvent medium, and insertion into another micelle. Extraction of the core block carries the unfavorable interaction between the core block segments and solvent at the interface, thus is rate-limiting.
The extraction of the core block involves the unfavorable interaction between the core block segments and solvent. Extracted PS core blocks should be entirely surrounded by solvent molecules and PEP blocks, therefore the enthalpically unfavorable interaction is the product of $\chi N_{\text{core}}$, where $\chi$ is the Flory-Huggins interaction parameter between the PS and medium (solvent + PEP). With the thermal activation over the enthalpic penalty, $\pi(N_{\text{core}})$ can be expressed as $\tau_{\text{Rouse}} \exp(\alpha \chi N_{\text{core}})$, where $\alpha$ is an unknown $O(1)$ prefactor.\cite{44,48,49} When the core block is already in contact with corona block or solvent due to the solvent penetration into the core region, the enthalpic penalty at the interface should be a fraction of $\chi N_{\text{core}}$. Consequently, the time correlation function for the extraction of PS core blocks from the micelle cores is given by

$$K(t, N_{\text{core}}) = \exp \left[ -t \frac{6\pi^2 kT}{N_{\text{core}}^2 b^2 \zeta} \exp(-\alpha \chi N_{\text{core}}) \right].$$  \hspace{1cm} (5.6)

This relation is analogous to the standard Kramers/Arrhenius expression for traversing the transition state. Since $K(t, N_{\text{core}})$ is a strong function of $N_{\text{core}}$ (an exponential for exponential) we expect polydispersity of core block length to play an important role in the exchange dynamics. Based on the molecular weight distribution produced during the polymerization of the block copolymers, we have modified $K(t, N_{\text{core}})$ using a Schulz-Zimm distribution function,

$$P(N_i) = \frac{z^{z+1}}{\Gamma(z+1)} \frac{N_i^{z-1}}{N_n^z} \exp \left( -\frac{z N_i}{N_n} \right),$$  \hspace{1cm} (5.7)

where $z = [(N_w/N_n)^{-1} - 1]^{-1}$, $N_w$ and $N_n$ are the weight and number average chain lengths,
and $\Gamma$ is the gamma function, resulting in the final relaxation function,

$$R(t) = \int_0^\infty P(N)K(t,N)dN.$$  \hfill (5.8)

Solid lines illustrated in Figure 5.8 are best fits to eq (5.8) by adjusting the thermodynamic penalty-related parameter $\alpha\chi$ and the polydispersity of the core block length $N_w/N_n$. The monomeric friction factor $\zeta(T)$ was estimated using reported rheology data for PS by shifting $T_g$ to 70 °C to account for plasticization of PS due to solvent penetration into the core.\textsuperscript{50} The statistical segment length was taken as 0.67 nm for PS.\textsuperscript{43} The fitting results are summarized in Table 5.3. The resulting values are reasonable comparing to those measured independently. The reported value of $\chi$ between PS and PEP, identical structure of repeat unit for squalane, was around 0.07,\textsuperscript{51} which gives $\alpha \approx 0.6$, consistent with theoretical expectation. For both systems, the resulting $N_w/N_n$ are relatively narrow, nearly consistent with the experimental values listed in Table 5.1.

Based on the proposed kinetic model, the molecular exchange kinetics are highly sensitive to both $\alpha\chi$ and polydispersity in the core block length. Figure 5.10 illustrates the sensitivity of this model to modest variations in core block polydispersity. Increasing $N_w/N_n$ from 1.0 to 1.04 leads to significant changes in $R(t)$, transforming the relaxation function from an exponential to a logarithmic decay. (Here, we note that a tenfold change in $\zeta$ leads to less than a 17% variation in the fitted value of $\alpha\chi$). In addition, the $\alpha\chi$ dependence of $R(t)$ is shown in Figure 5.8 for the PS-PEP-1 system. Varying this parameter between 0.03 and 0.06 shifts $R(t)$ by roughly five orders of magnitude along the time axis. Significantly, both systems yield nearly identical values, $\alpha\chi = 0.041$ and 0.042 for PS-PEP-1 and PS-PEP-2, respectively.
Table 5.3 Fitting results\textsuperscript{a} at $T = 125^\circ$C

<table>
<thead>
<tr>
<th></th>
<th>$\langle N_n \rangle$ (input)</th>
<th>$N_w/N_n$\textsuperscript{b} (fit)</th>
<th>$\alpha\chi$\textsuperscript{b} (fit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-PEP-1</td>
<td>255</td>
<td>1.08</td>
<td>0.041</td>
</tr>
<tr>
<td>PS-PEP-2</td>
<td>412</td>
<td>1.04</td>
<td>0.042</td>
</tr>
</tbody>
</table>

\textsuperscript{a}$\zeta = 1.71 \times 10^{-8}$ (N·s·m$^{-1}$), \textsuperscript{b} standard deviation is less than 1%

Figure 5.10 Sensitivity of calculated $R(t)$ to variations in core block polydispersity. Data are superimposed PS-PEP-2 ($T_{ref} = 125^\circ$C) results from Figure 3. Polydispersity of core block length: 1 (dash), 1.02 (dash-dot), 1.04 (solid), and 1.20 (dot).
Here, it is worthwhile to compare our model with that employed by Lund et al.,\textsuperscript{23,24} (originally developed by Halperin and Alexander)\textsuperscript{25} which couples a Poisson distribution in core block lengths, or a Gaussian distribution of activation energies, with the extraction of core blocks. They assumed the single chain insertion/expulsion mechanism is dominant over the micelle fusion/fission mechanism, consistent with our model. However, the thermodynamic penalty for the extraction of a core block was assumed to be proportional to $N_{\text{core}}^{2/3}$, rather than $N_{\text{core}}$, because core blocks were assumed to exist in a collapsed state after ejection from the micelles; this results limited solvent-(core polymer) segment contact. This concept, which combined with a finite polydispersity, produced relatively poor agreement with their experimental data. As an alternative explanation, necessity to rearrange core blocks prior to ejection was suggested to be responsible for the logarithmic decay of the relaxation time. This model is functionally similar to ours, however a key difference in our work is the investigation of diblock copolymers with different values of $N_{\text{core}}$, which directly exposes the hypersensitivity of $R(t)$ to this parameter after accounting for the effects of temperature. We have not assumed collapsed core blocks in modeling $R(t)$, implying that all ejected core segments can contact solvent molecules. As a consequence, the thermodynamic penalty of core block extraction should be proportional to $N_{\text{core}}$, instead of $N_{\text{core}}^{2/3}$.

Subsequently, their model was modified to include a prefactor in a thermodynamic penalty (corresponding to $a$ in our model) to intensify the $N_{\text{core}}$ dependence on exchange kinetics. The modified model, coupled with Poisson distribution in core block lengths, showed good agreement with their experimental data, qualitatively consistent with our conclusion.\textsuperscript{52}
5.5 Conclusion

In this chapter, the molecular exchange between diblock copolymer micelles was investigated as a function of temperature, concentration, and the core degree of polymerization using TR-SANS. The concentration independence rules out the micelle fusion/fission mechanism. The effect of temperature and core block length was isolated and quantified using time-temperature superposition principle. A logarithmic decay of the exchange kinetics was observed, consistent with the previous report by Lund et al.\textsuperscript{23,24} Based on these experimental results, we proposed that molecular exchange kinetics are governed by single chain exchange between micelles, which inherently involves unfavorable interaction between the core block segments and the medium. This proposed model consequently predicts that the kinetics display a hypersensitive to the core degree of polymerization, thus polydispersity, which is corroborated by the experimental data.

Our results provide a framework to understand micelle kinetics formed from block copolymers in a solution. The hypersensitivity of molecular exchange kinetics to the core block length explains the slower and frozen dynamics observed in block copolymer micelles regardless of the state of cores (e.g., glassy and rubbery), which is desirable for potential applications including a drug delivery vehicle and segregated storage. Furthermore our conclusions can be applicable to any block copolymer micelles independent of micelle morphologies (e.g., worm-like micelles and bilayered vesicles) and structures.
5.6 References and Notes


(46) Mutual-diffusion coefficient of polystyrene in toluene (less than 30 wt% of PS) was reported to be an order of $10^{-7}$–$10^{-11}$ cm$^2$s$^{-1}$, and self-diffusion coefficient of PS in PS matrix was reported to be an order of $10^{-17}$ cm$^2$s$^{-1}$: Kim, H.; Chang, T.; Yohanen, J.


Chapter 6

Molecular Exchange in Ordered Diblock Copolymer Micelles

6.1 Introduction

In Chapter 5, we characterized 1 vol% poly(styrene-\(b\)-ethylene-\(alt\)-propylene) (PS-PEP) in squalane by time-resolved small-angle neutron scattering (TR-SANS) and observed a quasi-logarithmic decay in relaxation times. As the concentration of spherical micelles formed by diblock copolymers increases, the micelles begin to overlap and eventually pack onto either face-centered cubic (fcc) or body-centered cubic (bcc) lattices, depending on the detailed form of the intermicellar potential.\(^1\)–\(^5\) Here, we consider whether the concentration of micelles affects single chain exchange kinetics. Provided that the micelle structure is independent of micelle concentration, the exchange rate is expected to be nearly independent of micelle concentration if the extraction of a single molecule is rate-limiting. In this chapter, we address molecular exchange kinetics in diblock copolymer micelles using 15 vol% polymer solutions of 50% hPS-PEP and 50% dPS-PEP in an isotopic squalane mixture. Under these conditions, a well-defined bcc phase exists. We have chosen a combination of experimental parameters (i.e., isotopic labeling) such that all interparticle SANS scattering initially vanishes, resulting in an intensity that is proportional to the square of the fraction of hPS (or dPS) chains in
the micelle cores. This condition mirrors the circumstances created for the previous study of dilute PS-PEP spherical micelles in squalane, where interparticle interference was negligible due to the low concentration as described in Chapter 5. The current results are discussed in comparison with the behavior of dilute solutions, and thereby provide fresh insights into the mechanisms that control molecular exchange in block copolymer micelles.

6.2 Experimental Section

6.2.1 Materials

Note that since this chapter includes the work on molecular exchange kinetics described in Chapter 5, the same materials were used. Two pairs of poly(styrene-\textit{b}-ethylene-\textit{alt}-propylene) (PS-PEP) diblock copolymers were prepared, and each pair includes deuterated polystyrene (dPS-PEP) and protonated polystyrene (hPS-PEP). Molecular characteristic of the four diblock copolymers are listed in Table 6.1.

An isotopic solvent mixture includes 42 vol\% protonated squalane (h-squalane) and 58 vol\% of deuterated squalane, which is formulated to exactly contrast match perfectly 50/50 mixed hPS and dPS micelle cores as described in Chapter 5.

6.2.2 Sample Preparation

15 vol\% polymer solutions with either hPS-PEP or dPS-PEP were prepared by dissolving the polymers in the isotopic squalane mixture with dichloromethane as a cosolvent, followed by removal of the dichloromethane at room temperature. The polymer solutions were then annealed for 5 min at 150 °C and 170 °C for PS-PEP-1 and PS-PEP-2, respectively. The annealing temperatures were selected to be well above (~50
### Table 6.1 Diblock copolymer characteristics

<table>
<thead>
<tr>
<th>Polymer</th>
<th>(N_{PS})^a</th>
<th>(N_{PEP})^b</th>
<th>(M_w/M_n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hPS-PEP-1</td>
<td>250</td>
<td>970</td>
<td>1.04</td>
</tr>
<tr>
<td>dPS-PEP-1</td>
<td>260</td>
<td>985</td>
<td>1.10</td>
</tr>
<tr>
<td>hPS-PEP-2</td>
<td>400</td>
<td>880</td>
<td>1.05</td>
</tr>
<tr>
<td>dPS-PEP-2</td>
<td>423</td>
<td>926</td>
<td>1.10</td>
</tr>
</tbody>
</table>

^a number of PS repeat units, ^b number of PEP repeat units

\(^{6}\)C) the temperature where molecular exchange was observed in dilute solution, yet still below the order-disorder transition as described in Chapters 4 and 5. The polymer solutions were then cooled down to room temperature where the PS cores become glassy. Subsequently, hPS-PEP and dPS-PEP polymer solutions were blended (50/50 by volume) using a cup-rotor mixer (CSI Co., MiniMax with a rotor diameter of 13 mm) at room temperature to produce “postmixed” specimens. “Premixed” specimens were prepared by codissolving hPS-PEP and dPS-PEP (50/50 by volume) in squalane with dichloromethane as a cosolvent, followed by removal of the latter.

### 6.2.3 Time-Resolved Small-Angle Neutron Scattering (TR-SANS)

TR-SANS experiments were performed with the NG7 30 m instrument at the Center for Neutron Research located at the National Institute of Standards and Technology, Gaithersburg, MD. Scattering data were acquired with a neutron wavelength \(\lambda\) of 7 Å and a wavelength spread \(\Delta\lambda/\lambda\) of 0.11. A sample to detector distance of 11 m was used to
provide a $q$ range of $0.005 \, \text{Å}^{-1} < q < 0.03 \, \text{Å}^{-1}$, where $q$ is the scattering wave vector defined as $q = 4\pi \lambda^{-1} \sin(\theta/2)$. A temperature-controlled electric heating block was used to maintain the sample temperature to within ±1 °C. 15 vol% polymer solutions (hPS-PEP, dPS-PEP, postmixed, and premixed specimens) were loaded in quartz cells with ca. 1–1.5 mm thickness and exposed for 5–10 min at room temperature. Then, postmixed specimens were heated to a target temperature, and monitored by SANS every 5 min. Two-dimensional scattering data were corrected for detector sensitivity, sample transmission, empty cell scattering and sample thickness, then azimuthally averaged and reduced to absolute intensity by the direct beam flux method. Data reduction was performed using the Igor package provided by NIST.°

6.2.4 Small-Angle X-ray Scattering (SAXS)

SAXS experiments were conducted with the equipment maintained by the DuPont-Northwestern-Dow Collaborative Access Team at Argonne National Laboratory. Radiation of 17 keV, corresponding to a wavelength $\lambda = 0.729 \, \text{Å}$, and a sample-to-detector distance of 6.6 m were employed. Temperature was controlled by an electric heater under a slightly positive pressure of helium. The specimens, loaded in aluminum DSC pans, were annealed at the target temperature for at least four minutes, followed by x-ray exposure for 0.5–1 s. Two-dimensional SAXS images, collected using a MAR-CCD detector, were azimuthally averaged to one dimensional plots of intensity versus $q$.

6.3 Background of SANS

The scattering cross section $d\Sigma(q)/d\Omega$ of $N$ spherical particles each composed of $z$
scattering centers in solution is given by\textsuperscript{8} (see Chapter 3)

\[ \frac{d\Sigma(q)}{d\Omega} = (\Delta \rho)^2 \frac{V^2}{V} \left\{ N z^2 P(q) + N^2 z^2 Q(q) \right\}, \quad (6.1) \]

in which \( P(q) \) and \( Q(q) \) are the intraparticle and interparticle contributions, \( V \) and \( v \) are the system volume and the scattering center volume, respectively, and \( \Delta \rho \) is the excess scattering length density of the scattering center against the background.

For a mixture of \( N_D \) deuterated and \( N_H \) protonated spheres, the scattering cross section can be expressed as

\[ \frac{d\Sigma(q)}{d\Omega} = (\Delta \rho_D)^2 \frac{V^2}{V} S_{DD}(q) + (\Delta \rho_H)^2 \frac{V^2}{V} S_{HH}(q) + 2 \Delta \rho_D \Delta \rho_H \frac{V^2}{V} S_{DH}(q) \quad (6.2) \]

where \( S_{ii}(q) \) are partial structure factors defined by

\[ S_{HH}(q) = N_H z^2 P(q) + N_H^2 z^2 Q_{HH}(q), \quad (6.3) \]

\[ S_{DD}(q) = N_D z^2 P(q) + N_D^2 z^2 Q_{DD}(q), \quad (6.4) \]

\[ S_{DH}(q) = N_H N_D z^2 Q_{DH}(q). \quad (6.5) \]

There is no intraparticle contribution for \( S_{DH}(q) \) because two scattering centers cannot belong to the same sphere. If the H-spheres and D-spheres are perfectly randomly distributed on a bcc lattice and any deuterium isotopic effects are negligible, it is reasonable to assume that \( Q_{HH}(q) = Q_{DD}(q) = Q_{DH}(q) = Q(q) \). If the spheres are not randomly distributed on the lattice sites, then this assumption fails.
When the system includes an equal amount of H-spheres and D-spheres \((N_H=N_D=N/2)\), eq (2) can be reduced to

\[
\frac{d\Sigma(q)}{d\Omega} = \left\{ (\Delta \rho_H)^2 + (\Delta \rho_D)^2 \right\} \frac{v^2 z^2 N}{2V} P(q) + (\Delta \rho_H + \Delta \rho_D)^2 \frac{v^2 z^2 N^2}{4V} Q(q), \tag{6.6}
\]

where \(P(q)\) and \(Q(q)\) are separated. Eq (6.6) can be reorganized using \(\Delta \rho_H = \rho_H - \rho_{\text{sol}}\) and \(\Delta \rho_D = \rho_D - \rho_{\text{sol}}\) as

\[
\frac{d\Sigma(q)}{d\Omega} = \left( \rho_D - \rho_H \right)^2 \frac{v^2 z^2 N}{4V} P(q) + \left( \frac{\rho_H + \rho_D}{2} - \rho_{\text{sol}} \right)^2 \left\{ \frac{v^2 z^2 N}{V} P(q) + \frac{v^2 z^2 N^2}{V} Q(q) \right\}. \tag{6.7}
\]

In eq (6.7), the first term is still the intraparticle scattering contribution with a different coefficient, which corresponds to the fluctuation between deuterated and protonated spheres. The second term, however, corresponds to the scattering obtained with fictitious spheres having an averaged scattering length density of deuterated and protonated spheres, i.e., \((\rho_H+\rho_D)/2\).8,9

When \(\rho_{\text{sol}}\) is designed to equal \((\rho_H+\rho_D)/2\) by blending protonated and deuterated solvent, the second term in eq (6.7) becomes zero, provided a completely random distribution of H-spheres and D-spheres is achieved. Under this condition, the intraparticle contribution (i.e., the spherical form factor) can be observed without interference of the interparticle contribution (i.e., Bragg scattering). Eq (6.7) is still satisfied, with appropriate modification of the coefficients, for arbitrary, non-spherical geometry (i.e., polymer chains) or for a ratio of H-spheres and D-spheres other than 1:1. This contrast matching technique, also known as the zero average contrast condition, has
been used with SANS to measure single chain conformation in ordered block copolymer melts\textsuperscript{10–13} and homopolymer melts and solutions.\textsuperscript{8,14–17}

6.4 Results and Analysis

6.4.1 SAXS

The SAXS patterns in Figure 6.1 were obtained from 15 vol% polymer solutions of hPS-PEP, dPS-PEP, premixed, and postmixed for (a) PS-PEP-1 and (b) PS-PEP-2 at room temperature, where there is no chain exchange between micelles (i.e., \( T < T_{g,PS} \)). All eight diblock copolymer solutions form well-defined spherical micelles in squalane, which are packed onto a bcc lattice as evidenced by the sequence of peak ratios \( q/q^* \) (\( q^* \) is the primary peak) of \( 1: \sqrt{2}: \sqrt{3}: \sqrt{4}: \sqrt{5}: \sqrt{6}: \sqrt{7} \) (for the postmixed specimen of PS-PEP-1; up to \( \sqrt{5} \) can be identified for the other specimens). The order-disorder transition for 10 wt% solutions of the same block copolymers occurs above 200 °C as described in Chapter 4. Therefore, all the block copolymer micelles (15 vol%) packed on bcc lattices at the temperatures of the TR-SANS measurements (SAXS data at higher temperatures are also provided in Figure 6.2). The mismatch in peak positions between hPS-PEP and dPS-PEP (9% and 17% in nearest neighbor radius \( R_{nn} = \sqrt{6\pi/(2q^*)} \) for PS-PEP-1 and PS-PEP-2, respectively) is attributed to the slight difference in block molecular weight. \( R_{nn} \) for postmixed and premixed specimens are the average of hPS-PEP and dPS-PEP, as expected.

Intraparticle scattering becomes dominant at higher \( q \) over interparticle scattering (i.e., Bragg scattering), as can be seen in Figure 6.1(a) and (b) for \( q > 0.03 \text{ Å}^{-1} \). We attempted to describe the former with the form factor \( P_s(q) \) of uniform spheres of radius \( R_c \).
Figure 6.1 SAXS patterns obtained from 15 vol% of (a) PS-PEP-1 and (b) PS-PEP-2 in squalane at room temperature: dPS-PEP, hPS-PEP, premixed, postmixed as shown in the legend. The representative data for both polymers are indexed to bcc morphologies. Solid curves in (b) are the fits to a form factor of polydisperse PS spheres in the squalane matrix. Data are vertically shifted for convenience.
Figure 6.2 SAXS patterns obtained from 15 vol% of (a) PS-PEP-1 at 120 °C and (b) PS-PEP-2 at 150 °C in squalane: dPS-PEP, hPS-PEP, premixed, postmixed as shown in the legend. The representative data for both polymers are indexed to bcc morphologies. Data are vertically shifted for convenience.
### Table 6.2 Micelle characteristics

<table>
<thead>
<tr>
<th></th>
<th>Calculated properties from bcc lattice</th>
<th>Fitting results&lt;sup&gt;b&lt;/sup&gt;</th>
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<tr>
<td></td>
<td>$q^*$ [Å&lt;sup&gt;-1&lt;/sup&gt;]</td>
<td>$R_{nn}$ [Å]</td>
</tr>
<tr>
<td>PS-PEP-1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>dPS-PEP</td>
<td>0.0131</td>
<td>295</td>
</tr>
<tr>
<td>hPS-PEP</td>
<td>0.0143</td>
<td>269</td>
</tr>
<tr>
<td>Premixed</td>
<td>0.0136</td>
<td>282</td>
</tr>
<tr>
<td>Postmixed</td>
<td>0.0136</td>
<td>282</td>
</tr>
<tr>
<td>PS-PEP-2</td>
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</tr>
<tr>
<td>dPS-PEP</td>
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<td>315</td>
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<td>hPS-PEP</td>
<td>0.0143</td>
<td>269</td>
</tr>
<tr>
<td>Premixed</td>
<td>0.0132</td>
<td>291</td>
</tr>
<tr>
<td>Postmixed</td>
<td>0.0132</td>
<td>291</td>
</tr>
</tbody>
</table>

<sup>a</sup> $v_{chain}$ for premixed and postmixed solutions was calculated by averaging the values of dPS-PEP and hPS-PEP.<sup>b</sup> Fit to the form factor.
In order to account for the effect of variation in sphere size, a Gaussian distribution was incorporated while fitting the scattering data. Two fitting parameters ($R_c$ and standard deviation $\sigma_R$) were adjusted using the Igor package provided by NIST.\textsuperscript{7} The adjusted theoretical curves show good agreement with the observed scattering data for PS-PEP-2 and the resulting parameters are provided in Table 6.2. We did not perform the fitting process for PS-PEP-1, since the scattering curves do not show distinct minima or maxima at higher $q$, leading to less confidence and precision in determining parameters.

$R_c$ also can be estimated by the known structural symmetry and diblock copolymer composition. The number density of micelles $n/V$ can be estimated as $2/a_{\text{bcc}}^3$, where $a_{\text{bcc}}$ is the lattice parameter of the bcc structure. The averaged aggregation number of the diblock copolymer in the micelles $N_{\text{agg}}$ can be computed from $n/V$, the polymer volume fraction in solution (= 15 vol%), and the volume of the single chain $\nu_{\text{chain}}$, assuming no free chains. Consequently, the core radius of the micelle $R_c$ can be computed as $R_c = (3
u_{\text{chain}}N_{\text{agg}}/4\pi)^{1/3}$ with the assumption of no solvent penetration into the core at room temperature. The structural properties of the micelles thus calculated from the SAXS patterns are summarized in Table 6.2.

Both fitted and calculated $R_c$ are approximately 20–30\% bigger than $R_c$ in 1 vol\% dilute solution (88 Å for PS-PEP-1 and 104 Å for PS-PEP-2). Spherical micelles prefer to avoid significant corona overlap at higher micelle concentration, particularly when ordered on a lattice, leading to solutions with lower number densities of micelles, higher aggregation numbers, and hence larger spherical cores.\textsuperscript{5}
6.4.2 SANS

Figure 6.3 displays the SANS data obtained from 15 vol% polymer solutions of hPS-PEP, dPS-PEP, premixed, and postmixed at 30 °C. Figure 6.3(a) shows the results for the PS-PEP-1 pair and Figure 6.3(b) shows the results for the PS-PEP-2 pair. For the hPS-PEP and dPS-PEP specimens, the SANS patterns reveal the bcc structure identified by the relative peak positions $q/q^*$ of $1:\sqrt{2}:\sqrt{3}$. The value of $q^*$ for each pair between SAXS and SANS are identical, as indicated by arrows denoting the observed $q^*$ in SAXS. However, SANS curves obtained from premixed and postmixed specimens show little or no evidence of bcc structure peaks. For premixed specimens this is due to negligible scattering contrast between the micelle cores and the medium, resulting in a masking out of the core contribution to the SANS intensity. Because of the bcc ordering part and the non-contrast matched micelle coronas, small peaks are evident and correspond with $q^*$ from SAXS (0.0136 Å$^{-1}$ and 0.0132 Å$^{-1}$ for PS-PEP-1 and PS-PEP-2, respectively), as indicated by arrows in Figure 6.3. Although fluctuations between deuterated and protonated PS chains in the cores are present, scattering from single PS core chains is also not detectable due to the overall low volume fraction of PS chains (ca. 4–5 vol%).

For the postmixed sample, the interparticle contribution (i.e., Bragg scattering) in SANS does not play a role under the experimental zero average contrast condition, as explained previously. This phenomenon can also be explained in analogous terms to crystal structures as observed in atomic binary solid solutions (i.e., AuCu$_3$)\cite{18,19}. When H-spheres and D-spheres are perfectly randomly distributed on bcc lattice sites, the probability of finding either an H-sphere or a D-sphere is 0.5. Therefore it is reasonable to assume that fictitious spheres having a scattering length density of $\Delta\rho_{avg} = (\Delta\rho_H + \Delta\rho_D)/2$ occupy the sites. Under this experimental condition, $\Delta\rho_{avg}$ becomes to zero.
Figure 6.3 SANS patterns obtained from 15 vol% of (a) PS-PEP-1 and (b) PS-PEP-2 in squalane at 30 °C: dPS-PEP (square), hPS-PEP (circle), postmixed (star), premixed (triangle), and solvent (diamond) as shown in legend. Solid curves are best fit to eq (6.9). Arrows indicate the position of $q^*$ observed in SAXS.
and the crystal symmetry is invisible against the matrix. Consequently, interparticle scattering does not contribute to the SANS intensity. As a result the coherent scattering cross section for the postmixed specimens with the assumption of hard sphere of radius $R_c$ and negligible corona scattering can be expressed as

$$\frac{d\Sigma(q)}{d\Omega} = \left(\frac{4\pi}{3}R_c^3\right)\phi_s\left(\rho_{\text{core}}(t) - \rho_{\text{sol}}\right)^2P_s(q), \quad (6.9)$$

where $\phi_s$ is the volume fraction of spheres, $\rho_{\text{core}}(t)$ is time-dependent scattering length density of the micelle cores, and $P_s(q)$ is the spherical form factor as defined in eq (6.8).

The solid lines in Figure 6.3 are the best fits to eq (6.9) for postmixed samples by adjusting $R_c$ and $\phi_s$. The resulting $R_c$ are 110 Å and 125 Å for PS-PEP-1 and PS-PEP-2, respectively, which are consistent with the fitted and calculated $R_c$ by SAXS for postmixed specimens. The fitted $\phi_s$ are 3.2 vol% and 5.0 vol% for PS-PEP-1 and PS-PEP-2, respectively. Considering the diblock copolymer composition, the PS volume fractions in the solution can be computed as 3.7 vol% and 5.5 vol% for PS-PEP-1 and PS-PEP-2, respectively, which shows reasonable agreement with the fitted values.

Here, it is worthwhile to discuss the way to produce the postmixed specimens, in which H-micelles and D-micelles are essentially perfectly randomly distributed as evidenced by SANS curves. Two types of micelles can be blended at room temperature ($T < T_{g,\text{core}}$) without chain exchange between the micelles using either a cosolvent or a mechanical mixer. For the former, the cosolvent is used to dilute the ordered solutions and to reorganize the micelles. Therefore, the cosolvent in this study should be highly PEP selective to avoid solvent-plasticized PS cores resulting in the possibility of chain exchange, and be easily removed to achieve the initially ordered state. This method,
however, was not chosen in this study due to difficulties in selecting an appropriate cosolvent satisfying the two conditions (data are not shown). Instead, a cup-rotor mixer with steel balls was used to blend isotopically segregated micelles. A MiniMAX mixer (CSI Co.) has been used to blend a small amount (~ 0.5 g) of polymer melts mechanically as described in Figure 6.4. The polymer blends can experience extensional flows and a wide range of shear rates with the help of the balls, resulting in well-dispersed mixtures. Mixing times were up to 30 min. Likewise, two kinds of bcc ordered micelles can be perfectly mixed using this instrument as evidenced by the SANS results. This study has provided the collateral benefit of demonstrating the remarkable efficiency of the MiniMAX mixer in creating uniform blends down to a length scale of less than 10 nm. To the best of our knowledge, this is the first published result of this kind.

![Schematic figure of the cup-rotor mixer (MiniMAX). Reproduced from Reference 20.](image)

**Figure 6.4** Schematic figure of the cup-rotor mixer (MiniMAX). Reproduced from Reference 20.
6.4.3 TR-SANS

Postmixed specimens containing 50% hPS-PEP and 50% dPS-PEP were heated to a target temperature and monitored by SANS every 5 min. Since the neutron scattering intensity is proportional to the contrast against background, the intensity decreases as copolymers are exchanged between micelles. Figure 6.5 illustrates representative scattering curves obtained from postmixed specimens during time evolution at 119.5 ºC and 156.5 ºC for PS-PEP-1 and PS-PEP-2, respectively. The intensity decreases rapidly during the early stage, followed by a significant reduction in the rate of exchange. In order to achieve annealing times longer than 3–4 hr, specimens were maintained at the target temperature outside the SANS beam line and reinserted periodically. More than 13 h are required to achieve statistically distributed hPS and dPS in the cores.

Since \( \rho_{\text{core}}(t) - \rho_{\text{sol}} \) in eq (6.9) is proportional to the volume fraction of hPS chains (or dPS chains) in the core, the scattering intensity is directly related to the extent of exchange. Therefore, the instantaneous state of exchange can be expressed by the normalized relaxation function \( R(t) \) as

\[
R(t) = \left( \frac{I(t) - I(\infty)}{I(0) - I(\infty)} \right)^{1/2},
\]

where \( I(0) \) and \( I(\infty) \) are the neutron scattering intensity of the initial state, obtained from the postmixed specimen at 30 ºC, and of the final state, obtained from the premixed specimen at the target temperature, respectively. Figure 6.6 presents \( R(t) \) plotted on a logarithmic time scale for PS-PEP-1 at 110 ºC, 119.5 ºC and 130.3 ºC, and for PS-PEP-2 at 144.5 ºC, 156.5 ºC, and 164.5 ºC. The logarithmic form of \( R(t) \) is consistent with our previous observations for the same copolymers in dilute solution as well as the results of
Figure 6.5 Time evolution of SANS patterns collected from a 15 vol% (a) dPS-PEP-1/hPS-PEP-1 50/50 mixture at 119.5 °C and (b) dPS-PEP-2/hPS-PEP-2 50/50 mixture at 156.5 °C. Initial measurements were obtained at 30 °C (filled circle), followed by the acquisition of SANS data every 5 min (shown in legend) at the target temperature. The statistically mixed core data were obtained from premixed specimens at the target temperature.
Figure 6.6 Relaxation function of (a) dPS-PEP-1/hPS-PEP-1 at 110 °C (square), 119.5 °C (circle), and 130.3 °C (triangle) and (b) dPS-PEP-2/hPS-PEP-2 at 144.5 °C (square), 156.5 °C (circle), and 164.5 °C (triangle). The straight lines are guides to the eye indicating logarithmic time dependence of relaxation decay.
Lund et al. on PEP-PEO in aqueous solution (see Chapter 8).\textsuperscript{21,22} This implies that the logarithmic decay is a result of single chain exchange that is hypersensitive to the core block length and therefore polydispersity, in a similar manner to the dilute solution.

It is worthwhile to compare $R(t)$ between the bcc ordered state and dilute solution to assess the expectation that the exchange rate is nearly independent of micelle concentration, based on the assumption that the extraction of the core block is rate-limiting. The time-temperature superposition principle was applied in order to account for the effect of temperature. The TR-SANS data presented in Figure 6.7 were shifted to individual master curves at a reference temperature $T_{\text{ref}}$ where the scattering intensities were monitored for both concentrations, i.e., $T_{\text{ref}} = 110$ °C for PS-PEP-1 and $T_{\text{ref}} = 145$ °C for PS-PEP-2, based on the shift factor $a_T = \tau(T)/\tau_{\text{ref}}(T_{\text{ref}})$ shown in the inset. Solid lines are best fits to eq (5.6) in Chapter 5 by adjusting the thermodynamic penalty-related parameter $\alpha_\chi$ and the polydispersity of the core block length. The monomeric friction factor $\zeta$ was estimated using reported rheology data for PS by shifting $T_g$ to 70 °C to account for plasticization of PS due to solvent penetration into the core.\textsuperscript{23} The statistical segment length was taken as 0.67 nm for PS.\textsuperscript{24} The fitting results are summarized in Table 6.3. As illustrated in Figure 6.7, exchange kinetics of the bcc ordered state are more than an order of magnitude slower than in dilute solution for both PS-PEP-1 and PS-PEP-2. This discrepancy is unexpected and discussed in the following section.
Figure 6.7 Comparison of time-temperature superposed $R(t)$ between dilute solution (open, regenerated from Chapter 5) and the bcc ordered state (filled) for (a) PS-PEP-1 at $T_{\text{ref}} = 110 \, ^\circ \text{C}$ [originally measured at 110 °C (filled circle), 119.5 °C (filled square) and 130.3 °C (filled triangle)] and (b) PS-PEP-2 at $T_{\text{ref}} = 145 \, ^\circ \text{C}$ [originally measured at 144.5 °C (filled square), 156.5 °C (filled circle), and 164.5 °C (filled triangle)]. Solid curves are best fit to eq (5.6). The shift factors $\alpha_T$ are shown in the inset.
Table 6.3 Fitting results for relaxation kinetics

<table>
<thead>
<tr>
<th></th>
<th>$\langle N_n \rangle$ (input)</th>
<th>$N_w/N_n$</th>
<th>$\alpha \chi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-PEP-1$^a$</td>
<td>Dilute solution</td>
<td>255</td>
<td>1.07</td>
</tr>
<tr>
<td></td>
<td>BCC ordered state</td>
<td>255</td>
<td>1.03</td>
</tr>
<tr>
<td>PS-PEP-2$^b$</td>
<td>Dilute solution</td>
<td>412</td>
<td>1.05</td>
</tr>
<tr>
<td></td>
<td>BCC ordered state</td>
<td>412</td>
<td>1.03</td>
</tr>
</tbody>
</table>

$^a T_{ref} = 110 \, ^\circ C, \zeta = 1.18 \times 10^{-7} \, N \, s \, m^{-1}, \quad ^b T_{ref} = 145 \, ^\circ C, \zeta = 2.41 \times 10^{-9} \, N \, s \, m^{-1}$

6.5 Discussion

We observed good agreement between the measured $R(t)$ for the bcc ordered solutions and the relaxation function estimated by our model, with reasonable values of the fitting parameters, consistent with the behavior of the dilute solutions. $R(t)$ for the bcc ordered solutions, however, is over an order of magnitude slower than for the corresponding dilute solutions, which is unexpected based on our assumption that the extraction of the core blocks is rate-limiting. We will investigate the sensitivity of the adjustable parameters in our model, followed by postulated reasons for these differences.

6.5.1 Sensitivity of Fitting Parameters

In our model, chain exchange kinetics are determined by three factors: polydispersity of core blocks, the unfavorable interaction between core block segments and solvents, and the mobility of core blocks. The polydispersity of core blocks is related to the broadness of relaxation times, resulting in a specific slope of the logarithmic decay at an intermediate time period. As the polydispersity increases, the exchange kinetics change
significantly: faster at shorter time due to shorter blocks, followed by slower at longer time due to longer blocks than a exponential decay observed with monodisperse polymers as shown in Figure 5.10 in Chapter 5. Therefore, we expect the slope to be independent of concentration when employing a single material. However, $R(t)$ for the bcc state with closer examination may be somewhat steeper than for the dilute solutions resulting in an apparent (fitted) polydispersity that is smaller for the ordered system.

**Figure 6.8** Sensitivity of calculated $R(t)$ to variation in interfacial tension $\alpha \chi$. Data are superimposed PS-PEP-1 ($T_{\text{ref}} = 110$ °C) results for dilute solutions (unfilled) and bcc ordered state (filled) from Figure 6. Lines are estimated $R(t)$ by eq (9) as a function of the values of $\alpha \chi$: 0.045 (solid), 0.0495 (dash), 0.054 (dash-dot), and 0.57 (dot) with fixed PDI (1.07) and $\zeta (=1.18 \times 10^{-7}$ N s m$^{-1}$).
According to eq (5.6) and eq (5.8) in Chapter 5, the unfavorable interactions between the core blocks and the matrix, expressed through $\chi$, directly influence the relaxation function $R(t)$. The exchange kinetics are highly sensitive to the magnitude of $a\chi$ due to the double exponential dependence, hence a 10% increase in $a\chi$ can induce approximately a 200% increase in the relaxation time as described in Figure 6.8. Therefore, the slower dynamics documented for the bcc system leads to an increase in the apparent value of $a\chi$ as shown in Table 6.3.

In the simplest description, $\chi$ measures the strength of the local interactions between polymer segments and solvent molecules independent of polymer chain length and polymer concentration in solution.\textsuperscript{25,26} However, $\chi$ values between nonpolar solvents and nonpolar polymers are typically higher than 0.3, while for miscible polymer blends $\chi \approx O(10^{-2})$. Milner et al. indicated that this behavior is mainly due to entropic contributions to $\chi$ associated with the translational degree of freedom in exploring free volume.\textsuperscript{27} They noted that the thermal expansion coefficients for solvents ($12 \times 10^{-4}$ K$^{-1}$) are typically a factor of 1.7 greater than those for polymers ($7 \times 10^{-4}$ K$^{-1}$) and this increment suggests solvent molecules can rattle more aggressively around the available free volume. Therefore, the entropic contribution decreases as the length of solvent molecules increases as evidenced by the thermal expansion coefficient. Considering the thermal expansion coefficient of squalane, a long saturated hydrocarbon solvent ($8.15 \times 10^{-4}$ K$^{-1}$), it is a reasonable assumption that squalane behaves more like polymers than small molecules.\textsuperscript{28} Similarly, Lund et al. reported that the calculated $\chi$ parameter between PS and $n$-alkanes decreases with longer hydrocarbon solvents up to $n=16$ using Hildebrand’s solubility parameters,\textsuperscript{29} consistent with our argument. Therefore, we assume that $\chi_{S\text{-squalene}}$ is similar to $\chi_{S\text{-EP}}$ because the segmental structure of squalane is identical to that of PEP.
Sakurai et al. obtained the temperature dependence of $\chi_{S-EP}$ using PS-PEP ($M_n = 7.4 \times 10^4$ g/mol and $f_{PS} = 0.128$, where $f_{PS}$ is the volume fraction of the PS block) solutions in dioctyl phthalate (DOP) by analyzing SAXS patterns with the random phase approximation. They estimated $\chi_{S-EP} = 0.07$ with a weak temperature dependence between 100 °C and 200 °C. Lai et al. measured order-disorder temperatures $T_{ODT}$ for three PS-PEP block copolymers ($2.0 \times 10^4$ g/mol $< M_w < 2.3 \times 10^4$ g/mol and $0.29 < f_{PS} < 0.35$), and reported a significantly larger and strongly temperature dependent segment-segment interaction parameter, $\chi_{S-EP} = 0.14$ at 100 °C and 0.09 at 200 °C. This kind of inconsistency in $\chi$ parameters estimated based on different experimental methods, in this case the structure factor from SAXS versus $T_{ODT}$, has been described before. Accepting a particular value for $\chi_{S-EP}$ directly influences our determination of the prefactor $\alpha$.

The prefactor $\alpha$ is related to the shape of the potential at the interface between the cores and the medium. In the strong segregation regime, the polymer blocks tend to be completely segregated, producing a square-like composition profile at the interface. At weaker segregation strengths this profile broadens due to interfacial mixing resulting in contact between core block segments and the medium (i.e., solvent molecules or corona block segments). Hence, the thermodynamic penalty associated with extracting a core block into the matrix is reduced to a fraction of $\chi N_{core}$, which is manifested as a smaller value of $\alpha$ in the analysis of the block copolymer exchange dynamics. Provided that $\chi_{S-EP}$ is approximately 0.1 at the experimental temperatures, the value of $\alpha$ ranges from 0.45 (PS-PEP-1) and 0.36 (PS-PEP-2) for dilute solutions to 0.57 (PS-PEP-1) and 0.41 (PS-PEP-2) for bcc ordered state, all consistent with theoretical expectations, i.e., lower than 1 and higher for the concentrated versus dilute solutions.

Diffusion of diblock copolymers in bcc ordered melt microstructures has been investigated using forced Rayleigh scattering (FRS), forward recoil spectrometry
All results have shown that diffusion is strongly influenced by the enthalpic factor $\chi N_{\text{core}}$, resulting in $D = D_0 \exp[-\alpha \chi N_{\text{core}}]$ where $D_0$ is the diffusion coefficient in the absence of any interactions. Yokoyama and Kramer measured the self-diffusion of sphere forming asymmetric poly(styrene-$b$-$2$-vinylpyridine) using FRES and reported $\alpha = 1.2$. Subsequent simulation results showed that $\alpha$ should be between 0 and 1. Cavicchi and Lodge also reported $\alpha$ between 0.27 and 1.34 based on FRS experiments with four asymmetric poly(ethylene-alt-propylene-$b$-dimethylsiloxane) diblock copolymers. While the variation in prior experimentally determined $\alpha$ values has not been resolved, they bracket the currently reported ones.

Based on Rouse dynamics, the longest relaxation time is inversely proportional to the mobility of core blocks as expressed by the monomeric friction factor $\zeta$ in eq (5.6) in Chapter 5. Due to the solvent plasticized core blocks, the mobility should be a function of the fraction of solvent molecules localized in the core. The $T_g$ of the PS core blocks is a quantitative indication of the solvent fraction in the micelle core, but accurate measurement of $T_{g,\text{PS}}$ is not feasible due to the small overall amount ($< 5$ vol% PS in the solutions). It was reported that the $T_{g,\text{PS}}$ for a mixture of PS-PI in squalane at lower polymer fraction ($< 40$ wt% PS in solutions) is nearly independent of concentration by differential scanning calorimetry, which suggests that the difference in the solvent fraction in the micelle cores between the two presently measured concentrations should be slight. Therefore, we have applied the same values of $\zeta$ to both concentrations for each diblock copolymer studied.

### 6.5.2 Postulated Reasons for Slower Dynamics

We observed that $R(t)$ for dilute, disordered solutions is nearly independent of the concentration between 0.5 vol% and 2 vol% of PS-PEP in squalane described in Figure
However, $R(t)$ for concentrated, ordered solutions (i.e., 15 vol% of PS-PEP in squalane) is more than an order of magnitude slower. The micelle structure and surroundings can influence chain exchange kinetics when their contributions become significant in comparison to the core block dynamics. Therefore, we propose possible explanations to account for the slower dynamics in terms of the solvent fraction in the core region, crowdedness of corona chains in the medium, and core radius.

The solvent plasticized core blocks provide both the higher mobility for core blocks and the reduced thermodynamic penalty of the chain extraction, simultaneously. As expected the probability of solvent penetration into the micelle cores is lower as the solvent fraction in the solutions decreases (i.e., 99 vol% and 85 vol% for dilute and concentrated solutions, respectively). This implies that the slower dynamics for bcc ordered solutions is attributed partly to the lower solvent fraction in the core region than the dilute solutions. However, the quantitative dependence of both the friction factor and thermodynamic incompatibility on the solvent fraction in the core region is not fully resolved particularly for dilute polymer micelle solutions.

The configuration of polymers being transported through the medium also has an influence on the exchange kinetics. In terms of the energy potential, grafted and confined corona blocks on micelle cores tend to adopt less stretched configurations by extraction to solvent media.\(^{41}\) The extracted polymers in dilute, disordered solutions have lower probability to interact with other corona blocks grafted on micelles than that for the concentrated, ordered solutions. Therefore, the driving force by corona blocks in concentrated solutions is entropically weaker, resulting in the slower chain extraction rate.

Since core blocks were at most weakly entangled and relaxed for dilute solutions (i.e., $R_c \sim N_{\text{core}}^{0.5}$) as described in Chapter 5, the Rouse dynamics were assumed to estimate
longest relaxation times in our model. The core radii for the bcc ordered solutions are 20–30% greater than for dilute solutions, indicating more stretched core blocks. The local chain dynamics on the nanosecond time scale are nearly independent of micelle concentration (i.e., ordered and disordered), measured by neutron spin echo experiments. Therefore, the longest relaxation time for the bcc ordered solutions would be greater than estimated by Rouse dynamics due to the longer path length of stretched chains, although this mechanism above is not likely to account for the order of magnitude increase.

6.6 Summary

To understand the concentration dependence of the chain exchange kinetics in block copolymer micelles, we investigated single molecular exchange between micelles packed onto bcc lattices by TR-SANS. SANS specimens were prepared with 15 vol% polymer solutions of 50/50 dPS-PEP/hPS-PEP in an isotopic squalane mixture. A perfectly random distribution of deuterium-rich and proton-rich micelles located on bcc lattice sites makes SANS intensities directly related to the fraction of exchanged chains without the contribution from the interparticle interaction. Logarithmic relaxation decay in bcc ordered solutions was observed, consistent with the behavior of dilute solutions, implying that the exchange mechanism for both concentrations have the same origin. However, the molecule exchange kinetics for the bcc ordered solutions are over an order of magnitude slower than for the corresponding dilute solutions. We postulate that the slower dynamics can be attributed to a lower solvent fraction in the cores, a longer diffusion path length for the core blocks, and a lower driving force for core block extraction induced by the corona blocks. These results provide more fundamental information necessary to
understand amphiphilic block copolymer micelle kinetics underlying the attainment of thermodynamically equilibrated structures.

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Chapter 7

Summary and Outlook

7.1 Thesis Summary

This research has focused on the structure and dynamics of block copolymer micelles formed by asymmetric poly(styrene-\textit{b}-ethylene-\textit{alt}-propylene) (PS-PEP) diblock copolymers in squalane, a highly selective solvent for PEP blocks. The micelles are composed of compact PS cores and highly swollen PEP coronas. Due to the increased glass transition temperature of the PS cores, the micelle structure is critically affected by the molecule exchange kinetics to reach the equilibrium state. The experimental results characterized by dynamic light scattering (DLS), rheology, and small-angle x-ray scattering (SAXS) demonstrate that the micelle structure observed is only weakly temperature dependent, and reproducible. Furthermore, the micelles begin to overlap and pack onto body-centered cubic lattices, as the copolymer concentration in solutions increases.

The temperature independence of the micelle structure may be attributed to either the equilibrium state or the slow or frozen molecule exchange. To understand the origin of this behavior, the molecule exchange kinetics in block copolymer micelles in dilute solutions (1 vol\% of copolymers) were investigated using time-resolved small-angle neutron scattering (TR-SANS) with isotopically labeled PS-PEP diblock copolymers dispersed in an isotopic squalane mixture, as described in Chapter 5. The form of the time
dependence of the molecule exchange is nearly concentration independent, quasi-logarithmic versus time, and highly sensitive to the core block length. Based on the observations, we proposed that molecule exchange kinetics are governed by single chain exchange between micelles, which inherently involves the unfavorable interaction between the core block segments and the medium. This proposed model consequently predicts that the kinetics display a hypersensitivity to the degree of polymerization of the core block, thus polydispersity, which is corroborated by the results.

These experiments were extended to ordered block copolymer micelles in concentrated solutions (15 vol% copolymers) as described in Chapter 6. The TR-SANS data for the concentrated solutions were manipulated analogous to the dilute solutions, because the intermicellar contribution in the scattered intensity was negligible under the experimental condition. The rate of molecular exchange obtained is more than an order of magnitude slower than for the dilute solutions, which is unexpected according to our model. The parameters in our kinetics model were revisited and three possible explanations for the slower dynamics were discussed in Chapter 6: the solvent fraction in the core region, driving force to extraction by coronas, and core radius.

### 7.2 Outlook

There are several potential future research directions related to molecular exchange kinetics in block copolymer micelles suggested by this thesis. The fundamental understanding derived from investigations of the well-known system should assist the design of other block copolymer micelles. A few possible future research directions are described. The first step would be to understand the relationship between the exchange rate and block copolymer micelle properties including the critical micelle temperature.
(CMT) or order-disorder transition temperature ($T_{ODT}$), glass transition temperature ($T_g$) of the core blocks, and block copolymer architecture.

As polymer concentration increases, $T_{ODT}$ for concentrated solutions increases up to $T_{ODT}$ for the neat block copolymers. This implies that the solvent selectivity apparently increases with increasing concentration. Here, the entropic contribution plays a dominant role in the increasing solvent selectivity, because the enthalpic contribution is nearly independent of the polymer concentration. $T_{ODT}$ has been considered as the onset of dissolution of copolymers in solutions. It was also observed that micelles are disordered, but not molecularly dissolved up to a particular temperature,\textsuperscript{1,2} potentially implying that CMT is also a function of the copolymer concentration. $T_{ODT}$ can be measured by SAXS and rheology, and CMT can be measured by DLS. Therefore, it would be interesting to perform the concentration dependent measurement resulting in a relationship between the $T_{ODT}$ or CMT and the temperature where the chain exchange occurs with a particular rate. This would provide more insight about the slower dynamics observed for concentrated, ordered solutions.

The solvent selectivity can be tuned by blending two different solvents. Figure 7.1 described the temperature dependence of hydrodynamic radius for 0.5 wt% SEP(42-60) in several mixtures of squalane, a highly selective solvent to PEP blocks, and phenyldodecane, a neutral solvent. Naturally, the CMT decreases with increasing fraction of phenyldodecane in the mixtures. Therefore the relationship between CMT–$T$ and the exchange rate can be determined. Here, $T_g$ of core blocks, influenced by the neutral solvent, can be independently estimated by extrapolating the values of $T_g$, core measured with various concentrated solutions using DSC.\textsuperscript{3}

Our conclusion in Chapter 5 should be applicable to several types of block copolymer micelles independent of shape and structure. In this work, we demonstrated the exchange
kinetics for micelles containing long and swollen coronas ($0.26 < f_{\text{core}} < 0.38$). Due to the sizable corona blocks, micelle fusion/fission does not come into play as described in Chapter 5. However the exchange process was expected to depend on the corona block length as well as core block length.\textsuperscript{4} Therefore, systematic investigation of the exchange kinetics with various block compositions, but fixed core block length, would provide more insight about the exchange kinetics. In addition, the exchange kinetics for worm-like micelles and vesicles formed by block copolymers has not been well documented due to experimental difficulties. TR-SANS is a powerful tool to investigate these micelle and vesicle dynamics as demonstrated in this Thesis and elsewhere.\textsuperscript{5,6}
Figure 7.1 (a) Temperature dependence of hydrodynamic radius ($R_h$) in the mixed solvents at 0.5 wt%: 75% squalane (open), 50% squalane (half filled), and 25% squalane (solid). Upper triangles are measure upon increasing temperature and down upon decreasing temperature. (b) The critical micelle temperature (CMT) as a function of the squalane fraction in the binary mixtures.
### 7.3. References


Chapter 8

Supporting Information

8.1 Phase Diagram of SEP(42-60)

In this study, we investigated the phase diagram of poly(styrene-\textit{b}-ethylene-\textit{alt}-propylene) (with $N_{\text{PS}} = 400$ and $N_{\text{PEP}} = 880$, designated SEP(42-60)) in squalane, highly selective to PEP blocks, as a function of temperature and concentration using small-angle x-ray scattering (SAXS). SEP(42-60) was prepared by anionic polymerization and selective saturation as described in Chapter 4. SAXS specimens were prepared by dissolving the copolymer in squalane with dichloromethane, followed by removal of the dichloromethane at atmospheric pressure. Before loading in aluminum DSC pans, the specimens were annealed at higher temperature (~160 °C), followed by slowly cooling down. SAXS experiments were performed at the DND-CAT beam line at the Argonne National Laboratory using 17 keV radiation, corresponding to a wavelength $\lambda$ of 0.729 Å, and a sample-to-detector distance of 6.5 m. The sample temperature was managed by an electric heater under a slightly positive pressure of helium between room temperature and 300 °C. Two-dimensional SAXS images were azimuthally averaged to one-dimensional plot of intensity vs wavevector ($q$).

8.1.1 Lamellae (LAM)

The volume fraction of PS blocks is calculated as 0.356 at 140 °C from the densities
of PEP (0.790 g/cm$^3$) and PS (0.969 g/cm$^3$), accordingly a lamellar morphology is expected.$^1$ Figure 8.1 illustrates SAXS patterns of (a) 100 wt% and (b) 88 wt% and (c) 80 wt% of SEP(42-60) diblock copolymers in squalane at multiple temperatures. The sequence of peak ratio $q/q^*$ ($q^*$ is the primary peak) of 1:2:3:4:5:6:7 indicates a lamellar morphology for all three specimens between room temperature and 200 ºC or 300 ºC. Each specimen shows that peaks are broad at 30 ºC, and become sharper and clearer as the temperature increases. The poorly ordered structure at room temperature is attributed to the glassy PS domain ($T_{g,PS}$ ~ 100 ºC), coupled with deformation during specimen loading at room temperature. At higher temperatures, a greater mobility of the SEP block copolymers can result in well-ordered lamellae. It is also observed that the position of $q^*$ slightly increases with increasing temperature, indicating that the domain spacing ($d=2\pi/q^*$) decreases. Since the incompatibility between PS and PEP blocks is attenuated as temperature increases ($\chi_{S-EP} \sim 1/T$), the entropy of mixing becomes comparable to the enthalpy of the unfavorable interaction. Therefore, PS and PEP blocks form a relaxed configuration at the interface. However, the order-disorder transition was not observed in our measurements due to the generically strong incompatibility between the PS and PEP blocks.

It is interesting that the weak appearance of peaks located at 3$q^*$ and 6$q^*$, and complete absence of 7$q^*$ scattering for the 100 wt% and 80 wt% SEP(42-60) solutions, respectively, were observed. Since the scattering center is specified by the distribution of the scattering length density, the distribution of lattice points ($z(r)$) should be convoluted with the scattering length density of the scattering centers ($\rho_u(r)$), resulting in $\rho(r) = \rho_u(r) * z(r)$. Therefore, the scattering intensity, which is a square of the Fourier transform of $\rho(r)$, can be expressed as
\[ I(q) \propto |F(q)Z(q)|^2 \]  

(8.1)

where \( F(q) \), called the structure factor, is the Fourier transform of \( \rho_u(r) \), and \( Z(q) \), called as the lattice factor, is the Fourier transform of \( z(r) \).\textsuperscript{3,4} For one dimensional lamellar, the \( Z(q) \) are 1 and 0 where \( q = 2\pi h/d \) and \( q \neq 2\pi h/d \), respectively, where \( h \) is an integer. Therefore, the scattering intensity for one-dimensional centro-symmetric lamellae can be described as

\[ I(h) \propto \left| \int_0^{\frac{1}{2}} \rho(x) \left( \cos(2\pi hx) + \cos(-2\pi hx) \right) dx \right|^2. \]  

(8.2)

where \( x = r/d \). For strongly segregated lamellae, the electron density field can be given as

\[ \rho(x) = \begin{cases} 
\rho_A & : x \in [0,f] 
\rho_B & : x \in (f,0.5] 
\end{cases} \]  

(8.3)

in which \( f \) is volume fraction of A block. According to the given \( \rho(x) \), Eq (9.2) can be reorganized as

\[ I(h) \propto \left| \frac{1}{h\pi} \left( \rho_B \sin(h\pi) + (\rho_A - \rho_B) \sin(2fh\pi) \right) \right|^2. \]  

(8.4)

Therefore, the position of extinct peaks is dependent on the block volume ratio. For example, regardless of the values of \( \rho \), peaks at \( q/q^* = 2n \) (\( n \) is an integer) disappear for perfectly symmetric two-domain lamellae \( (f = 0.5) \).\textsuperscript{4} Based on eq (8.4), volume fractions
Table 8.1 Calculated volume fraction of PS domain where peaks are disappear for lamellae

<table>
<thead>
<tr>
<th>Miller index ($h$)</th>
<th>Volume fraction of PS$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>0.25</td>
</tr>
<tr>
<td>3</td>
<td>0.33</td>
</tr>
<tr>
<td>4</td>
<td>0.25, 0.375</td>
</tr>
<tr>
<td>5</td>
<td>0.30, 0.40</td>
</tr>
<tr>
<td>6</td>
<td>0.25, 0.33</td>
</tr>
<tr>
<td>7</td>
<td>0.285, 0.36</td>
</tr>
<tr>
<td>8</td>
<td>0.25, 0.312, 0.375</td>
</tr>
</tbody>
</table>

$^a$
Figure 8.1 SAXS patterns of SEP(42-60) in squalane at (a) 100 wt%, (b) 88 wt%, and (c) 80 wt% upon heating. The sequence of peak ratio $q/q^*$ indicates a lamellar morphology for the three specimens. Data are vertically shifted for convenience.
of PS domain (between 0.25 and 0.4) where the peak at \( q/q^* \) are expected to be extinct for perfectly segregated lamellae can be calculated as illustrated in Table 8.1, using \( \rho_{PS} = 0.886 \times 10^{10} \text{ cm}^{-2} \) and \( \rho_{PEP} = 0.766 \times 10^{10} \text{ cm}^{-2} \). \( 7q^* \) for 80 wt% SEP(42-60) solution (\( f_{PS} = 0.285 \)) is expected to be extinct, consistent with the data. For 100 wt% (\( f_{PS} = 0.356 \)) and 88 wt% (\( f_{PS} = 0.313 \)) solutions, \( 3q^* \) and \( 6q^* \) are expected to be weaker, consistent with the data, however \( 7q^* \) and \( 8q^* \) are observed to be strong, inconsistent with this calculation.

### 8.1.2 Hexagonally Packed Cylinder (HEX)

As the amount of solvent increases, the phase transitions \( \text{LAM} \rightarrow \text{G} \rightarrow \text{HEX} \) can be predicted.\(^5\,6\) Since the G window is typically narrow, it is not surprising that this phase was not observed with SEP(42-60) in squalane in our study. Figure 8.2 illustrates SAXS patterns from (a) 67 wt%, (b) 59 wt%, (c) 49 wt% and (d) 40 wt% SEP(42-60) solutions in squalane. The SAXS patterns from four specimens show the sequence of peak ratio \( q/q^* \) of \( 1 : \sqrt{3} : \sqrt{4} : \sqrt{9} : \sqrt{12} : \sqrt{13} : \sqrt{16} : \sqrt{19} \), indicating a two-dimensional hexagonally packed cylinder morphology with a long-range order. Similar to the lamellar samples, broad Bragg peaks were observed at 30 °C due to a combination of glassy PS domains and sample loading history where equilibration is impractical. Chain mobility increases with increasing temperature, leading to well-ordered structure evidenced by the sharp Bragg peaks. Consistent with the lamellar samples, the position of \( q^* \) increases with increasing temperature due to relaxed configurations of each block at higher temperatures. \( T_{ODT} \) was not also observed in our experiment up to 300 °C.

In general, scattering patterns include the intraparticle contribution (i.e., form factor) and the interparticle contribution (i.e., Bragg scattering). The interparticle scattering is dominant at lower \( q \), while the intraparticle scattering is at higher \( q \). Some Bragg peaks
disappear near the minimum of the form factor at intermediate $q$. In Figure 8.2, a fluctuation in scattering intensities at $q > 0.02$ Å$^{-1}$ is attributed to the intraparticle scattering. Accordingly, we attempted to describe the SAXS patterns with the form factor $P_c(q)$ of uniform cylinder of radius $R_c$ and length $L$,

$$P_c(q, R_c, L) = \frac{\pi}{2} \int_0^\pi \Psi(q, R_c, L, \alpha) \sin \alpha d\alpha$$

(8.5)

where

$$\Psi(q, R_c, L, \alpha) = \frac{2J_1(qR_c \sin \alpha)}{qR_c \sin \alpha} \sin \left(\frac{(qL \cos \alpha)/2}{qL \cos \alpha}/2\right),$$

(8.6)

and $J_1$ is the first order Bessel function of the first kind. The characteristic equation, $J_1(qR_c) = 0$, indicates that the distinct first minima reflects the core radius of the cylinder. For example, $q^* = 0.0214$ Å$^{-1}$ for 67 wt% solution at 100 °C gives $R_c = 179$ Å, which was then used as an initial guess in the detailed model. Two fitting parameters ($R_c$ and $L$) were adjusted using the Igor package provided by NIST. Solid lines are best fit to the form factor, and show reasonable agreement with the data. The length of cylinders is mostly dependent on sample history, and not a thermodynamic parameter, thus I do not consider the fitting parameter $L$. The resulting $R_c$ are in reasonable agreement with the initial guesses and summarized in Table 8.2.

The unit cell dimensions ($a_{HEX}$) for two-dimensional hexagonal structure are related to $q^*$ by $a_{HEX} = 4\pi/(\sqrt{3}q^*)$, and $a_{HEX}$ at 100 °C are also illustrated in Table 8.2. Geometrically, a volume fraction of PS domain forming cylinder core can be estimated
Figure 8.2 SAXS patterns of SEP(42-60) in squalane at (a) 67 wt%, (b) 59 wt%, (c) 49 wt%, and (d) 40 wt% upon heating. The sequence of peak ratio $q/q^*$, indicated by arrows, shows that four specimens are ordered into hexagonally packed cylinder, and solid lines are best fit to cylindrical form factor. Data are vertically shifted for convenience.
Table 8.2 Characteristics of 2D hexagonal-packed cylinder

<table>
<thead>
<tr>
<th>Sample</th>
<th>$q_{\text{min}}$ [Å$^{-1}$]</th>
<th>$R_c$ [Å]</th>
<th>$R_c^b$ [Å]</th>
<th>$q^*$ [Å$^{-1}$]×</th>
<th>$a_{\text{HEX}}$ [Å]×</th>
<th>$f_{PS}$×</th>
<th>$f_{PS}$×</th>
</tr>
</thead>
<tbody>
<tr>
<td>67 wt%</td>
<td>0.0214</td>
<td>179</td>
<td>182</td>
<td>0.00947</td>
<td>766</td>
<td>0.21</td>
<td>0.23</td>
</tr>
<tr>
<td>59 wt%</td>
<td>0.0227</td>
<td>169</td>
<td>173</td>
<td>0.00947</td>
<td>766</td>
<td>0.19</td>
<td>0.21</td>
</tr>
<tr>
<td>49 wt%</td>
<td>0.0239</td>
<td>160</td>
<td>163</td>
<td>0.00926</td>
<td>783</td>
<td>0.16</td>
<td>0.16</td>
</tr>
<tr>
<td>40 wt%</td>
<td>0.0251</td>
<td>152</td>
<td>152</td>
<td>0.00905</td>
<td>801</td>
<td>0.13</td>
<td>0.13</td>
</tr>
</tbody>
</table>

a calculated by the characteristic equation, b fitting results,

c $q^*$ at 100 ºC, d the unit cell dimension at 100 ºC

e the volume fraction of PS domain, which is calculated from $R_c$ and $a_{\text{HEX}}$ geometrically,
f the volume fraction of PS block, which is calculated from the block compositions and the amount of added squalane

by the areal ratio of cylinder core and hexagonal matrix. The estimated values shown in Table 8.2 are reasonably consistent with the volume fraction of PS block calculated from the block composition and the amount of added squalane in solutions.

8.1.3 Body-Centered Cubic Spheres (BCC)

Figure 8.3 shows SAXS patterns for (a) 30 wt%, (b) 20 wt%, (c) 10 wt% (reproduced from Chapter 4), (d) 7 wt%, and (e) 6.5 wt% of SEP(42-60) solution in squalane upon heating. The sequence of peak ratios $q/q^*$ of $1 : \sqrt{2} : \sqrt{3} : \sqrt{4} : \sqrt{5} : \sqrt{6} : \sqrt{7} : \sqrt{8}$ indicates the body-centered cubic (BCC) morphology with a long-range order. A peak at $q/q^*$ of
\( \sqrt{7} \) distinguishes a BCC morphology from a simple cubic morphology. Contrary to the concentrated solutions, the position of \( q^* \) decreases smoothly with increasing temperature for all five specimens, where squalane is the major component. The increase in domain spacing \( (d=2\pi/q^*) \) is attributed to the increase of the squalane specific volume with increasing temperature, consistent with the results in Chapter 4 where the adjusted lattice parameters are nearly independent of temperature. We observed the order-disorder transition at near 30 ºC only for the 6.5 wt% solution as evidenced by disappearing Bragg peaks.

Similar to the SAXS patterns associated with hexagonally packed cylinders, a form factor dominates over a structure factor (i.e., Bragg scattering), as can be seen in Figure 8.3 for \( q > 0.03 \text{ Å}^{-1} \). Therefore, we also attempted to fit the data with the form factor of uniform sphere of radius \( R_s \),

\[
P_s(q) = \frac{3\left(\sin(qR_s) - qR_s \cos(qR_s)\right)}{(qR_s)^3}.
\]

The distinct first minima in the form factor is related to \( R_s \) by the characteristic equation: \( qR_s = \tan(qR_s) \). One fitting parameter \( (R_s) \) was adjusted using the Igor package provided by NIST.\(^8\) The solid curve is best fit to the form factor for 30 wt% SEP(42-60) solution, and shows reasonable agreement with the data.
Figure 8.3 SAXS patterns of SEP(42-60) in squalane at (a) 30 wt%, (b) 20 wt%, (c) 10 wt%, (d) 7 wt%, and (e) 6.5 wt% upon heating. The sequence of peak ratio \(q/q^*\) indicates body-centered cubic morphology, and solid line is best fit to spherical form factor.
Table 8.3 Characteristics of body-centered cubic spheres

<table>
<thead>
<tr>
<th>Sample</th>
<th>$q_{\text{min}}$ [Å$^{-1}$]</th>
<th>$R_c^a$ [Å]</th>
<th>$R_c^b$ [Å]</th>
<th>$q^* [Å^{-1}]^c$</th>
<th>$a_{\text{bcc}}$ [Å]$^d$</th>
<th>$f_{\text{PS}}$ $^e$</th>
<th>$f_{\text{PS}}$ $^f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 wt%</td>
<td>0.0327</td>
<td>138</td>
<td>139</td>
<td>0.0143</td>
<td>621</td>
<td>0.094</td>
<td>0.11</td>
</tr>
<tr>
<td>20 wt%</td>
<td>0.0379</td>
<td>119</td>
<td>-</td>
<td>0.0145</td>
<td>612</td>
<td>0.061</td>
<td>0.071</td>
</tr>
<tr>
<td>10 wt%</td>
<td>0.0399</td>
<td>113</td>
<td>-</td>
<td>0.0120</td>
<td>740</td>
<td>0.039</td>
<td>0.036</td>
</tr>
<tr>
<td>7 wt%</td>
<td>0.0392</td>
<td>115</td>
<td>-</td>
<td>0.0107</td>
<td>830</td>
<td>0.022</td>
<td>0.025</td>
</tr>
<tr>
<td>6.5 wt%</td>
<td>0.0394</td>
<td>114</td>
<td>-</td>
<td>0.0107</td>
<td>832</td>
<td>0.022</td>
<td>0.023</td>
</tr>
</tbody>
</table>

$^a$ calculated by the characteristic equation, $^b$ fitting results, $^c$ $q^*$ at 100 ºC, $^d$ the unit cell dimension at 100 ºC
$^e$ the volume fraction of PS domain, which is calculated from $R_c$ and $a$ geometrically,
$^f$ the volume fraction of PS block, which is calculated from the block compositions and the amount of added squalane

The lattice parameter of a bcc morphology ($a_{\text{bcc}}$) can be computed as $a_{\text{bcc}} = \sqrt[4]{2(2\pi/q^*)}$, and such values are illustrated in Table 8.3 for 100 ºC. Geometrically, a volume fraction of a PS domain forming spheres can be estimated by the ratio of sphere to cubic unit cell volumes. The estimated values are shown in Table 8.3, reasonably consistent with the volume fraction of the PS block calculated from the block composition and the amount of added squalane in solutions.
8.1.4 Summary

We investigated the phase transitions of SEP(42-60) solutions in squalane as a function of temperature and concentration using SAXS. As described in Figure 8.4, LAM $\rightarrow$ HEX $\rightarrow$ BCC transitions were observed as the overall volume fraction of PS decreases, consistent with previous SCFT results in the strong segregation regime (i.e., $\chi N \approx 100$ for our study). In the SCFT result, LAM $\rightarrow$ HEX and HEX $\rightarrow$ BCC occur near $f \approx 0.3$, and 0.12, respectively, which shows good agreement with our data. The loci of order-order transitions are nearly vertical shown in Figure 8.4 because squalane is a highly selective solvent and this system is in the strong segregation regime. For the same reasons, the order-disorder transition was not observed except at 6.5 wt% solution. Below 6.5 wt%, spherical micelles are disordered as indicated by shaded area shown in Figure 8.4. A detailed description of the disordered micelles is provided in Chapter 4.

Figure 8.5 summarizes the results of (a) the domain spacing and (b) the core radius as a function of the weight fraction of the copolymer in solutions, measured at 100 ºC. For the HEX morphology, as the solvent is added, the domain spacing increases and the core radius decreases. The PEP domain can be expanded by the addition of squalane due to solvent selectivity. Increasing the PEP domain size can cause the entropic loss of PEP blocks if the PS core radius is fixed. Therefore, the solution tends to increases the number of cores to relieve this entropic penalty, although this can increase the interfacial area between the PS domains and the matrix (PEP + squalane).

For the BCC morphology, we observed that the core radius of spherical micelles below 10 wt% is nearly independent of the polymer concentration as discussed in chapter 4, consistent with Lodge et al. on poly(styrene-$b$-isoprene) in tetradecane and diethyl phthalate. However, the micelle structure becomes a function of the polymer concentration above 10 wt%, consistent with the results from 15 vol% (Chapter 6). This
Figure 8.4 Phase diagram of SEP(42-60) in squalane as a function of the weight fraction of polymer and the volume fraction of PS. Shaded area denotes disordered micelle. The lines are drawn as guidance to eye indicating the estimated locus between two morphologies.

Figure 8.5 (a) Primary $q^*$ and domain spacing, and (b) $q$ of first minimum and core radius as a function of weight fraction of SEP(42-60) in squalane at 100 °C.
implies that the crowdedness of micelles can be buffered by corona chains below 10 wt%, however entropic loss due to the crowdedness should be compensated with enthalpic gain by decreasing the surface area per chain, thus increasing the core radius above 10 wt%.

8.2 Model Fitting to Data Obtained by Lund et al.

Lund et al. investigated the molecular exchange of poly(ethylene-alt-propylene-b-ethylene oxide) (PEP-PEO) in mixtures of water and N,N-dimethylformamide (DMF) using time-resolved small-angle neutron scattering (TR-SANS).\textsuperscript{11,12} We attempted to fit their data with the our model discussed in Chapter 5. Data obtained by Lund et al. were reproduced using the “Data Thief” software, which converts data points in figures into numerical values.

Eq (5.7) was used to fit the data obtained by Lund et al. as described in Figure 8.6. Two parameters (PDI of core block length and \( \alpha \chi \)) were adjusted to optimize the fits. The monomeric friction factor (\( \zeta \)) was calculated based on simulated prediction at 55°C shown in Figure 8.7.\textsuperscript{13} Here, increase of chain mobility due to solvent penetration into the core region was not considered because \( T_g \) of the PEP core in dilute solution was not provided. A PEP statistical segment length of 0.76 nm was taken from the literature.\textsuperscript{1} Table 8.4 summarizes the parameters associated with fitting \( R(t) \) shown in Figure 8.6. It seems that two data set show similar slopes, but different positions, which is attributed to different interfacial tension between PEP core block segments and solvent (i.e., \( \alpha \chi \)). Adjusted PDI shows a reasonable agreement with reported PDI for core block lengths (~ 1.06). According to the reported interfacial tension (\( \gamma \)) between PEP and water/DMF (\( X_{\text{DMF}} = 0.3 \) at 20 °C) of 20 mN/m,\textsuperscript{14} \( \chi \) can be calculated via Helfand and Tagami theory.
### Table 8.4 Fitting Results

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>$N_{PEP}$</th>
<th>$\zeta$ (N s/m)</th>
<th>PDI</th>
<th>$\alpha \chi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X_{DMF}=0.25$</td>
<td>55</td>
<td>18</td>
<td>$6.06 \times 10^{-10}$</td>
<td>1.03</td>
</tr>
<tr>
<td>$X_{DMF}=0.30$</td>
<td>55</td>
<td>18</td>
<td>$6.06 \times 10^{-10}$</td>
<td>1.03</td>
</tr>
</tbody>
</table>

* : standard deviation is less than 1%

in which $\gamma = kT/a^2(\chi/6)^{0.5}$ where $a$ is a lattice length.\(^\text{15}\) Here, $a$ was estimated to be 3.9 Å as a mean segmental length between water and DMF, leading to $\chi = 3.4$ (thus, $\alpha \sim 0.4$). In addition, $\alpha \chi$ should increase as the fraction of DMF in the mixture decreases.
Figure 8.6 Left: Master curves of chain exchange kinetics at reference temperature of 55 °C for PEP-PEO in water/DMF at $X_{\text{DMF}} = 0.25$ (circle) and $X_{\text{DMF}} = 0.30$ (square) measured at several temperatures (42, 47, 55, 60, 65 °C). Solid lines are best fit to Eq (5.7). Right: shift factor for $X_{\text{DMF}} = 0.25$ (red) and $X_{\text{DMF}} = 0.30$ (blue).

Figure 8.7 Temperature dependence of the monomeric friction factor of PEP block. Square: experimental data using neutron spin echo, Solid line: simulation prediction by J. Luettmert-Strathmann.
8.3 References


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