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著者(和文)	Wylie Kevin Lawrence
Author(English)	Kevin Lawrence Wylie
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Doctoral Dissertation

**Tailoring the Self-Assembly of Block Copolymers by
Functionalizing the Block Interface**

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Kevin Wylie



Department of Materials Science and Engineering

School of Materials and Chemical Technology

Tokyo Institute of Technology

Table of Contents

Chapter 1 General Introduction	1
1.1 Block Copolymers	1
1.2 Block Copolymer Self-Assembly	1
1.3 Block Copolymer Theory and Simulation	5
1.4 Strategies for Tuning Block Copolymer Self-Assembly	8
1.4.1 High- χ Polymers	9
1.4.2 Modifying Block Copolymers	10
1.4.3 Multiblock Copolymers	11
1.4.4 Side-Chain Liquid Crystal Polymers	13
1.5 Overview of This Dissertation	15
1.6 References	18
Chapter 2 Synthesis and Bulk Characteristics of PS- <i>b</i> -PGMA- <i>b</i> -PMMA Triblock Terpolymers Containing a Short Reactive Middle Block	26
2.1 Introduction	26
2.2 Experimental Section	28
2.2.1 Reagents	28
2.2.2 General Procedure for the Synthesis of PSGM by Living Anionic Polymerization	29
2.2.3 Synthesis of PSGM _{OH} via the Thiol-Epoxy Reaction	29

2.2.4 Synthesis of PSGM _F via the Thiol-Epoxy Reaction.....	30
2.2.5 Synthesis of PGMA- <i>b</i> -PMMA via Anionic Living Polymerization.....	30
2.2.6 Characterization Methods	31
2.3 Results and Discussion	32
2.3.1 Synthesis and Post-Functionalization of PSGM.....	32
2.3.2 Estimation of Interaction Parameters.....	36
2.3.3 Bulk Morphology Characterization	42
2.4 Conclusion	47
2.5 References	48
Chapter 3 Morphological Study of Functionalized PS- <i>b</i> -PGMA- <i>b</i> -PMMA Triblock Terpolymers Using Simulation.....	54
3.1 Introduction.....	54
3.2 Experimental Section	55
3.2.1 Theory	55
3.2.2 General Algorithm for Solving the SCFT Equations.....	57
3.2.3 Computational Details.....	58
3.3 Results and Discussion	59
3.3.1 Comparison of Simulated and Experimental Results.....	59
3.3.2 Construction of Linear ABC Triblock Phase Diagrams	66
3.4 Conclusion	74

3.5 References	75
Chapter 4 Self-Assembly of Side-Chain Liquid Crystal Functionalized PS- <i>b</i> -PGMA- <i>b</i> -PMMA Triblock Terpolymers.....	79
4.1 Introduction.....	79
4.2 Experimental Section	80
4.2.1 Reagents	80
4.2.2 Synthesis of PSGM _{LC} via the Thiol-Epoxy Reaction.....	81
4.2.3 Characterization Methods	81
4.3 Results and Discussion	82
4.3.1 Synthesis of Side-Chain Liquid Crystal Containing PSGM.....	82
4.3.2 Estimation of Interaction Parameters.....	84
4.3.3 Liquid Crystal behavior of PGMA _{LC}	86
4.3.4 Bulk Morphology Characterization	88
4.4 Conclusion	95
4.5 References	96
Chapter 5 Synthesis and Bulk Characteristics of Block Copolymers Containing a Functional 1,1-Diphenylethylene Derivative.....	100
5.1 Introduction.....	100
5.2 Experimental Section	102
5.2.1 Reagents	102

5.2.2 Synthesis of 1,1-Diphenylethylene Derivatives via the Wittig Reaction	102
5.2.3 Synthesis of (<i>tert</i> -Butyldimethylsilyl)acetylene Derivatives	103
5.2.4 Synthesis of 1-(3-Butenyl)-4-(1-phenylvinyl)benzene	104
5.2.5 Synthesis of PS- <i>b</i> -PMMA Containing Functional DPE Derivatives via Anionic Polymerization.....	105
5.2.7 Deprotection of TBDMS-containing PS- <i>b</i> -PMMA.....	106
5.2.8 Post-Functionalization of PS- <i>b</i> -PMMA via the Thiol-Ene Reaction	107
5.2.9 Post-Functionalization of PS- <i>b</i> -PMMA via the Thiol-Yne Reaction	108
5.2.10 Post-Functionalization of PS- <i>b</i> -PMMA by Amine Quaternization	108
5.2.11 Poly(styrene- <i>r</i> -methyl methacrylate- <i>r</i> -2-hydroxyethyl methacrylate) via Free Radical Polymerization.....	109
5.2.12 Preparation of Thin Film Samples	110
5.2.13 Characterization Methods.....	110
5.3 Results and Discussion	111
5.3.1 Synthesis of Functional 1,1-Diphenylethylene Derivatives.....	111
5.3.2 Synthesis and Post-Functionalization of PS- <i>b</i> -PMMA Diblock Copolymers with a Functionalized DPE Derivative.....	114
5.3.3 Bulk Morphology Characterization	119
5.3.4 Thin-Film Morphology Characterization	126
5.4 Conclusion	127

5.5 References	129
Chapter 6 General Conclusion	133
List of Publications and Presentations.....	137
Publications Related to this Dissertation	137
List of Presentations	137
Acknowledgement.....	139

Chapter 1

General Introduction

1.1 Block Copolymers

Block copolymers (BCPs) are a widely studied material because of their many interesting properties and applications. The simplest type of block copolymer is the linear A-B diblock copolymer which is composed of two different homopolymers that are covalently bonded which generally requires the use of a controlled polymerization method to obtain precise molecular architectures. Since the discovery of living anionic polymerization by Szwarc et al. in 1956,¹ block copolymers have been able to be synthesized in a simple and economical way resulting in the rapid expansion of knowledge in this field. Block copolymers are not only limited to linear diblocks however, with the advance in synthetic techniques, multiblock copolymers, star polymers, branched polymers, cyclic polymers and more have been produced experimentally.² To date, many more controlled polymerization techniques have been developed which allow for new and interesting combinations of monomers and chain topologies.³⁻⁵

1.2 Block Copolymer Self-Assembly

One of the most interesting properties of block copolymers is their ability to spontaneously self-assemble into periodic domains with a characteristic length on the order of several to tens of nanometers.⁶ This process is driven by the minimization of the Gibbs free energy (1) of the polymer melt and is therefore a balance between the enthalpy of mixing chemically dissimilar blocks and the entropy of the conformation of the chains, as proposed by Flory and Huggins.^{7,8} For example, if the dissimilarity of the blocks is low, the decrease in entropy as a result of phase-separation is larger than the decrease in enthalpy, favoring a disordered mixed state. In

contrast, as the incompatibility of the blocks increases, the melt will phase separate to minimize the enthalpy of mixing despite a small entropic penalty due to chain stretching.

$$\Delta G = \Delta H - T\Delta S \quad (1)$$

In contrast to the simple mixing of homopolymers, the individual blocks in a copolymer are covalently bonded so they cannot completely phase separate as blends of homopolymers will. Instead, they form periodic domains at the nanometer scale. Using mean field theory, Leibler demonstrated that the self-assembled morphology depends only on three experimental parameters: the degree of polymerization (N), the volume fractions (f) and the Flory-Huggins interaction parameter (χ).⁹ Work by Leibler and others also demonstrated that for a given composition, there is a critical value of χN below which the melt will be disordered due to insufficient segregation strength.^{9,10} The classical morphologies of self-assembled diblock copolymers are, in order of increasing volume fraction, *bcc* spheres, hexagonal cylinders, the bicontinuous gyroid phase, and lamellae (Figure 1-1). In the symmetric diblock case (i.e. $f_A = f_B = 0.5$) the critical χN for self-assembly reaches its minimum at 10.5 and results in a lamellar morphology (Figure 1-2a).

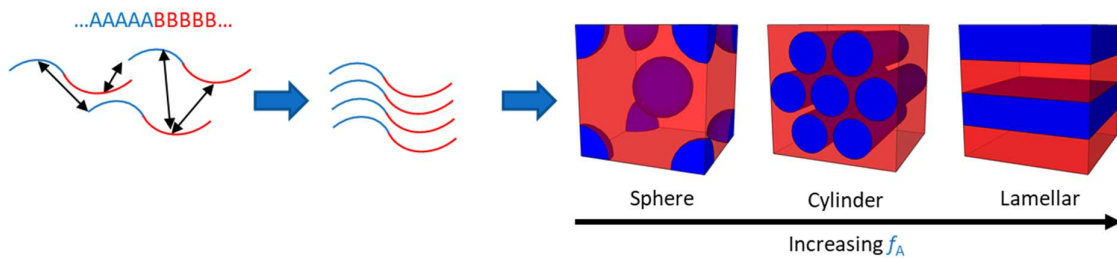


Figure 1-1. Illustration of polymer phase separation.

Furthermore, the magnitude of the χ parameter depends on temperature as described by

$$\chi = \alpha T^{-1} + \beta \quad (2)$$

where α is the enthalpic contribution and β is the entropic contribution. The characteristic length (d) of the periodic domains scales as

$$d \propto N^{\frac{1}{2}} \quad (3)$$

in the weak-segregation limit ($\chi N \approx 10$) (Figure 1-2b), meaning changes in χ have no effect on d , and

$$d \propto \chi^{\frac{1}{6}} N^{\frac{2}{3}} \quad (4)$$

in the strong-segregation limit ($\chi N \rightarrow \infty$) (Figure 1-2c), meaning changes in one or both of χ and N influence d .^{9,11,12}

While the phase diagram shown above in Figure 1-2a was derived from theoretical calculations of self-assembled diblock copolymers, extensive experimental work by Khandpur et al. has shown that the experimentally derived phase diagram shares many of the same features and trends (Figure 1-3) including the existence of the Ia3d gyroid phase at low χN .

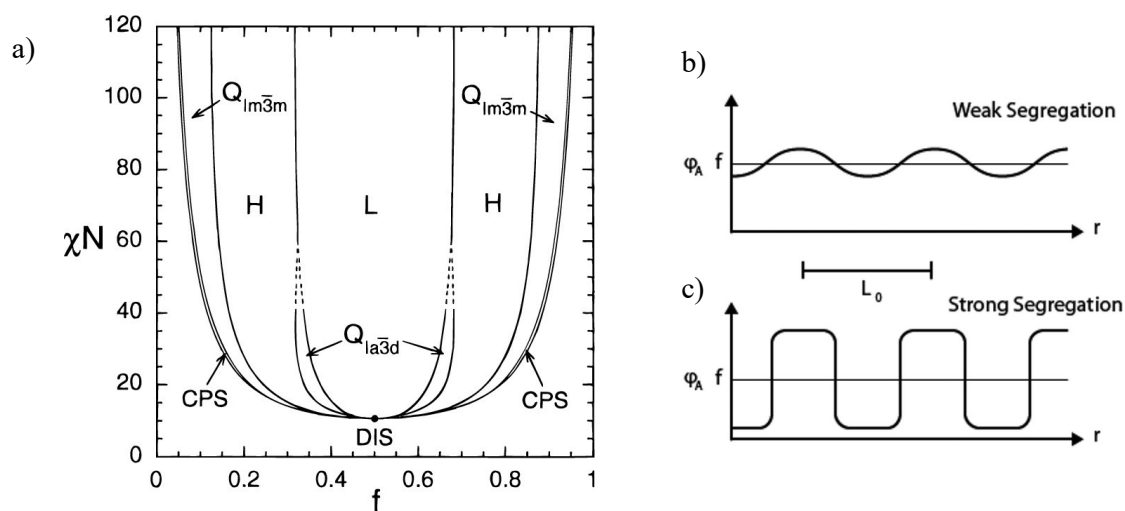


Figure 1-2. a) Theoretical diblock copolymer phase diagram. Copyright 2020 American Chemical Society. Reprinted with permission.¹⁰ b) Illustration of 1D composition profile of a diblock copolymer in each of the weak and strong segregation regimes. Copyright 2020 Annual Reviews. Reprinted with permission.¹²

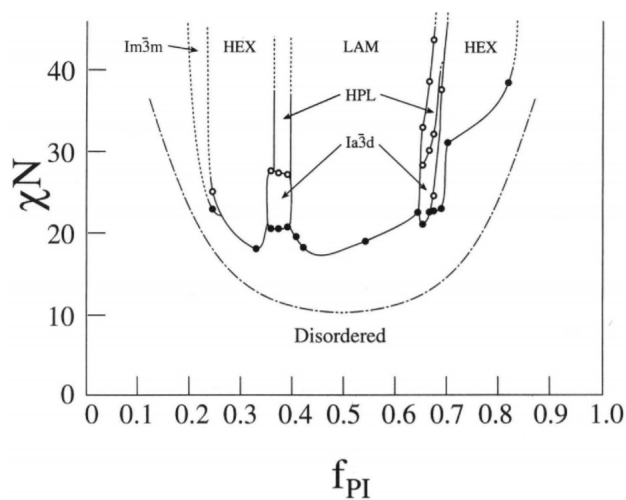


Figure 1-3. Experimentally determined phase diagram of diblock poly(styrene-*block*-isoprene). Copyright 2020 American Chemical Society. Reprinted with permission.¹³

1.3 Block Copolymer Theory and Simulation

As the complexity of the polymer in question increases, so too does the number of experimental variables that must be controlled to build a general understanding of its self-assembly behavior. As a result, polymer theory and simulation become more and more useful to efficiently explore the phase behavior of polymer self-assembly. Unfortunately however, due to the size of the molecules being studied, fully atomistic models and more coarse-grained bead-spring models are unsuitable for the study of BCP self-assembly.¹⁴ Luckily, polymers can be accurately modeled as infinitely thin Gaussian chains where the interactions between dissimilar blocks can be represented by a single χ parameter and the conformational entropy can be represented by a simple stretching energy (Figure 1-4a). In fact, because of their size, the effect of random fluctuations becomes negligible so BCPs are accurately described using mean-field calculations (Figure 1-4b).¹⁵

The first application of mean-field theory to BCPs, commonly called self-consistent field theory (SCFT), was performed by Helfand in 1975.^{16,17} In this representation, the many-body problem posed by a melt of BCP chains can be reduced to a one-body problem subject to time-averaged interaction fields. As a result, SCFT is accurate for well-ordered microstructures because the fluctuations in the potential fields are small relative to their magnitude.¹⁵ However, one drawback to this approach is that the free energy of the morphology must be solved numerically due to the self-consistent nature of its solution.¹⁸

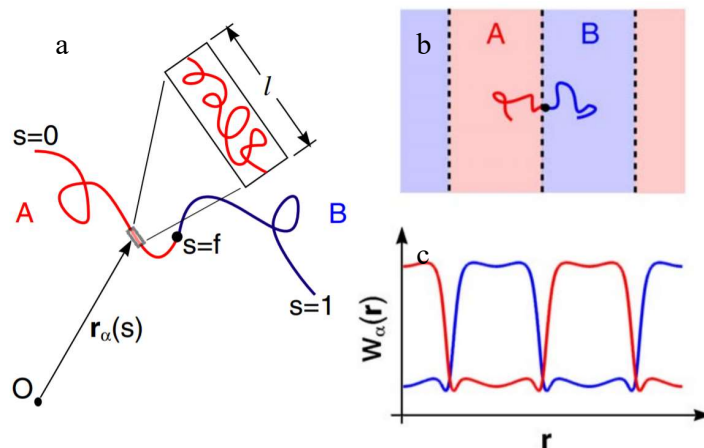


Figure 1-4. a) Illustration of a flexible Gaussian chain characterized by the curve $\mathbf{r}_\alpha(s)$ relative to an arbitrary position O. The coarse-grained segment represents a random coil of the polymer chain of length l . b) Illustration of mean-field theory where one macromolecule is modeled in an interaction field described by $w_\alpha(\mathbf{r})$. c) Graphical representation of the strength of the mean-fields $w_\alpha(\mathbf{r})$ as calculated using SCFT. Copyright 2020 IOP Publishing. Reprinted with permission.¹⁵

By introducing the limiting case of weak segregation in 1980, Leibler demonstrated the first analytical solution to the set of SCFT equations and in doing constructed the first phase diagram for BCP self-assembly.⁹ However, this approach is accurate only for $\chi N \leq 12$ and has largely been superseded by more modern implementations of SCFT. A second analytical solution to the SCFT equations was introduced by Semenov in 1985, using the limiting case of strong segregation as $\chi N \rightarrow \infty$.¹¹ In this regime, the chains are completely phase-separated except for a very narrow region around the interface. The advantage to this approach lies in the fact that the interaction energy and stretching energy of the chains can be completely decoupled. Though this approach is not analytical for experimentally accessible degrees of segregation, it still provides a useful approach for the discovery of new stable phases.

The first general implementation of SCFT without any limitations in χN was demonstrated by Matsen and Schick in 1994.¹⁹ They reasoned that since self-assembled structures of block copolymers are periodic in one or more dimensions, the set of SCFT equations should be solvable in reciprocal space using a series of truncated Fourier basis functions. This so-called spectral approach has proven to be very powerful for computing the free energy of a given phase and thus its stability,¹⁰ but is not suitable for the discovery of new phases with unknown symmetry. Subsequently, Drolet and Fredrickson introduced a real-space approach to solving the set of SCFT equations simulating linear ABCA tetrablock polymers to demonstrate the existence of previously undiscovered phases.²⁰ Their approach has the distinct advantage of not requiring an assumed symmetry of the morphology, and can therefore be used to discover new self-assembled phases but is computationally more demanding for the same level of accuracy in the free energy as the spectral approach. Building upon these previous works, a third technique for solving the SCFT equations was developed by Tzeremes et al. which combines some of the advantages of both the spectral and the real-space approaches.^{21,22} Like the real-space approach of Drolet and Fredrickson, it does not require a priori knowledge of the morphology, but it provides a gain of about an order of magnitude in computation time for the same level of accuracy as the real-space method of Drolet and Fredrickson.

As SCFT has matured and become more robust, it has become an invaluable tool for the design and discovery of new polymeric materials beyond the classical coil-coil model for BCPs. Simulation of liquid-crystal (LC) BCPs, which incorporate liquid-crystalline molecules either in the backbone or as pendant side-chains, have been developed based on the SCFT framework that allow for the accurate simulation of self-assembled rod-coil or wormlike polymer chains.²⁴⁻²⁶ With new tools like the open-source Polymer Self-Consistent Field package developed by Morse et al. (Figure 1-5),²³ BCP simulation has been made accessible

to researchers without a background in computational chemistry and simulation, further expanding the usefulness and scope of SCFT.

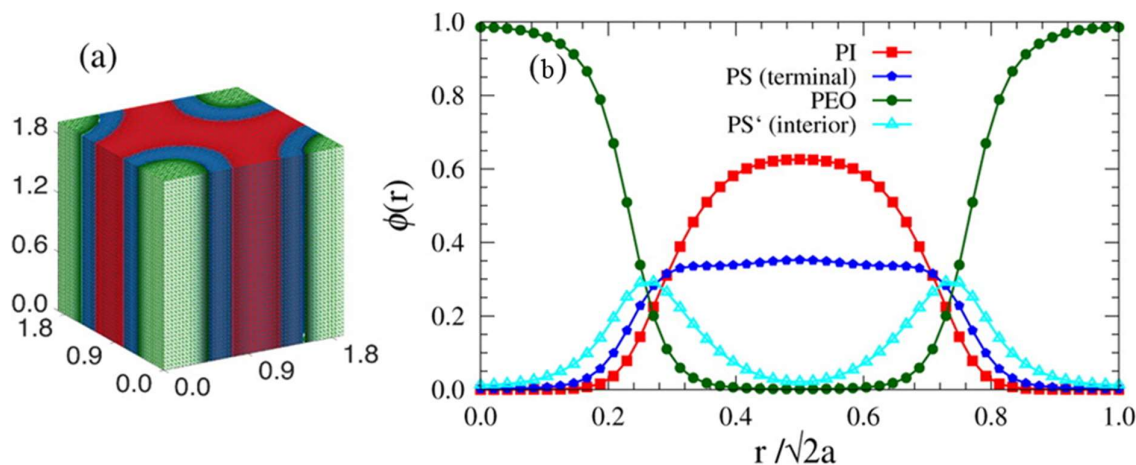


Figure 1-5. Example of a) a simulated morphology using SCFT and b) volume fraction profiles produced using the Polymer Self-Consistent Field package developed by Morse et al. Copyright 2020 American Chemical Society. Reprinted with permission.²³

1.4 Strategies for Tuning Block Copolymer Self-Assembly

Because BCPs have such varied and interesting morphologies, their potential applications include microelectronics,²⁷ nanopatterning,^{28–30} and porous materials among others.^{31,32} These applications require precise control of the morphology of the copolymer and repeatability across samples which in turn requires a comprehensive understanding of the variables that affect self-assembly. As discussed previously, for diblock copolymers, this largely depends on three variables: the degree of polymerization (N), the volume fractions (f), and the χ parameter. As seen in the phase diagram in Figure 1-2, The primary means to tune the self-assembled morphology is to change the volume fractions of the blocks. Additionally, since the characteristic periodic length d scales as $d \propto \chi^n N^m$ where $n = 0$ and $m = 1/2$ in the weak-segregation limit, and $n = 1/6$ and $m = 2/3$ in the strong-segregation limit,^{9,11,12} one or both

of χ and N can be increased or decreased to increase or decrease the size of the morphology in question. However, this is subject to the constraint that the product χN must remain above the minimum value of 10.5 in the symmetric lamellar case to self-assemble.^{9,12} Although f and N can be easily changed experimentally, χ is constant for a given pair of monomers. As a result, several different strategies for altering the self-assembly behavior of BCPs have been investigated, ranging from using different monomers to chemically altering one or more of the blocks to change some properties of the BCP.

1.4.1 High- χ Polymers

The primary means for tuning the morphology of polymers such that d decreases is to use pairs of monomers that have large χ which in turn decreases the minimum N required for self-assembly.³³ Since χ is in essence a measure of the chemical dissimilarity of a given pair of monomers, typical high- χ BCPs are for example poly(styrene-*block*-dimethylsiloxane) (PS-*b*-PDMS) which combines organic and inorganic components,³⁴ or poly(styrene-*block*-4-vinylpyridine) (PS-*b*-P4VP) which combines non-polar and polar components.³⁵

Silicon-containing BCPs in particular are attractive for nanopatterning applications because of their intrinsic etch contrast resulting from the inorganic silicon component in addition to their high χ parameters.³⁶ However, the large chemical difference between the blocks makes it difficult to achieve perpendicular orientation in thin films which necessitates the use of solvent vapor annealing or top-coats to control the interfaces.^{37–40} While these techniques are effective for producing the desired orientation, they introduce more processing steps which increases the cost and complexity of producing BCP thin films. As a result, design of high- χ BCPs that incorporate some form of surface energy control has become an increasingly important area of study. One method is to incorporate fluorine or hydroxyl groups to a silicon-containing BCP, to balance the interfacial energies and achieve controlled orientation with little change in χ .^{41,42}

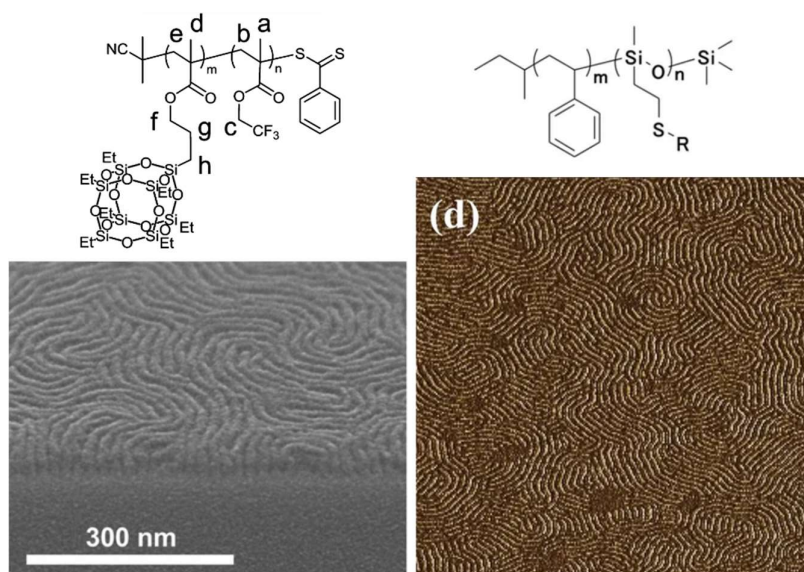


Figure 5-6. a) Introduction of a fluorine-containing block. Copyright 2020 American Chemical Society. Reprinted with permission.⁴² b) a hydroxyl groups to a silicon BCP to balance the surface energies. Copyright 2020 Springer Nature. Reprinted with permission.⁴¹

To date, several polymers with self-assembled domains with $d < 10$ nm have been demonstrated which follow the motifs of organic-inorganic or polar-non-polar monomer pairs, demonstrating the strength of this approach for tuning d .³³ However, selection of monomer pairs requires much guesswork and experimentation since no model or theory can accurately predict the magnitude of χ and changes in χ alone for a diblock copolymer will not usually produce changes in the self-assembled morphology. Since χ is also predetermined for a given pair of monomers, many BCPs are necessary to cover a wide range of d , further increasing the experimental demands.

1.4.2 Modifying Block Copolymers

Recently, an increasingly interesting area of study is the design of modifiable BCPs where the self-assembly behavior can be tailored to a desired application. The modification can take the form of post-polymerization functionalization to change χ or f of the BCP or blends of

BCPs with additives, homopolymers, or other BCPs. These approaches are able to modify the domain spacing and the morphology of the BCP independently of the as-synthesized values of f , N , and χ .

Functionalization of the block junction points and chain-ends specifically of BCPs has been shown theoretically to have a significant effect on their self-assembly behavior.⁴³ Experimental studies by Pispas et al. and Luo et al. using strongly interacting zwitterions at the block junction of several BCPs have demonstrated the clear de-mixing of the outer blocks as a result of the ionized junction which has the effect of increasing the effective χ (χ_{eff}).^{44,45} Similarly, Woo et al. demonstrated that the introduction of a short, dissimilar middle-block to PS-*b*-PMMA can significantly reduce the minimum accessible d to 16.7 nm,⁴⁶ while Yoshida et al. demonstrated that the addition of very polar oligosaccharides to the chain-end of PS-*b*-PMMA can also considerably reduce the minimum accessible d to 11.5 nm.⁴⁷ Modification of BCPs is not only limited to changes in χ_{eff} , however. For example, Schöps et al. have shown that by controlling the ionic interactions of a zwitterionic BCP by using ionic salts, they could switch between hexagonally packed cylinders and lamellae.⁴⁸ Furthermore, Kim et al. showed the simultaneous control of surface energy and χ_{eff} by selective epoxidation of one block.⁴⁹ All of these studies utilized some form of post-polymerization modification which permitted the fine-tuning of the chemical properties of a BCP to tune the self-assembly behavior as desired.

1.4.3 Multiblock Copolymers

Because of their relative simplicity, the self-assembly behavior of diblock copolymers has been extensively explored both experimentally and theoretically.^{9,18,50–52} Moving beyond diblock copolymers to tri- and multiblock copolymers increases the experimental parameter space from three to six or more depending on the number of blocks. As a result, the range of accessible morphologies and domain sizes is markedly increased compared to the diblock case.²

For linear triblocks, the number of independent parameters increases from three to six (χ_{AB} , χ_{BC} , χ_{AC} , f_A , f_B , N) which results in many more morphologies not previously seen for diblock copolymers.⁵³ Previous experimental studies have discovered many phases not possible using diblocks such as “decorated” lamellae,^{54,55} core-shell cylinders,^{56,57} tetragonal cylinders,⁵⁸ and other more complex morphologies.^{59,60} These studies have shown that the interesting new phases are a result of both the magnitude and the relation between the increased number experimental variables. For example, the interaction parameters of the two covalently bound blocks (χ_{AB} , χ_{BC}) relative to that of the outer blocks (χ_{AC}) has been found to have a significant effect on the resultant morphology.^{53,55} This relationship can be generally classified into two categories: “frustrated” triblocks where $\chi_{AC}N < \chi_{AB}N$ or $\chi_{BC}N$, and “non-frustrated triblocks” where $\chi_{AC}N > \chi_{AB}N$ and $\chi_{BC}N$.^{61–63} Frustrated triblocks have an increased probability of an A/C interface being formed despite the lack of a covalent connection between these blocks which gives rise to much more complex morphologies than the non-frustrated case.^{54,64} Non-frustrated systems on the other hand are characterized by a general lack of A/C interfaces as seen in core-shell structures or the orthorhombic *Fddd* network phase.^{65–67} In contrast, diblocks cannot show this type of complex behavior because there is only one χ parameter.

Similarly, for a given set of χ parameters, many more phases are accessible by changes in f for a multiblock than the diblock case which can typically only access four or five distinct phases. Using SCFT, Guo et al. demonstrated that there are at least 20 distinct stable or meta-stable phases possible for a frustrated linear triblock with $\chi_{AB} = \chi_{BC} = 35$ and $\chi_{AC} = 10$ (Figure 1-7).⁶⁸ Multiblock polymers thus present an effective way to produce varied morphologies analogous to those found in diblocks in addition to many other complex phases only possible with multiblocks. However, their enriched self-assembly behavior is somewhat offset by the relative difficulty in synthesizing and characterizing multiblocks compared to simple diblocks. Additionally, because their self-assembly behavior is much more complex and therefore less

well understood, it is more difficult to predict the self-assembled morphology for a given polymer.

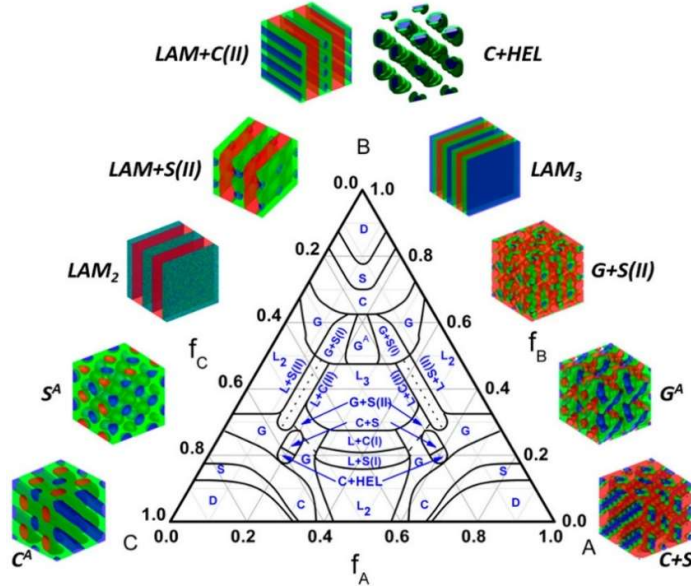


Figure 1-7. Phase diagram of a model frustrated linear ABC triblock terpolymer constructed using SCFT at constant χ . Copyright 2020 American Physical Society. Reprinted with permission.⁶⁸

1.4.4 Side-Chain Liquid Crystal Polymers

Liquid crystals (LC) are another phase of condensed matter with characteristic length scales on the order of nanometers, between those of polymers and individual atoms, and possess anisotropy in all phases of liquid crystal ordering. By introducing LC mesogens to one block of a BCP therefore produces a material with molecular scale ordering in addition to the mesoscale ordering of BCP domains. This complex interplay between the LC and coil domains results in a diverse phase diagram with periodic ordering at multiple length scales.^{69,70} Figure 1-8c below illustrates this concept where the mesoscale lamellar distance d is shown vertically

and is composed of the LC block length (l_A) and the coil block length (l_B), while the LC block also shows an intermolecular periodic spacing in the horizontal direction.⁷¹

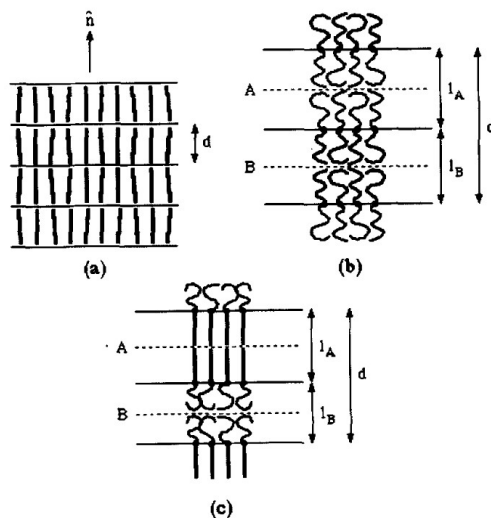


Figure 1-8. Schematic of a) smectic ordering of LC domains, b) lamellar ordering of a coil-coil BCP, and c) the combined LC-coil ordering of an LCBCP. Copyright 2020 John Wiley and Sons. Reprinted with permission.⁷¹

LC BCPs can be further subdivided into main-chain liquid crystal (MCLC) BCPs, where the mesogen is incorporated into the backbone of the polymer, and side-chain liquid crystal (SCLC) BCPs where the mesogen is pendant to the main chain. Both types exhibit the interplay between the LC and coil blocks discussed previously, but SCLC BCPs have a richer phase diagram because the flexibility of the SCLC backbone is mostly maintained which results in a competition between orientational ordering due to the LC mesogens and the conformational entropy of coil-like polymer chains.^{25,26} This behavior can be tuned further by increasing or decreasing the spacer length, thereby providing another experimental technique towards modifying the self-assembly behavior of block copolymers.

1.5 Overview of This Dissertation

Molecular Design			
Short, Reactive Middle Block Degree of Polymerization = 1 or 5-7			
Chapter	Polymer Studied	Focus of Study	Conclusion
Chapter 2 DP _B = 5-7	 PSGM	R = (PSGM _{OH}) R = (PSGM _F) Small Molecules	PSGM Lam. PSGM _F Hex. Cyl. PSGM _{OH} Tet. Cyl.
Chapter 3 DP _B = 5-7	 General Case	$w(\mathbf{r}) = N \sum \chi \phi(\mathbf{r}) + \xi(\mathbf{r})$ Simulation	Phase Diagram
Chapter 4 DP _B = 5-7	 PSGM	R = Liquid Crystal	PSGM _{LC} Double Tet. Cyl. Unit Cell
Chapter 5 DP _B = 1	 PS-PMMA	 Small Molecules	d = 27.7 nm d = 26.0 nm

This thesis focuses on the molecular design of block copolymers containing a reactive middle block that can be used to tailor the self-assembled morphology by post-polymerization functionalization of the interface. The molecular design presented herein offers the ability to tune the interaction parameters between the middle and outer blocks arbitrarily thereby

tailoring the self-assembled morphology as desired and independently of the other factors affecting self-assembly of block copolymers. The effect of changes in the interaction parameters are therefore isolated and are investigated in depth using both experimentation and simulation.

In Chapter 2, a novel poly(styrene-*block*-glycidyl methacrylate-*block*-methyl methacrylate) (PS-*b*-PGMA-*b*-PMMA) triblock terpolymer which contains a short, reactive middle block was designed and functionalized using several strongly dissimilar thiols to modify the χ_{AB} and χ_{BC} interaction parameters without changing the volume fractions of each block nor the degree of polymerization. The synthetic route for obtaining this polymer is discussed along with the morphological analysis of the resultant changes in self-assembled morphologies by transmission electron microscopy (TEM) and small-angle x-ray scattering (SAXS). By modifying χ_{AB} and χ_{BC} only, we demonstrate the impact this has on self-assembly and the broad applicability this approach can have for tailorable BCPs.

In Chapter 3, simulations were carried out using self-consistent field theory to further examine the experimental results obtained in the Chapter 2. The simulated morphologies were found to match closely with the experimental ones so the scope of the study was expanded to construct phase diagrams of frustrated linear triblock terpolymers with short, strongly-interacting middle blocks. We demonstrate that both the magnitude and the relationship between the three χ parameters of a linear triblock has a strong effect on the self-assembled morphology. The simulation method is discussed in detail and the simulated morphologies and phase diagrams are compared with experimental results from Chapter 2. We demonstrate that by combining theoretical simulation with a small number of experimental results for validation, it is possible to quickly and efficiently construct a comprehensive understanding of self-assembly behavior for a given BCP.

In Chapter 4, the effect of liquid-crystalline ordering on self-assembly was investigated using PS-*b*-PGMA-*b*-PMMA synthesized in Chapter 2 where the middle block was functionalized with fluorinated alkyl chain side-chain liquid-crystals. The resultant morphology which has previously never been reported for linear triblocks is discussed and analyzed extensively using TEM and SAXS. By functionalizing the block interface with liquid-crystalline molecules, we demonstrate the significant impact of ordering at two different length scales can have on self-assembly.

In Chapter 5, we investigate the effect of tailoring the block junction on self-assembly by synthesizing a series of poly(styrene-*block*-methyl methacrylate) (PS-*b*-PMMA) diblock copolymers containing exactly one functional 1,1-diphenylethylene (DPE) derivative at the block junction and functionalize them by post-polymerization functionalization. Using a variety of different strongly dissimilar molecules, the block interface was functionalized and the resultant change in self-assembly behavior was characterized in the bulk state using SAXS and in thin films using atomic force microscopy (AFM). We demonstrate that the introduction of a single small molecule at the block junction can have an effect on self-assembly in both the bulk and thin film state though the mechanism is not fully understood.

Finally, in Chapter 6 the results of this work are summarized, and future prospects and perspectives are discussed.

1.6 References

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Chapter 2

Synthesis and Bulk Characteristics of PS-*b*-PGMA-*b*-PMMA

Triblock Terpolymers Containing a Short Reactive Middle Block

2.1 Introduction

Block copolymers are a widely studied class of material because of their intrinsic ability to self-assemble into ordered nanoscale structures.¹⁻³ As a result, they have garnered much attention for applications such as nanopatterning,⁴⁻⁶ microelectronics,⁷ and porous materials.^{8,9} Accordingly, understanding the underlying mechanism of self-assembly and the key factors which affect it is becoming increasingly central to research in this field.

For the simplest type of block copolymers, linear AB-type diblock copolymers, the phase diagram of possible morphologies has been extensively explored since the morphology depends primarily on only three variables: the degree of polymerization (N), the volume fractions of each block (f), and the Flory-Huggins interaction parameter (χ_{AB}).¹⁰⁻¹⁴ In contrast, linear ABC triblock terpolymers (triBCPs) have a much richer phase diagram arising from the larger parameter space provided by three interaction parameters (χ_{AB} , χ_{BC} , χ_{AC}), two independent volume fractions (f_A, f_B), and one degree of polymerization. Previous experimental studies of the triBCP phase diagram have discovered many stable bulk structures like “decorated” lamellae,^{15,16} core-shell cylinders,^{17,18} and other more complex morphologies in addition to those that are comparable to AB diblocks.¹⁹⁻²¹

On the other hand, investigation of the linear triblock phase diagram using theory and simulation has increasingly played an important role in the discovery of new phases. Early theoretical work by Zheng and Wang demonstrated the usefulness of this approach by constructing phase diagrams in which the predicted phases matched closely with previous experimental results.²² More recently, self-consistent field theory (SCFT) has been a powerful

tool for the study of block copolymers, revealing new complex phases and aiding in the understanding of experimental results.^{23–25}

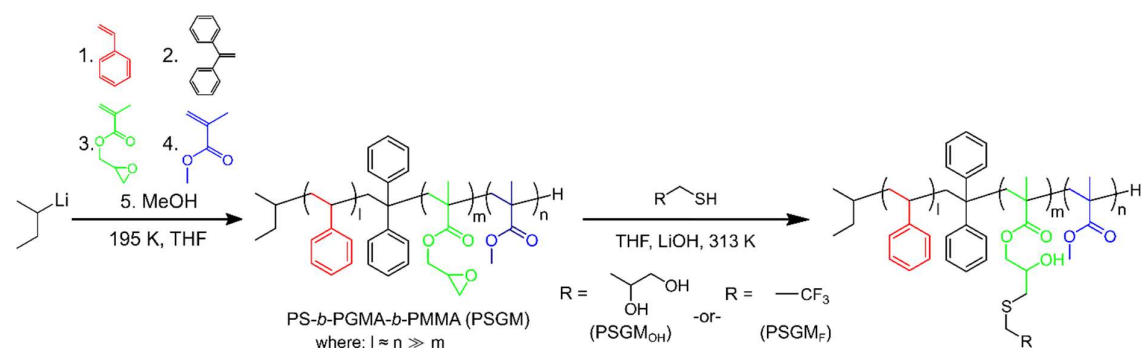
These experimental and theoretical studies have shown that both the magnitude and the relation between the experimental variables becomes non-trivial in the triblock case. First, the interaction parameters of the two covalently bound blocks (χ_{AB}, χ_{BC}) relative to that of the outer blocks (χ_{AC}) has been found to have a significant effect on the resultant phase diagram.^{16,22} This relationship can be generally classified into two categories: “frustrated” triblocks where $\chi_{AC}N < \chi_{AB}N$ or $\chi_{BC}N$, and “non-frustrated triblocks” where $\chi_{AC}N > \chi_{AB}N$ and $\chi_{BC}N$.^{26–28} Frustrated triblocks have an increased probability of an A/C interface being formed despite the lack of a covalent connection between these blocks which gives rise to much more complex morphologies than the non-frustrated case.^{15,23} Non-frustrated systems on the other hand are characterized by the lack of A/C interfaces as seen in core-shell structures or the orthorhombic *Fddd* network phase.^{29–31}

Although many experimental studies have been undertaken using a variety of triBCPs, they typically only investigate a single monomer trio which in turn fixes the interaction parameters except in rare cases such as the hydrogenation of poly(butadiene).¹⁶ In light of recent work by our group and others,^{32–35} it is clear that a fundamental understanding of the effect of changing the interaction parameters by adding a small middle block or otherwise modifying it is increasingly necessary.

In this chapter we present a newly designed poly(styrene-*block*-glycidyl methacrylate-*block*-methyl methacrylate) (PSGM) containing a short, reactive PGMA middle block which is easily functionalized by thiols and amines allowing us to functionalize the middle block with different small molecules.³⁶ We demonstrate that we can effectively tune the χ_{AB} and χ_{BC} interaction parameters using this technique and in so doing, change the self-assembled morphology and explore the χ_{AB} - χ_{BC} parameter space with unchanging χ_{AC} . Four PSGM triblock terpolymers

were synthesized and functionalized with two different thiols yielding a total of 12 experimental samples with four different $\chi_{AC}N$ (Scheme 2-1). The bulk morphology of each of the triblock terpolymers was characterized by small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). Thus, by combining living anionic polymerization with the thiol-epoxy reaction, we were able to efficiently produce a small library of well characterized polymers to investigate the effect of changing χ_{AB} and χ_{BC} on the self-assembled morphology.

Scheme 2-1. Synthesis of PS-*b*-PGMA-*b*-PMMA (PSGM) by Anionic Polymerization and Functionalization via the Thiol-Epoxy Reaction



2.2 Experimental Section

2.2.1 Reagents

Lithium chloride (LiCl) was purchased from Kanto Chemical Co. and dried by heating under reduced pressure immediately before use. Styrene, 1,1-diphenylethylene (DPE), glycidyl methacrylate (GMA), and methyl methacrylate (MMA) were purchased from Tokyo Chemical Industry. Styrene, GMA, and MMA were first distilled over calcium hydride (CaH₂) under reduced pressure and then distilled a second time over di-*n*-butylmagnesium, CaH₂, and trioctylaluminum respectively. DPE was distilled over *n*-butyllithium. All other reagents and

solvents were purchased from Kanto Chemical Co. Inc, Tokyo Chemical Industry or Sigma-Aldrich and used as received.

2.2.2 General Procedure for the Synthesis of PSGM by Living Anionic Polymerization

To an oven-dried flask under argon gas were added LiCl (34.7 mg, 0.819 mmol) and 40 ml of THF. The flask was cooled to 195 K and *sec*-butyllithium (*sec*-BuLi) (1.05 M in hexanes) was added until a yellow color remained indicating the endpoint of impurity titration. The flask was removed from the cold bath and allowed to slowly warm to room temperature at which point the yellow color disappeared. The flask was once again cooled to 195 K and *sec*-BuLi (0.11 ml, 0.11 mmol) was added followed immediately by styrene (1.40 ml, 12.2 mmol) resulting in an orange color and stirred for 30 min. DPE (0.10 ml, 0.57 mmol) was then added, changing the color to dark red, and stirred for 30 min. GMA (0.15 ml, 1.1 mmol) was then added, causing the color to disappear, and stirred for a further 30 min. Finally, MMA (1.60 ml, 15.0 mmol) was added and stirred for 30 min before being terminated by the addition of degassed methanol. The polymer was precipitated in 500 ml of cold methanol and collected by filtration. The collected solid was dried under reduced pressure overnight at 313 K (2.52 g, 85% yield). ¹H NMR (400 MHz, chloroform-*d*, δ , ppm): 7.22-6.85 (br, *m*-, *p*-aromatic), 6.82-6.25 (br, *o*-aromatic), 4.28 (s, -(C=O)O-CH₂-), 3.78 (s, -(C=O)O-CH₂-), 3.59 (s, -(C=O)O-CH₃), 3.21 (s, -CH₂-CH(CH₂)-O-), 2.83 (s, -CH₂-CH(CH₂)-O-), 2.62 (s, -CH₂-CH(CH₂)-O-), 2.20-1.67 (br, -CH₂-CH-, -CH₂-C(CH₃)-), 1.54-1.22 (br, -CH₂-CH-), 1.05-0.75 (br, -CH₂-C(CH₃)-).

2.2.3 Synthesis of PSGM_{OH} via the Thiol-Epoxy Reaction

A general procedure for the functionalization of PSGM_{OH} is presented here.³⁶ PSGM (149.2 mg, 7.1 μ mol) and 1-thioglycerol (7.7 mg, 71 μ mol) were dissolved in 1 ml THF. LiOH_{aq} (0.05 M, 0.07 ml, 3.6 μ mol) was then added to initiate the reaction. The resulting solution was stirred

at 313 K for 3 h. The polymer was precipitated in 50 ml of cold methanol and filtered a minimum of three times to remove residual thiol. The resultant solid was dried under reduced pressure overnight at 313 K (112.6 mg, 75% yield). ^1H NMR (400 MHz, chloroform-*d*, δ , ppm): 7.22-6.85 (br, *m*-, *p*-aromatic), 6.82-6.25 (br, *o*-aromatic), 4.04 (m, $-(\text{C}=\text{O})\text{O}-\text{CH}_2-$), 4.04 (m, $-\text{CH}_2-\text{CH}(\text{CH}_2)-\text{OH}$), 3.62 (m, $-\text{S}-\text{CH}_2-\text{CH}-$) 3.59 (s, $-(\text{C}=\text{O})\text{O}-\text{CH}_3$), 3.48 (m, $\text{S}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{OH}$), 2.73 (m, $-\text{CH}_2-\text{S}-\text{CH}_2-$), 2.20-1.67 (br, $-\text{CH}_2-\text{CH}-$, $-\text{CH}_2-\text{C}(\text{CH}_3)-$), 1.54-1.22 (br, $-\text{CH}_2-\text{CH}-$), 1.05-0.75 (br, $-\text{CH}_2-\text{C}(\text{CH}_3)-$).

2.2.4 Synthesis of PSGM_F via the Thiol-Epoxy Reaction

A general procedure for the functionalization of PSGM_F is presented here.³⁶ PSGM (187 mg, 9.0 μmol) and 2,2,2-trifluoroethanethiol (25.1 mg, 216 μmol) were dissolved in 1 ml THF. LiOH_{aq} (0.05 M, 0.08 ml, 3.8 μmol) was then added to initiate the reaction. The resulting solution was stirred at 313 K for 3 h. The polymer was precipitated in 50 ml of cold methanol and filtered a minimum of three times to remove residual thiol. The resultant solid was dried under reduced pressure overnight at 313 K (0.111 g, 58% yield). ^1H NMR (400 MHz, chloroform-*d*, δ , ppm): 7.22-6.85 (br, *m*-, *p*-aromatic), 6.82-6.25 (br, *o*-aromatic), 4.07 (m, $-(\text{C}=\text{O})\text{O}-\text{CH}_2-$), 4.07 (m, $-\text{CH}_2-\text{CH}(\text{CH}_2)-\text{OH}$), 3.59 (s, $-(\text{C}=\text{O})\text{O}-\text{CH}_3$), 3.24 (m, $-\text{CH}(\text{OH})-\text{CH}_2-\text{S}-$), 2.84 (br $-\text{S}-\text{CH}_2-\text{CF}_3$), 2.20-1.67 (br, $-\text{CH}_2-\text{CH}-$, $-\text{CH}_2-\text{C}(\text{CH}_3)-$), 1.54-1.22 (br, $-\text{CH}_2-\text{CH}-$), 1.05-0.75 (br, $-\text{CH}_2-\text{C}(\text{CH}_3)-$).

2.2.5 Synthesis of PGMA-*b*-PMMA via Anionic Living Polymerization

To an oven-dried flask under argon gas were added LiCl (70.4 mg, 1.7 mmol) and 20 ml of THF. The flask was cooled to 195 K and *sec*-butyllithium (*sec*-BuLi) (1.04 M in hexanes) was added until a yellow color remained indicating the endpoint of impurity titration. The flask was removed from the cold bath and allowed to slowly warm to room temperature at which point the yellow color disappeared. The flask was once again cooled to 195 K and *sec*-BuLi (0.37 ml, 0.38 mmol) was added followed immediately DPE (0.10 ml, 0.57 mmol), changing the

color to dark red, and stirred for 30 min. GMA (0.25 ml, 1.9 mmol) was then added, causing the color to disappear, and stirred for a further 30 min. Finally, MMA (0.70 ml, 6.6 mmol) was added and stirred for 30 min before being terminated by the addition of degassed methanol. The polymer was precipitated in 500 ml of cold hexane and collected by filtration. The collected solid was dried under reduced pressure overnight at 313 K (0.9463 g, 95% yield). ^1H NMR (400 MHz, chloroform-*d*, δ , ppm): 4.28 (s, $-(\text{C}=\text{O})\text{O}-\text{CH}_2-$), 3.78 (s, $-(\text{C}=\text{O})\text{O}-\text{CH}_2-$), 3.59 (s, $-(\text{C}=\text{O})\text{O}-\text{CH}_3$), 3.21 (s, $-\text{CH}_2-\text{CH}(\text{CH}_2)-\text{O}-$), 2.83 (s, $-\text{CH}_2-\text{CH}(\text{CH}_2)-\text{O}-$), 2.62 (s, $-\text{CH}_2-\text{CH}(\text{CH}_2)-\text{O}-$), 2.20-1.67 (br, $-\text{CH}_2-\text{CH}-$, $-\text{CH}_2-\text{C}(\text{CH}_3)-$), 1.54-1.22 (br, $-\text{CH}_2-\text{CH}-$), 1.05-0.75 (br, $-\text{CH}_2-\text{C}(\text{CH}_3)-$).

2.2.6 Characterization Methods

The ^1H nuclear magnetic resonance (NMR) spectra were recorded on a JEOL 400 MHz instrument using deuterated chloroform at ambient temperature. The number-average and weight-average molecular weights (M_n and M_w) were measured by size-exclusion chromatography (SEC) using a Shodex GPC-101 equipped with a refractive index detector and a LF-804 column (Showa Denko) with THF as the eluent at 313 K for PSGM_F samples and PSGM_{OH} samples were measured on a Viscotek GPC-1000 system equipped with a TDA 302 triple detector (Malvern Instruments Ltd., UK) and a TSKgel α -M column (Tosoh Corp., Japan) with *N,N*-dimethylformamide (DMF) containing 0.05 M lithium bromide as the eluent at 313 K. Bulk samples were prepared by slow evaporation of chloroform solutions followed by thermal annealing at 453 K for 24 h. Bulk SAXS measurements were performed at the BL40B2 beamline of SPring-8 with a wavelength of 1.00 Å and a sample-to-detector distance of 2.0 m. SAXS thermal experiments were performed on a Bruker NanoSTAR (50 kV/ 50 mA) with a wavelength of 1.54 Å and a sample-to-detector distance of 1.0 m equipped with a TCPU-H heating stage and a Våntec-500 detector. Samples were placed in quartz glass capillaries (wall thickness 0.1 mm) for measurement. The SAXS profiles were collected using a cooling process

beginning from 250 °C and cooled at a rate of 1 °C min⁻¹. At each measurement temperature, the sample was held for 15 min and exposed to X-ray radiation for 15 min to collect the spectrum. Background spectra were collected for each sample by exposing an empty glass capillary for 15 min. Transmission electron microscopy (TEM) (H-7650 Hitachi High Tech) was used to examine ultrathin samples prepared by room temperature ultramicrotomy (Leica EM UC7) and stained by ruthenium tetroxide (RuO₄).

2.3 Results and Discussion

2.3.1 Synthesis and Post-Functionalization of PSGM

Several symmetric PSGM triBCPs were synthesized by sequential living anionic polymerization in the presence of excess LiCl under an inert atmosphere.^{37–39} The molecular weight and dispersity of the polymers were determined by SEC at 313 K using THF as an eluent and calibrated with PS standards. The volume fraction of each block was calculated by integrating the ¹H NMR peaks and the densities of 1.05, 0.805, and 1.18 g cm⁻³ for PS, PGMA, and PMMA respectively.⁴⁰ Despite the low mole fraction of the middle PGMA block, the characteristic peaks of the epoxide group could be clearly distinguished at 4.28, 3.78, 3.59, 2.83, and 2.62 ppm providing a simple means to calculate the volume fraction of the PGMA block (Figure 2-1). The triBCPs used investigated had molecular weights ranging from 10.2 to 20.9 kg mol⁻¹ with volume fractions of the middle PGMA block controlled to be in the range of $f_B = 0.05$ -0.1 and the outer blocks having symmetric volume fractions (Table 2-1).

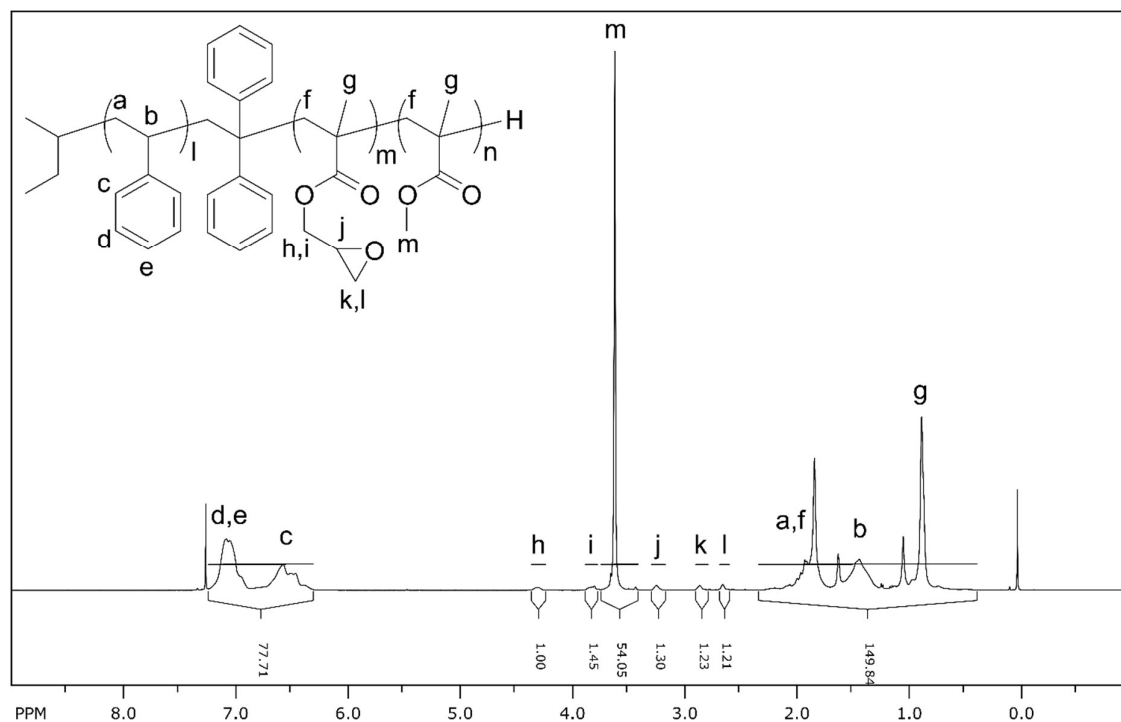


Figure 2-1. Representative ^1H NMR spectrum of PS-*b*-PGMA-*b*-PMMA

Table 2-1. Sample Characteristics of Parent PS-*b*-PGMA-*b*-PMMA Triblock Terpolymers

Sample ^a	M_n^b (kg mol ⁻¹)	$\bar{D}^b$	f_{PS}^c	f_{PGMA}^c	f_{PMMA}^c	Morphology ^d	d^e (nm)
PSGM21	20.9	1.15	0.47	0.07	0.46	Lamellar	19.3
PSGM18	17.7	1.16	0.44	0.10	0.46	Disorder	-
PSGM15	14.7	1.18	0.46	0.11	0.43	Disorder	-
PSGM10	10.2	1.27	0.47	0.05	0.48	Disorder	-

^aNumbers indicate the molecular weights of the triBCPs

^bDetermined by SEC in THF using PS standards

^cDetermined by ^1H NMR analysis

^dDetermined by SAXS peak ratios

^eDetermined by position of primary scattering peak

The PSGM triBCPs were functionalized by ring-opening the epoxide moieties using either 1-thioglycerol or 2,2,2-trifluoroethanethiol in THF with LiOH as catalyst to yield PSGM_{OH} or PSGM_F respectively according to the procedure of Gadwal et al.^{36,41–43} The reaction was found

to proceed quantitatively as determined by ^1H NMR where the five characteristic glycidyl peaks (4.28, 3.78, 3.59, 2.83, and 2.62 ppm) disappeared and were replaced by broad peaks in the range of 4.2-3.8 ppm and 3.2-2.2 ppm depending on the thiol (Figure 2-2). The density of each of the two functionalized PGMA_s was estimated using the group contribution method of Fedors and calculated to be 1.50 and 1.43 g cm⁻³ for PGMA_{OH} and PGMA_F respectively.⁴⁴ The volume fractions of the functionalized polymers are summarized in Table 2-2.

Table 2-2. Sample Characteristics of Functionalized PS-*b*-PGMA-*b*-PMMA Triblock Terpolymers

Sample ^a	f_{PS}^b	f_{PGMA}^b	f_{PMMA}^b	Morphology ^c	d^d (nm)
PSGM21_{OH}	0.47	0.06	0.47	Lamellar	25.0
PSGM21_F	0.47	0.07	0.46	Hexagonal cylinders	18.7
PSGM18_{OH}	0.45	0.10	0.45	Mixed morphology	18.4
PSGM18_F	0.44	0.10	0.46	Hexagonal cylinders	16.2
PSGM15_{OH}	0.47	0.10	0.43	Tetragonal cylinders	16.6
PSGM15_F	0.46	0.11	0.43	Hexagonal cylinders	15.2
PSGM10_{OH}	0.47	0.05	0.48	Disorder	-
PSGM10_F	0.46	0.05	0.49	Disorder	-

^aNumbers indicate the molecular weights of the triBCPs; subscripts OH and F indicate functionalization by 1-thioglycerol or 2,2,2-trifluoroethanethiol respectively

^bDetermined ^1H NMR analysis with densities calculated by the group contribution method⁴⁴

^cDetermined by SAXS peak ratios

^dDetermined by position of the primary scattering peak

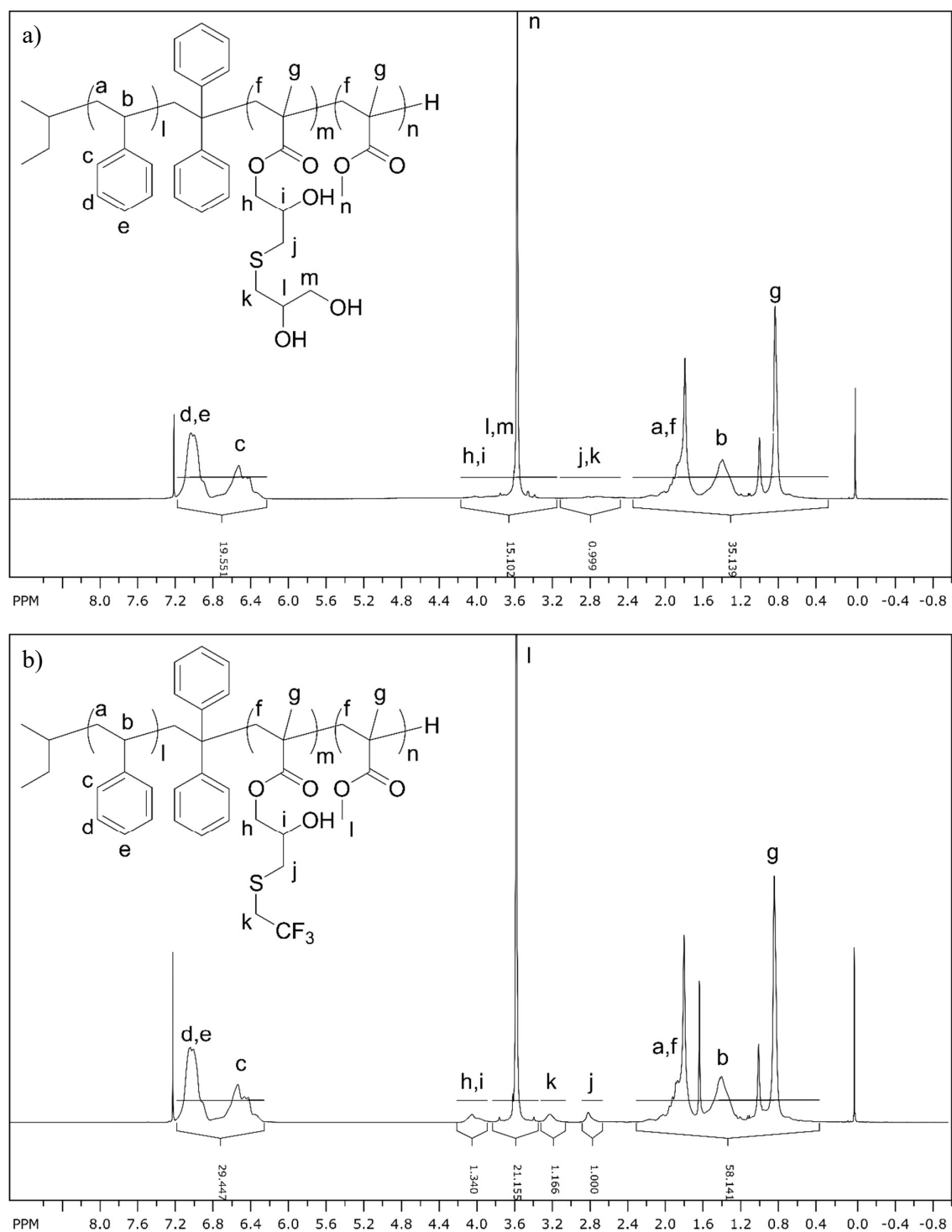


Figure 2-2. Representative ¹H NMR spectrum of a) PSGM_{OH} and b) PSGM_F.

The thiols used in this study were chosen because we expected that the addition of a strongly dissimilar polar or fluorinated functional group would have a significant effect on the χ

parameters between the middle and outer blocks.^{33,34,45} Additionally, the volume fractions remained nearly constant as did the degree of polymerization so we could directly compare the effect that changes in χ had on self-assembly before and after modification.

2.3.2 Estimation of Interaction Parameters

Before analyzing the morphological behavior of the bulk samples however, it is necessary to first determine the effective χ (χ_{eff}) for each monomer pair because the relationship between them has a significant impact on self-assembly for triblock terpolymers. Each of the 7 binary interaction parameters were estimated using the random phase approximation (RPA),^{11,50,51} or taken from literature where available.^{49,52} To estimate the interaction parameters (χ) experimentally, low molecular weight diblock or triblock terpolymers were synthesized and functionalized with the appropriate thiol. The polymers were then analyzed by SAXS over a range of temperatures in the disordered state and their scattering behavior was fitted using RPA analysis to determine the temperature dependence of each of the χ parameters which takes the form $\chi = \alpha T^{-1} + \beta$ where αT^{-1} is the enthalpic contribution and β is the entropic contribution. The intensity (I) of the first order scattering peak was fitted using

$$I_{AA}(q) = K \frac{F_{AA}(q)}{\Delta(q)}$$

Where K is a proportionality constant which is unimportant in the fitting process and $F(q)$ is an expression which depends on all χ_{ij} and chain structure factors S_{ij} for $(ijk) \in \{(ABC), (BCA), (CAB)\}$ and is given by:

$$F_{AA}(q) = C_{ABC}(q) - 2\chi_{AB}A(q)$$

where

$$\begin{aligned} A(q) &= S_{AA}(q)S_{BB}(q)S_{CC}(q) + 2S_{AB}(q)S_{AC}(q)S_{BC}(q) \\ &\quad - [S_{AC}^2(q)S_{BB}(q) + S_{BC}^2(q)S_{AA}(q) + S_{AB}^2(q)S_{CC}(q)] \\ C_{ABC} &= S_{AA}(q)[S_{BB}(q) + S_{CC}(q) + 2S_{BC}(q)] - [S_{AB}(q) + S_{AC}(q)]^2. \end{aligned}$$

The denominator is given by:

$$\Delta(q) = S(q) + \sum_{(ijk)} [2\chi_{ij}B_{ijk}(q) - A(q)(\chi_{ij}^2 - 2\chi_{ij}\chi_{ik})]$$

where

$$B_{ijk}(q) = S_{ij}^2(q) + S_{ij}(q)[S_{ik}(q) + S_{jk}(q) + S_{kk}(q)] - S_{ii}(q)S_{jj}(q) - S_{ii}(q)S_{jk}(q) - S_{jj}(q)S_{ik}(q) - S_{ik}(q)S_{jk}(q).$$

For a linear block copolymer, the single chain structure factors are given by:

$$S_{ii}(q) = \frac{2\bar{N}f_i^2}{x_i^2} (x_i - 1 + [x_i(\lambda_i - 1) + 1]^{-(\lambda_i-1)^{-1}}) \text{ for } i \in \{A, B, C\}$$

$$S_{ij}(q) = \frac{\bar{N}f_i f_j}{x_i x_j} (1 - [x_i(\lambda_i - 1) + 1]^{-(\lambda_i-1)^{-1}})(1 - [x_j(\lambda_j - 1) + 1]^{-(\lambda_j-1)^{-1}}) \text{ for } ij \in \{AB, BC\}$$

$$S_{ik}(q) = \frac{\bar{N}f_i f_k}{x_i x_k} (1 - [x_i(\lambda_i - 1) + 1]^{-(\lambda_i-1)^{-1}})(1 - [x_k(\lambda_k - 1) + 1]^{-(\lambda_k-1)^{-1}}) \left([x_j(\lambda_j - 1) + 1]^{-(\lambda_j-1)^{-1}} \right) \text{ for } ik = AC \text{ and } j = B$$

where

$$\bar{N} = \frac{\sum_i v_i N_i}{(\prod_i v_i)^{n-1}}$$

$$x_i = \frac{N_{i,n} b_i^2}{6} q^2$$

$$\lambda_i = \lambda = \left(\frac{M_w}{M_n} - 1 \right) \left(\sum_i w_i^2 \right)^{-1} + 1$$

and f_i is the volume fraction of the i th monomer, v_i is the molar volume (in $\text{cm}^3 \text{ mol}^{-1}$) of the i th monomer, N_i is the degree of polymerization of the i th block, $N_{i,n}$ and $N_{i,w}$ are the number-average and weight-average molar masses of the i th block respectively, λ_i is the dispersity of the i th block, b_i is the statistical segment length of the i th monomer ($\sim 0.68 \text{ nm}$ for PS and ~ 0.74

nm for PMMA),⁴⁶ and n is the number of different monomers (i.e. 2 for diblocks and 3 for triblocks). All degrees of polymerization were normalized to a reference volume of 118 Å³.

The value of each pairwise interaction parameter were determined by the best fit of the scattering profile using the above equations at each temperature for each of the four polymers listed in Table 2-3 and Table 2-4. For the diblock case, four parameters were fitted: K , χ_{AB} , b_A , and b_B . For the triblock case, two of the three χ parameters were held constant at each temperature using their previously determined temperature dependencies and the following five parameters were fitted: K , χ , b_A , b_B , and b_C . Triblocks were used for three of the four cases because the molecular weight of the diblock necessary for RPA would have been either prohibitively large (PGMA-PMMA and PGMA_F-PMMA) or small (PS-PGMA_{OH}). The temperature dependencies were then obtained by linear regression using the equation $\chi = \beta + \alpha T^{-1}$ where αT^{-1} is the enthalpic contribution and β is the entropic contribution and T is given in kelvin (Figure 2-3 to Figure 2-6) and are listed in Table 2-5 as well as the χ_{eff} at 453 K, the annealing temperature used in this study.

Table 2-3. Physical parameters of the polymers used for RPA analysis.

Polymer Used	M_n (kg mol ⁻¹)	f_A	f_B	f_C	λ_A	λ_B	λ_C	N_A	N_B	N_C
PS-PGMA-PMMA	17.7	0.43	0.07	0.50	1.29	1.29	1.29	102	15	86
PS-PGMA_{OH}- PMMA	10.4	0.47	0.05	0.51	1.46	1.46	1.46	61	3	66
PGMA_{OH}-PMMA	4.0	0.43	0.57	-	1.36	1.36	-	10	35	-
PS-PGMA_F-PMMA	15.4	0.46	0.11	0.43	1.32	1.32	1.32	93	9	90

Table 2-4. Physical parameters of the monomers used for RPA analysis.

Monomer	Molar Mass (g mol ⁻¹)	Density (g cm ⁻³)	Molar Volume (cm ³ mol ⁻¹)
Styrene	104.15	1.05	99.2
GMA	142.15	0.805	177
GMA_{OH}	250.31	1.50 ^a	167
GMA_F	258.26	1.43 ^a	181
MMA	100.12	1.184	84.6

^aEstimated using the group contribution method⁴⁴

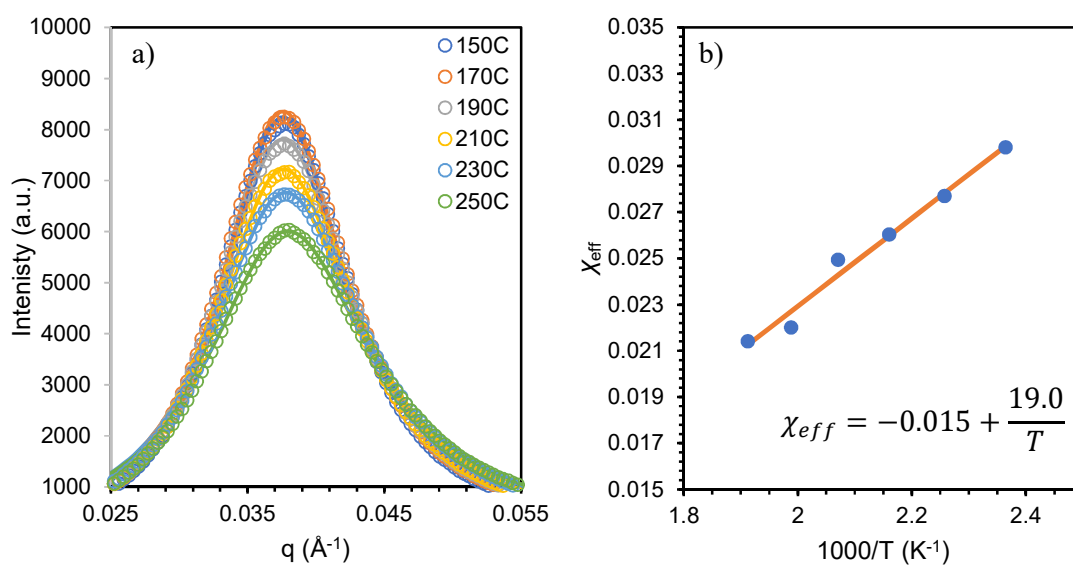


Figure 2-3. a) Fitting of PS-PGMA-PMMA using RPA and b) temperature dependence of $\chi_{GMA-MMA}$.

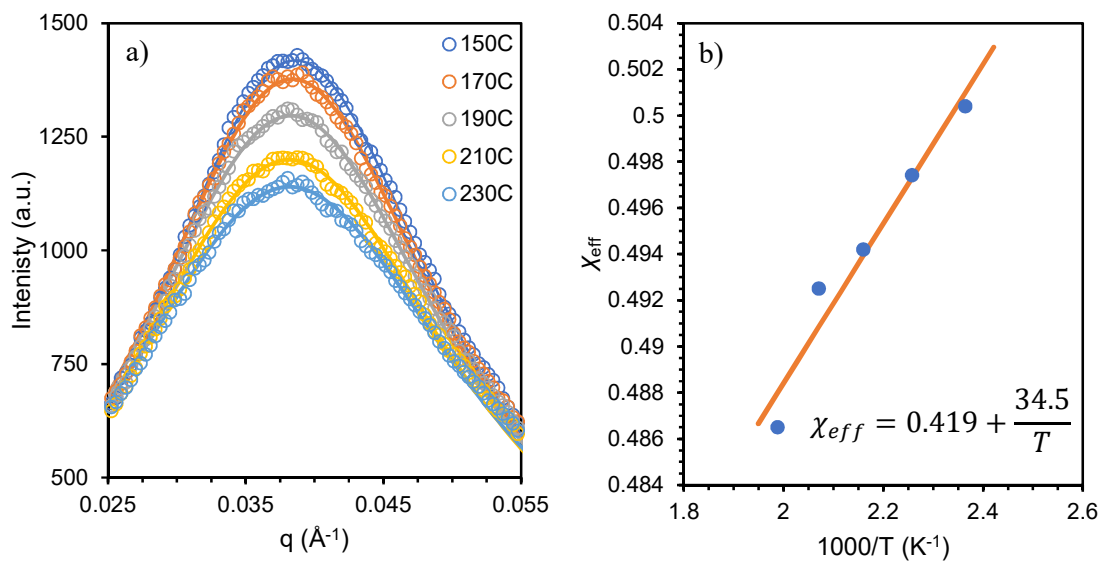


Figure 2-4. a) Fitting of PS-PGMA_{OH}-PMMA using RPA and b) temperature dependence of $\chi_{\text{S-GMA-OH}}$.

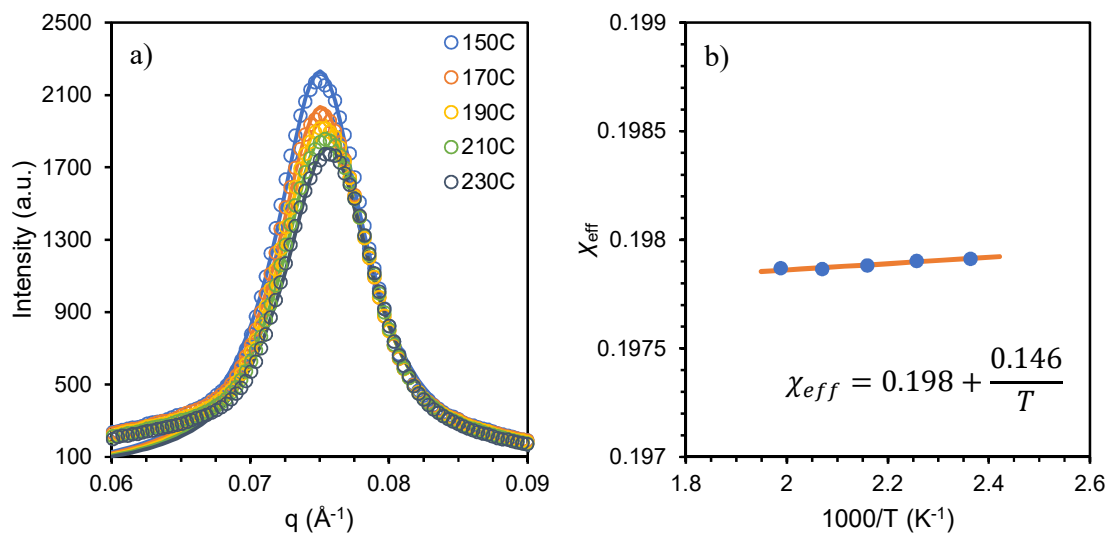


Figure 2-5. a) Fitting of PGMA_{OH}-PMMA using RPA and b) temperature dependence of $\chi_{\text{MMA-GMA-OH}}$.

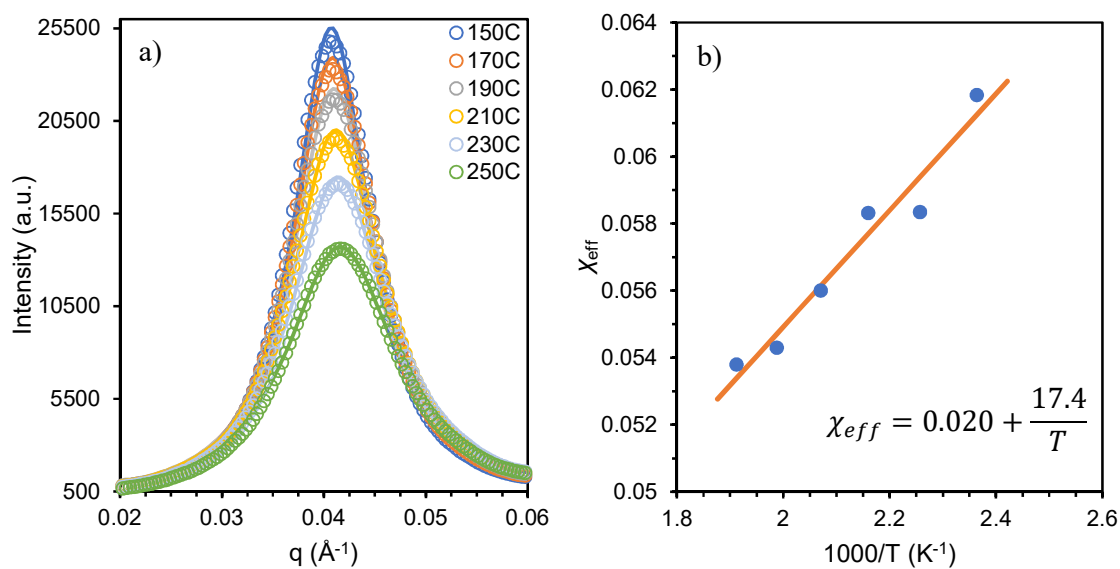


Figure 2-6. a) Fitting of PS-PGMA_F-PMMA using RPA and b) temperature dependence of $\chi_{\text{MMA-GMA-F}}$.

Table 2-5. Summary of the Temperature Dependent Pairwise Interaction Parameters Estimated by RPA

Monomer Pair ^a	β	α	χ_{eff} at 453 K
S-MMA^b	0.0282	4.46	0.0380
S-GMA^c	0.098	16.0	0.133
MMA-GMA^d	-0.015	19.0	0.0268
S-GMA_{OH}^d	0.419	34.5	0.495
GMA_{OH}-MMA^e	0.198	0.146	0.198
S-GMA_F^c	0.126	19.4	0.169
GMA_F-MMA^d	0.020	17.4	0.0585

^aS = styrene, MMA = methyl methacrylate, GMA = glycidyl methacrylate, subscripts OH and F indicate functionalization by 1-thioglycerol or 2,2,2-trifluoroethanethiol respectively

^bFrom Zhao et al.⁵²

^cFrom Yoshimura et al.⁴⁹

^dCalculated using a triblock terpolymer

^eCalculated using a diblock copolymer

As expected, the functionalization of the PGMA block had a significant effect on the χ of each monomer pair with χ_{AB} varying from 0.133 (S-GMA) to 0.495 (S-GMA_{OH}) and χ_{BC} varying from 0.0268 (GMA-MMA) to 0.198 (GMA_{OH}-MMA). Of the four χ parameters measured in this study, those of S-GMA_{OH} and GMA_{OH}-MMA both showed very low temperature dependence. This is the result of the extensive hydrogen bonding of GMA_{OH} which increases the entropic contribution to χ and is in agreement with previous studies using strongly hydrogen bonding monomers.^{47,48} Since χ_{AC} (S-MMA) remains the same for all samples, it is clear that in all cases the triblock terpolymers should exhibit frustrated self-assembly as defined by χ_{AC} smaller than at least one of χ_{AB} or χ_{BC} . While segregation strength is strictly measured as the product of χN , in this case since N does not change after functionalization, a direct comparison of the magnitude of each of the χ parameters is equivalent to a comparison of the segregation strength. Furthermore, in contrast to the diblock case where there is only one value of χN , for the triblock case there are three and it is this interplay that causes the interesting morphologies seen previously.²²

2.3.3 Bulk Morphology Characterization

Bulk samples for SAXS and TEM analysis were prepared by slow evaporation of solutions of the polymers in chloroform followed by thermal annealing under reduced pressure at 453 K for 24 h. 1D SAXS spectra were obtained by subtracting the background and azimuthally integrating the 2D scattering profiles taken at room temperature. The domain spacing (d) of each sample was determined by the position of the first-order scattering peak q^* ($d = 2\pi q^{*-1}$) and the morphologies by the ratio of q^* to the higher order peaks. The samples were also observed directly by TEM after microtoming and staining with RuO₄.

PSGM21 was found to self-assemble into a lamellar (LAM) morphology with peak ratios 1:2:3 and $d = 19.3$ nm (Figure 2-7a,b,c). 1-Thioglycerol modified PSGM21_{OH} was also found to be lamellar with peak ratios 1:2:3:4:5:6 but $d = 25.0$ nm (Figure 2-7d,e). Since d scales with

both χ and N which is unchanged,^{14,29} this leftward shift is consistent with the large increase in both $\chi_{\text{S-GMA}}$ from 0.133 to 0.495 and $\chi_{\text{MMA-GMA}}$ from 0.0268 to 0.198 at 453 K determined previously (Table 2-5). Interestingly, the SAXS spectrum of 2,2,2-trifluoroethanethiol modified PSGM21_F indicated that it had become hexagonally packed cylinders (HEX) with peak ratios of $1:\sqrt{3}:2:\sqrt{7}:\sqrt{12}$ and $d = 18.7$ nm (Figure 2-7a) despite the unchanged, symmetric A/C volume fractions, demonstrating that χ also plays an important role in influencing the morphology. The TEM image of PSGM21_F (Figure 2-7f) and its Fourier transform also clearly show HEX packing with an angle between the two indicated vectors of 119° which is very near to the ideal angle of 120° (Figure 2-7g).

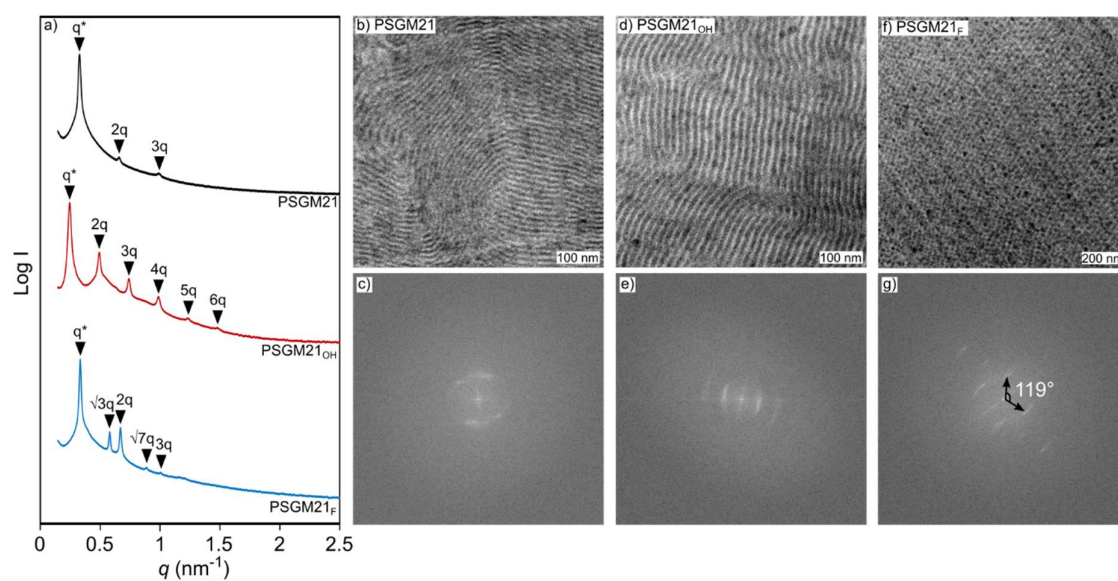


Figure 2-7. a) SAXS spectra of PSGM21 and its functional derivatives, b) TEM image of PSGM21, c) Fourier transform of the TEM image of PSGM21, d) TEM image of PSGM21_{OH}, e) Fourier transform of the TEM image of PSGM21_{OH}, f) TEM image of PSGM21_F, and g) Fourier transform of the TEM image of PSGM21_F. The SAXS spectra have been shifted vertically for clarity.³⁵

In contrast to the diblock case where there is only one χ , in the triblock case there is a complex interplay between the three χ parameters that has a strong influence on the morphology as seen in Figure 2-7 where changes in χ_{AB} and χ_{BC} alone induced changes in the predicted morphology from LAM to HEX. This phenomenon will be discussed further in the following chapter.

As molecular weight decreased to 17.7 kg mol^{-1} for PSGM18, SAXS analysis of the unmodified sample revealed that it was disordered with only a broad first-order peak (Figure 2-8a) and no apparent morphology in the TEM image (Figure 2-8b,c). However, the SAXS spectrum of PSGM18_F indicated HEX morphology with peak ratios $q^*:q$ of $1:\sqrt{3}:2:\sqrt{7}$ and $d = 16.2 \text{ nm}$ (Figure 2-8a,f). The Fourier transform of the TEM image of PSGM18_F indicates an angle of 118° between the two indicated vectors which matches closely the expect angle of 120° for HEX packing (Figure 2-8g). The SAXS spectrum of PSGM18_{OH} on the other hand, has peaks with the ratio $q^*:q$ of $1:\sqrt{2}:2:3$ with $d = 18.4 \text{ nm}$ which may be the result of tetragonally packed cylinders.^{49,50} However, the peaks are comparatively broader, which indicates larger deviation from the ideal paracrystalline lattice or overlapping peaks from a mixed morphology.⁵⁰ Additionally, the TEM image and its Fourier transform do not show any clear ordered morphologies due to poor contrast as a result of incomplete phase separation (Figure 2-8d,e).

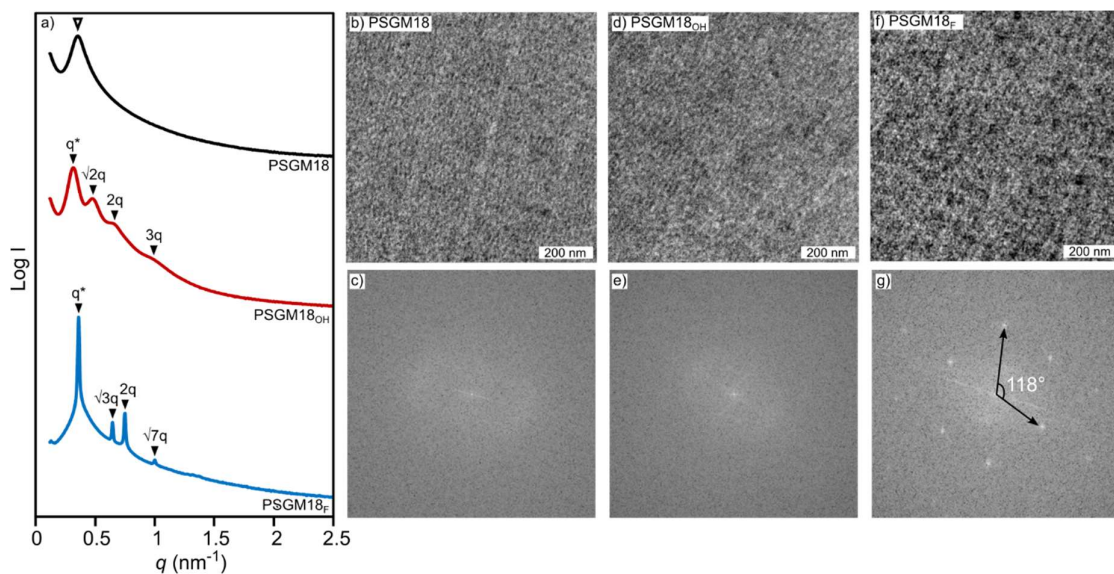


Figure 2-8. a) SAXS spectra of PSGM18 and its functional derivatives, b) TEM image of PSGM18, c) Fourier transform of the TEM image of PSGM18, d) TEM image of PSGM18_{OH}, e) Fourier transform of the TEM image of PSGM18_{OH}, f) TEM image of PSGM18_F, and g) Fourier transform of the TEM image of PSGM18_F. The SAXS spectra have been shifted vertically for clarity.³⁵

As the molar mass continues to decrease, PSGM15 was found to be disordered (Figure 2-9a,b,c) like PSGM18. SAXS analysis of PSGM15_{OH} revealed the characteristic peak ratios of $q^*:q$ of $1:\sqrt{2}:2:\sqrt{5}:\sqrt{8}:\sqrt{10}$ consistent with tetragonally packed cylinders with $d = 16.6$ nm (Figure 2-9a). TEM images of this sample also show clear tetragonal packing (Figure 2-9d) consistent with the predicted morphology (Figure 2-9d). The Fourier transform of the TEM image of PSGM15_{OH} indicates an angle of 95° between the two indicated vectors which is close to the ideal angle of 90° for tetragonal packing (Figure 2-9c). Like previous fluorinated samples, the experimental results from PSGM15_F clearly show HEX cylinders with SAXS peak ratios $q^*:q$ of $1:\sqrt{3}:2$ and $d = 15.2$ nm along with HEX packing observed by TEM (Figure 2-9e). The Fourier transform of the TEM image of PSGM15_F also indicates an angle of 125°

between the two indicated vectors, close to the expected value of 120° for HEX packing (Figure 2-8f).

Finally, SAXS analysis of PSGM10 and its functionalized derivatives PSGM10_{OH} and PSGM10_F (Figure 2-10) indicate that all samples are disordered as characterized by a single broad peak.

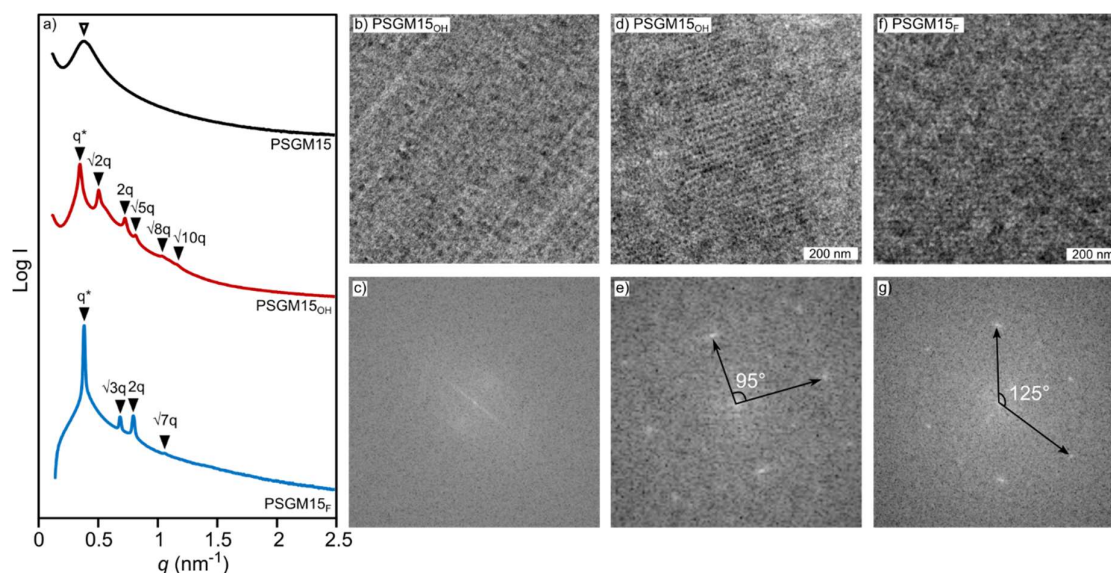


Figure 2-9. a) SAXS spectra of PSGM15 and its functional derivatives, b) TEM image of PSGM15, c) Fourier transform of the TEM image of PSGM15, d) TEM image of PSGM15_{OH}, e) Fourier transform of the TEM image of PSGM15_{OH}, f) TEM image of PSGM15_F, and g) Fourier transform of the TEM image of PSGM15_F. The SAXS spectra have been shifted vertically for clarity.³⁵

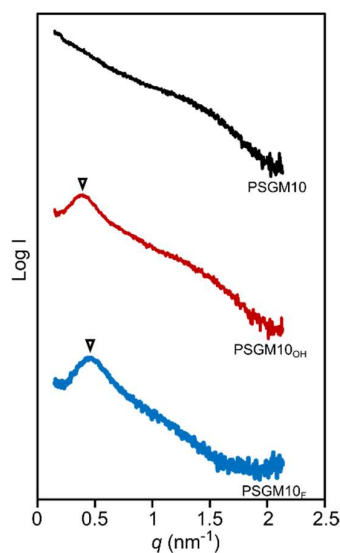


Figure 2-10. SAXS spectra of PSGM10 and its functionalized derivatives. The spectra have been shifted for clarity.³⁵

2.4 Conclusion

In this study, we have presented a new triblock poly(styrene-*block*-glycidyl methacrylate-*block*-methyl methacrylate) terpolymer which has a short, reactive glycidyl methacrylate middle block that we used to explore the χ_{AB} - χ_{BC} parameter space and in doing so, clearly demonstrated the profound effect changes in χ have on the self-assembly behavior of triblock terpolymers. By introducing strongly dissimilar small molecules to the middle block, we could vary χ_{AB} and χ_{BC} experimentally while keeping all other parameters nearly constant which, to the extent of our knowledge, has never been investigated previously. Observed morphologies included lamellae, hexagonal cylinders, and tetragonal cylinders as confirmed by SAXS and TEM. Our experimental results demonstrated that it is possible to alter the self-assembled morphology solely by changing χ which led us to conclude that both the magnitude and the relationship between the three interaction parameters is vital in understanding the self-assembly behavior of linear triblock terpolymers.

2.5 References

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Chapter 3

Morphological Study of Functionalized PS-*b*-PGMA-*b*-PMMA

Triblock Terpolymers Using Simulation

3.1 Introduction

As discussed in previous chapters, block copolymers are a particularly interesting class of soft material due to their inherent ability to self-assemble into periodic ordered structures on the scale of several to tens of nanometers. The formation of these periodic structures depends on several experimental parameters such as the Flory-Huggins interaction parameter (χ), the volume fraction (f) and the degree of polymerization (N). Typically, the effect that these parameters have on self-assembly is determined experimentally which is both time-consuming and costly. Therefore, the prediction of the self-assembly behavior of polymers by theory and simulation would be an invaluable tool for the discovery of new materials.

While other fields often make use of fully atomistic models or bead-spring models,¹ these are unsuitable for polymers due to their size. In 1975, Helfand extended the mean-field theory, commonly called self-consistent field theory (SCFT), to block copolymers.^{2,3} This approach is well suited for polymers which can be modeled as a continuous gaussian chain in a chemical potential field. In 1980, Leibler introduced an analytical solution to the set of SCFT equations by constraining it to the weak segregation region commonly referred to as the weak-segregation theory (WST).⁴ Then, in 1985, Semenov introduced a new theory for generating analytical expressions of the set of SCFT equations by examining the strong segregation regime where χN goes to infinity called the strong segregation theory (SST).⁵

The first general implementation of SCFT without any limitations in χN was demonstrated by Matsen and Schick in 1994.⁶ Since the self-assembled structures of block copolymers are periodic in one or more dimensions, the authors were able to solve the set of SCFT equations

in reciprocal space using a series of truncated Fourier basis functions. This spectral approach has proven to be very powerful for computing the free energy of a given phase and thus its stability,⁷ however it relies on prior knowledge of the symmetry of the phase in question and so is generally unsuitable for discovering new phases. To address this, Drolet and Fredrickson applied a real-space approach to solving the set of SCFT equations which removes the restriction of an assumed symmetry and can therefore be used to discover new self-assembled phases.⁸

More recently, a third technique for solving the SCFT equations was developed by Tzeremes et al. which combines some of the advantages of both the spectral and the real-space approach.^{9,10} Namely, it does not require a priori knowledge of the morphology like in the real-space method, but is more computationally efficient like the spectral method. This pseudo-spectral technique provides a gain of about an order of magnitude in computation time for the same level of accuracy as the real-space method of Drolet and Fredrickson.

In this chapter, we apply the pseudo-spectral technique to solve the SCFT equations of a linear ABC triblock terpolymer and compare the results to the experimentally determined morphologies from Chapter 2. We demonstrate that the simulated and experimental results are in good agreement, so we extend our simulation to generate phase diagrams consisting of 100 simulations for each of the polymers studied by varying χ_{AB} and χ_{BC} at constant χ_{AC} . Using this method, we demonstrate the pronounced effect that both the magnitude and relationship of the three χ parameters have on the self-assembly behavior of linear ABC triblock terpolymers.¹¹

3.2 Experimental Section

3.2.1 Theory

For the general case, consider a melt of n multiblock copolymers where each polymer is composed of N segments where $f_i N$ forms the i th block. The interaction between dissimilar

blocks is given by the Flory-Huggins interaction parameter χ_{ij} . The free energy per chain F (in units of $k_B T$) is given by:⁶

$$F = -\ln\left(\frac{Q}{V}\right) + \frac{N}{2V} \sum_i \sum_{j \neq i} \chi_{ij} \int d\mathbf{r} \phi_i(\mathbf{r}) \phi_j(\mathbf{r}) - \frac{1}{V} \sum_i \int d\mathbf{r} w_i(\mathbf{r}) \phi_i(\mathbf{r}) + \frac{1}{V} \sum_i \int d\mathbf{r} \xi_i(\mathbf{r}) \phi_i(\mathbf{r}) \quad (1)$$

Where V is the dimensionless volume of the system, $\phi_i(\mathbf{r})$ is the volume fraction of species i at position $\mathbf{r}$, $w_i(\mathbf{r})$ is the mean-field energy of species i being at position $\mathbf{r}$, and Q is the single-molecule partition function. $\xi_i(\mathbf{r})$ is the Lagrangian multiplier that enforces the condition of incompressibility

$$\sum_i \phi_i = 1 \quad (2)$$

The free energy described in (1) is minimized with respect to $w_i(\mathbf{r})$ and $\phi_i(\mathbf{r})$ which gives

$$w_i(\mathbf{r}) = N \sum_{j \neq i} \chi_{ij} \phi_j(\mathbf{r}) + \xi_i(\mathbf{r}) \quad (3)$$

The partition function Q is calculated from

$$Q = \int q(\mathbf{r}, s) q^\dagger(\mathbf{r}, s) d\mathbf{r} = \int q(\mathbf{r}, 1) d\mathbf{r} \quad (4)$$

Where $q(\mathbf{r}, s)$ and $q^\dagger(\mathbf{r}, s)$ are the partial partition functions, often called “propagators”, of a block copolymer constrained to having its s th segment at a position $\mathbf{r}$. Since the polymers are described by random-walk statistics in chemical potential fields, the propagators can be described using the modified diffusion equations (MDEs):¹²

$$\frac{\partial q(\mathbf{r}, s)}{\partial s} = N \frac{b^2}{6} \nabla^2 q(\mathbf{r}, s) - w(\mathbf{r}, s) q(\mathbf{r}, s) \quad (5)$$

$$-\frac{\partial q^\dagger(\mathbf{r}, s)}{\partial s} = N \frac{b^2}{6} \nabla^2 q^\dagger(\mathbf{r}, s) - w(\mathbf{r}, s) q^\dagger(\mathbf{r}, s) \quad (6)$$

where the field and the statistical segment length b are defined as

$$w(\mathbf{r}, s) = \begin{cases} w_A(\mathbf{r}) & \text{for } 0 < s < f_A \\ w_B(\mathbf{r}) & \text{for } f_A < s < f_A + f_B \\ \dots & \dots \end{cases} \quad (7)$$

and

$$b = \begin{cases} b_A & \text{for } 0 < s < f_A \\ b_B & \text{for } f_A < s < f_A + f_B \\ \dots & \dots \end{cases} \quad (8)$$

The monomer densities can then be calculated by

$$\phi_i(\mathbf{r}) = \frac{V}{Q} \int_{s_{\text{lower}}}^{s_{\text{upper}}} q(\mathbf{r}, s) q^\dagger(\mathbf{r}, s) ds \quad (9)$$

where s_{lower} and s_{upper} are the lower and upper bounds respectively of the part of the polymer containing species i . Equations (2), (3), (4), (5), (6), and (9) then form the set of self-consistent equations used to find the free energy of a given system. For a more complete discussion of SCFT applied to block copolymers, the reader can consult one of several excellent reviews of the subject.^{12–15}

3.2.2 General Algorithm for Solving the SCFT Equations

As mentioned previously, in this work we used the pseudo-spectra approach to solve the set SCFT equations.^{9,10} The general algorithm for finding a self-consistent solution is as follows:

1. The potential fields w_i are initialized to a random guess in the range of $[-1 \ 1]$ using a random number generator.
2. Solve the MDEs (5) and (6) using the split-step Fourier method.
3. Calculate the partition function Q using (4) and find the new densities $\phi_i(\mathbf{r})$ using (9).
4. Update the Lagrangian $\xi_i(\mathbf{r})$ by combining equations (2) and (3). E.g. for a diblock copolymer

$$\xi(\mathbf{r}) = \frac{w_A + w_B}{2} - \frac{\chi_{AB} N}{2} \quad (10)$$

5. Calculate the free energy using (1). If the change in free energy is below some threshold (typically on the order of 10^{-6} to 10^{-10}) the solution has converged.
6. If above the threshold, calculate the values of the new fields at step $n + 1$ by iterating using a Picard-type algorithm with the results from step n :

$$w_i^{n+1}(\mathbf{r}) = w_i^n(\mathbf{r}) + \lambda \left(N \sum_{j \neq i} \chi_{ij} \phi_j(\mathbf{r}) + \xi(\mathbf{r}) - w_i^n(\mathbf{r}) \right) \quad (11)$$

where λ is a small positive number.

7. Return to step 2 until convergence is achieved.

This algorithm will continue until the free energy converges to a local minimum. The linear mixing parameter λ determines the degree of mixing between the new and old solutions of the mean field values and is in the range $0 < \lambda \leq 1$ where a value of mixing means using only the new solution with no mixing. As λ increases, the algorithm will speed up at the expense of becoming less stable. Typically, λ is chosen to be ≤ 0.1 .

3.2.3 Computational Details

In this study, the simulated polymers were assumed to be monodisperse with temperature independent densities and identical statistical segment lengths. A grid size of 64×64 was used for the 2D SCFT calculations with a minimum contour step of $\Delta s = 0.005$ and periodic boundary conditions. The simulations were performed using the pseudo-spectral method developed by Rasmussen and Kalosakas starting from random initial conditions followed by Anderson acceleration once a stable morphology could be identified (typically at changes in the free energy $\leq 1 \times 10^{-6}$).^{10,16} The simulations were implemented in MATLAB version 2019b and calculations were performed on an Intel Xeon CPU E5-2690V2 3.00 GHz or an Intel Xeon CPU Gold 6130 2.10 GHz.

3.3 Results and Discussion

The simulations carried out in this study were performed using the split-step Fourier pseudo-spectral method first employed by Tzeremes et al.⁹ This method combines the strengths of the full spectral method, namely accuracy, with the speed and flexibility of real-space methods. In general, the computational cost of the pseudo-spectral scales as $O(M \log M)$ where M is the number of basis functions or equivalent grid points compared to the spectral method which scales as $O(M^3)$.^{13,17} Convergence can also be sped up using Anderson mixing which was first applied to SCFT by Thompson et al.¹⁶ By building up a history of solutions from previous iteration steps, convergence can be sped up by setting $\lambda = 1$ once a sufficient number of histories have been generated. However, if insufficient histories are available or the histories are not good estimates the result may become unstable, so care must be taken when setting the threshold for Anderson mixing. In this work we switched to Anderson mixing once a stable morphology could be identified, which typically occurred at changes in the free energy $\leq 1 \times 10^{-6}$.

3.3.1 Comparison of Simulated and Experimental Results

Using SCFT, we were able to simulate the self-assembly behavior of the experimental samples and compare them directly, allowing us to check the accuracy of our simulations. The bulk triblock terpolymer samples used in this section were synthesized as described in the previous chapter and their physical characteristics are listed in Table 3-1.

Table 3-1. Input parameters for SCFT calculations.

Simulated Sample Code	f_A	f_B	f_C	Degree of Polymerization (N)	χ_{AC}
PSGM21	0.465	0.07	0.0465	267	0.0380
PSGM18	0.45	0.1	0.45	227	0.0380
PSGM15	0.45	0.1	0.45	190	0.0380
PSGM10	0.475	0.05	0.475	130	0.0380

As discussed in the previous chapter, PSGM21 and 1-thioglycerol modified PSGM21_{OH} were found to self-assemble into lamellar (LAM) morphologies with $d = 19.3$ nm and $d = 25.0$ nm respectively (Figure 3-1a,b). On the other hand, 2,2,2-trifluoroethanethiol modified PSGM21_F self-assembled into hexagonally packed cylinders (HEX) with $d = 18.7$ nm (Figure 3-1a,c) despite the unchanged, symmetric A/C volume fractions.

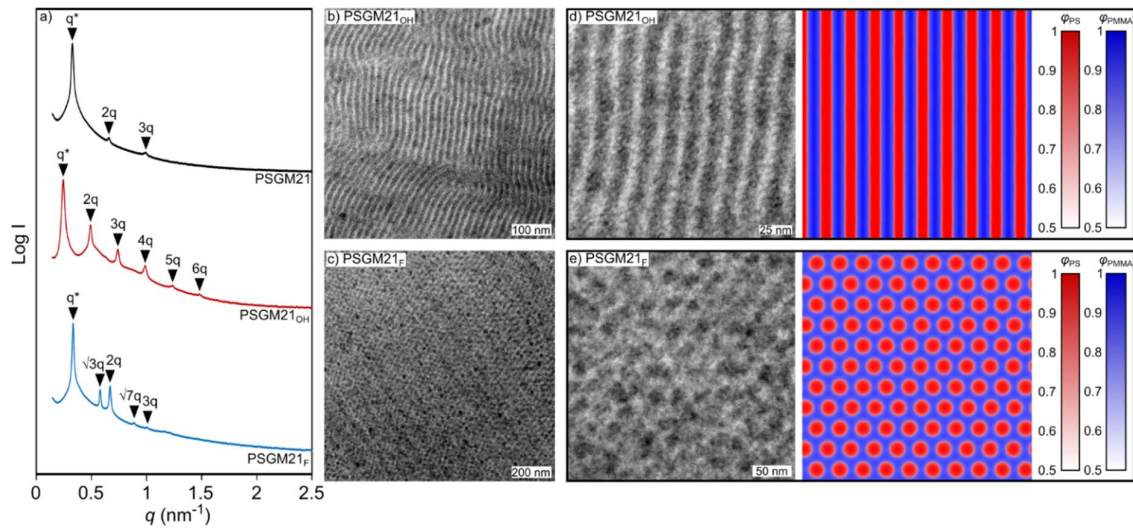


Figure 3-1. a) SAXS spectra of PSGM21 and its functional derivatives, b) TEM image of PSGM21_{OH}, c) TEM image of PSGM21_F, d) comparison of the PSGM21_{OH} experimental result to the morphology predicted by SCFT, and e) comparison of the PSGM21_F experimental result to the morphology predicted by SCFT. The SAXS spectra have been shifted vertically for clarity.¹¹

Using the previously determined χ , N , and volume fractions (Table 3-1, Table 2-5), the morphologies of PSGM21, PSGM21_{OH}, and PSGM21_F were simulated using the pseudo-spectral method developed by Rasmussen and Kalosakas combined with Anderson mixing.^{10,16} The morphologies predicted by SCFT matched closely with our experimental results and revealed only two distinct PS and PMMA phases even though $\chi_{S-GMAOH}$ is largest (Figure 3-1d,e). By examining the one-dimensional compositional profiles (Figure 3-2b, Figure 3-3b), we found that the PGMA block is completely mixed with the PMMA block because of its lower χ . Since the PGMA block contains some number of hydroxy groups which will be stained by RuO₄, this explains the poor contrast in many of the TEM images. In contrast to the diblock case where there is only one χ , in the triblock case there is a complex interplay between the three χ parameters that has a strong influence on the morphology as seen in Figure 3-1 where changes in χ_{AB} and χ_{BC} alone induced changes in the predicted morphology from LAM to HEX.

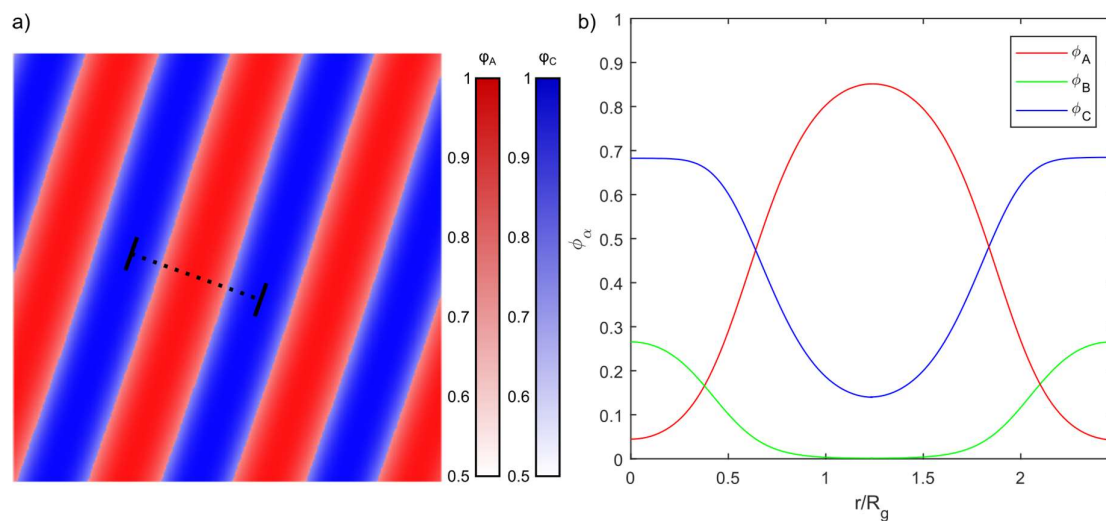


Figure 3-2. a) Morphology of PSGM21_{OH} LAM phase calculated using SCFT at $\chi_{AB}N = 131$, $\chi_{BC}N = 52.5$ and $\chi_{AC}N = 10.2$ and b) 1D composition profile along the dotted line in units of R_g .

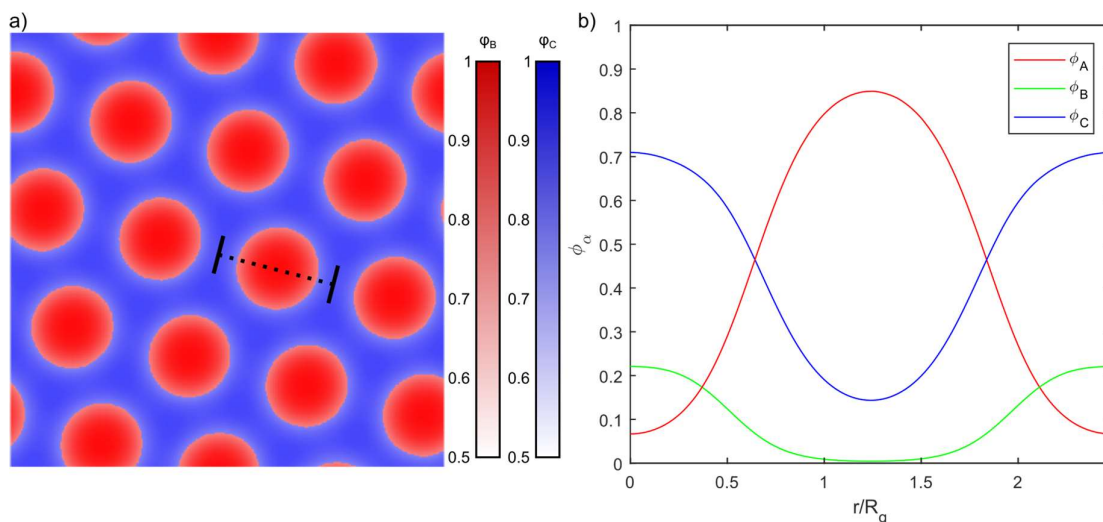


Figure 3-3. a) Morphology of PSGM21_F HEX phase calculated using SCFT at $\chi_{AB}N = 44.8$, $\chi_{BC}N = 15.5$ and $\chi_{AC}N = 10.2$ and b) 1D composition profile along the dotted line in units of R_g .

The observed morphologies for PSGM18, PSGM18_{OH}, and PSGM18_F were analyzed using SAXS and found to be disordered, poorly ordered tetragonal cylinders, and HEX cylinders respectively (Figure 3-4). Using the experimental parameters (Table 2-1, 2-2, 2-3), the self-assembly behavior was simulated as before and was found to be in agreement with our experimental results. In particular, the expected morphology for PSGM18_{OH} is predicted to be tetragonal cylinders which supports our conclusions from the previous chapter. Unfortunately, the TEM contrast is relatively poor due to the partial staining of the PGMA block so the comparison is less clear than that of PSGM21.

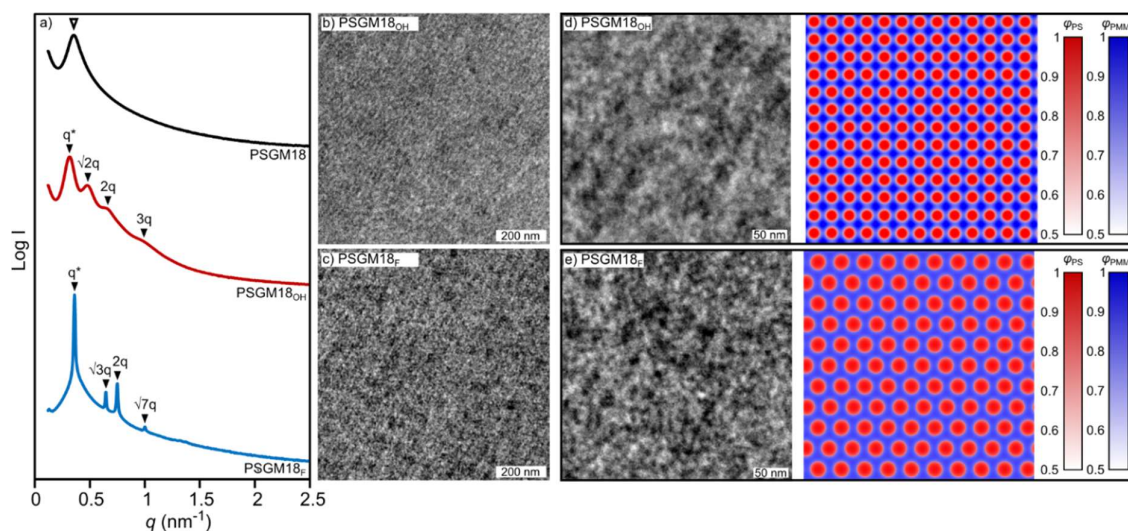


Figure 3-4. a) SAXS spectra of PSGM18 and its functional derivatives, b) TEM image of PSGM18_{OH}, c) TEM image of PSGM18_F, d) comparison of the PSGM18_{OH} experimental result to the morphology predicted by SCFT, and e) comparison of the PSGM18_F experimental result to the morphology predicted by SCFT. The SAXS spectra have been shifted vertically for clarity.¹¹

Like PSGM18, the observed morphologies of PSGM15, PSGM15_{OH}, and PSGM15_F were found to be disordered, tetragonal cylinders, and HEX cylinders respectively (Figure 3-5). Once again, the experimental results were compared with the morphologies predicted by SCFT. In this case, the simulated morphologies of PSGM15 and PSGM15_{OH} were in close agreement with the experimental results, but the SCFT simulation predicted disorder for PSGM15_F which is clearly not the case for the experimental result (Figure 3-5a,c).

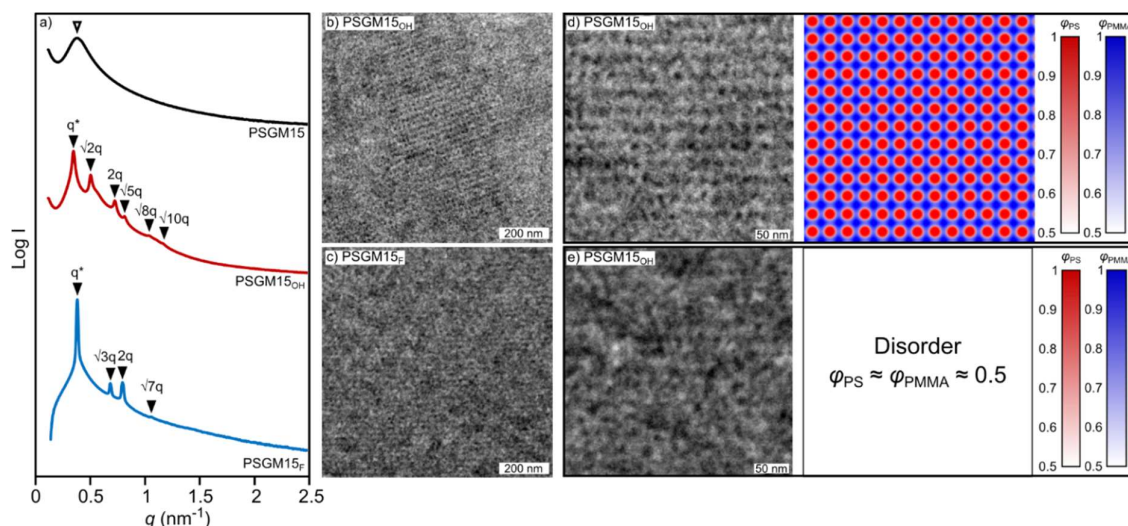


Figure 3-5. a) SAXS spectra of PSGM15 and its functional derivatives, b) TEM image of PSGM15_{OH}, c) TEM image of PSGM15_F, d) comparison of the PSGM15_{OH} experimental result to the morphology predicted by SCFT, and e) comparison of the PSGM15_F experimental result to the morphology predicted by SCFT. The SAXS spectra have been shifted vertically for clarity.¹¹

Since the SCFT simulations assume perfectly monodisperse chains with no volume asymmetry, we turned to the random-phase approximation (RPA) for triblock terpolymers, taking into account molar mass dispersity and segment volume asymmetry to explain this discrepancy.^{18,19} By setting all variables equal to their experimentally derived values we found that the experimental value of $\chi_{S-GMAF}N = 32.4$ is in fact larger than the predicted value of $\chi_{AB}N = 30.3$ at the stability limit (Figure 3-6a). Earlier studies have shown that dispersity can have an effect on the self-assembly behavior; particularly for triblocks where a disperse sample reduces the entropy of microphase separation.²⁰⁻²² Applying the same RPA analysis to PSGM15 (Figure 3-6b), which has similar χ , N and f , shows that the critical $\chi_{AB}N = 33.1$ is indeed larger than that of the experimental value $\chi_{S-GMA}N = 25.3$ and so is in agreement with the observed disordered morphology.

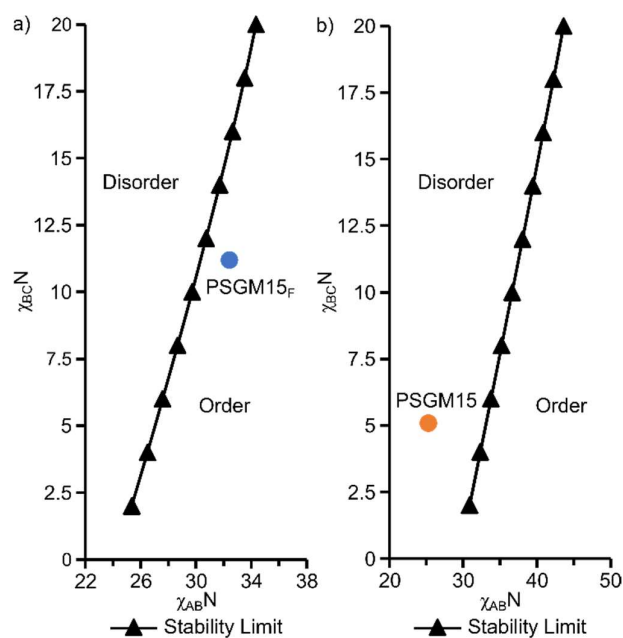


Figure 3-6. Calculation of the order-disorder transition with the RPA for a) PSGM15-F and b) PSGM15 using the experimentally determined dispersity, normalized degree of polymerization, and volume fractions.

Finally, SAXS analysis of PSGM10 and its functionalized derivatives PSGM10_{OH} and PSGM10_F (Figure3-7a) indicate that all samples are disordered which is in agreement with the simulated results at $\chi_{AC}N = 4.94$ (Figure3-7b).

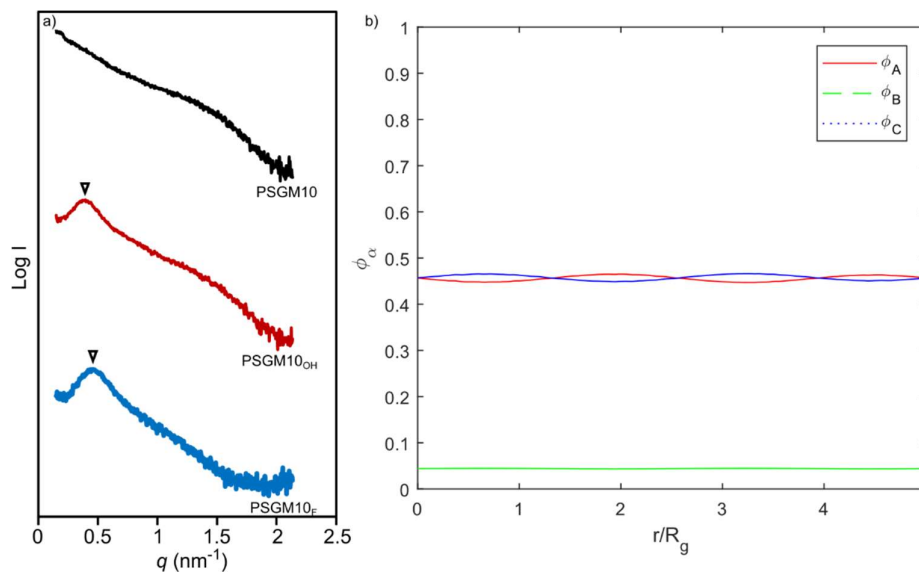


Figure3-7. a) SAXS spectra of PSGM10 and its functionalized derivatives and b) 1D composition profile of PSGM10 indicating a disordered structure. The spectra have been shifted for clarity.¹¹

3.3.2 Construction of Linear ABC Triblock Phase Diagrams

Since our simulated results were generally found to be in good agreement with the experimental results, we then expanded the scope of our simulations and systematically varied χ_{AB} and χ_{BC} to examine their effect on the self-assembly behavior over a wider range and to construct phase diagrams for each of the linear terpolymers studied.

The phase diagram corresponding to PSGM21 at $\chi_{AC}N = 10.1$ is shown in Figure 3-8 below. As expected, our experimental results, which span a large range of $\chi_{AB}N$, are in close agreement with the simulated phase diagram. Beyond the classical phases of HEX cylinders and LAM, A/C lamella with spheres at the interface (hereafter, *Is* phase) is predicted at very large $\chi_{AB}N$ and $\chi_{BC}N$ (Figure 3-9a). This phase of linear triblocks has previously been found to be stable for $f_B < 0.17$, above which cylinders will form at the A/C interface.²³

In contrast to the diblock case where there is only one χ , in the triblock case there is a complex interplay between the three χ parameters that has a strong influence on the morphology as seen

in Figure 3-8 where changes in χ_{AB} and χ_{BC} alone induced changes in the predicted morphology. The phase diagram can generally be subdivided into three regions, symmetric about the line $\chi_{AB} = \chi_{BC}$. When $\chi_{AB} \approx \chi_{BC} \gg \chi_{AC}$ the triblock will form the *ls* phase, when $\chi_{AB} > \chi_{BC} > \chi_{AC}$ HEX cylinders will tend to form, and when $\chi_{AB} \gg \chi_{BC} \geq \chi_{AC}$ LAM is preferred.

One possible explanation for this change in interfacial curvature is to consider the local density profile near the interface. In the *ls* case, $\chi_{AB} \approx \chi_{BC}$ and is very large with respect to χ_{AC} , which favors a distinct B domain to reduce the interface with both A and C. The 1D profile of this phase (Figure 3-9b) shows a local volume fraction of the B domain to exceed 0.6 even though the average f_B is less than 0.1. Next, consider the LAM case, where only one of χ_{AB} or χ_{BC} is large. If, for example, χ_{AB} is largest, as is the case with the experimental results, the B block will minimize the contact with the A block by stretching away from the A/C interface and mixing with the B block (Figure 3-2b). Though this has a clear penalty on the free energy by reducing the entropy caused by this chain stretching, it is more than made up for by the lowering of the A/B interfacial tension which in turn lowers the internal energy.

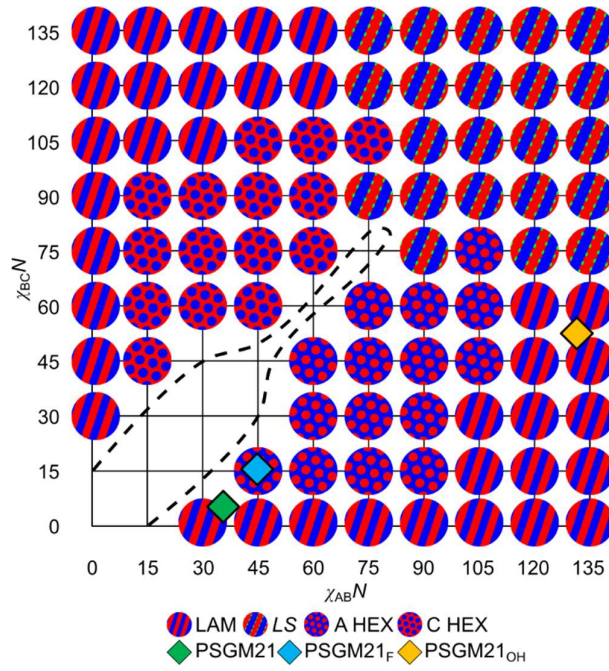


Figure 3-8. PSGM21 phase diagram calculated using SCFT at $\chi_{AC}N = 10.14$, $f_A = f_B = 0.465$, and $f_C = 0.07$ where each grid point represents a simulated result. Dashed lines indicating the extent of disordered region are meant solely as a visual aid.¹¹

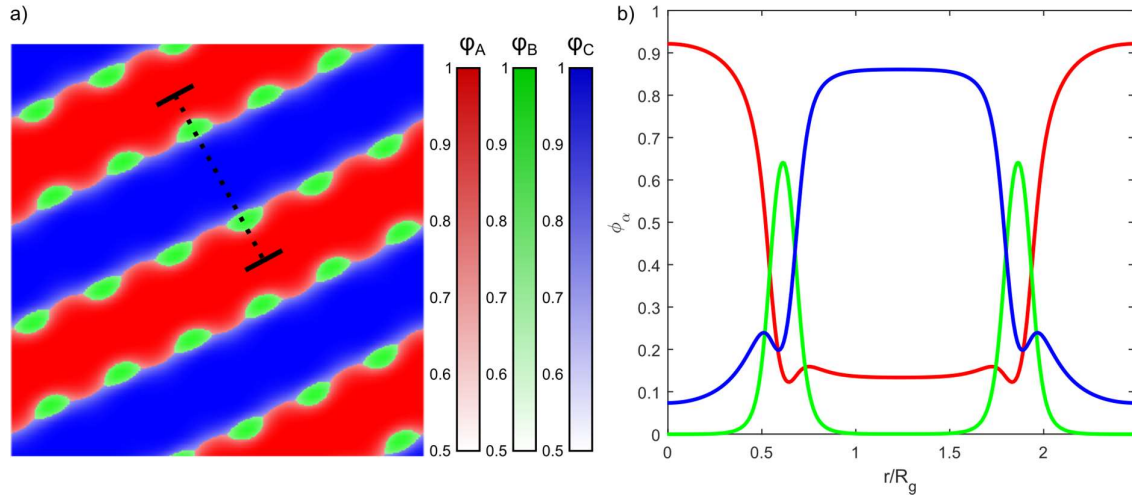


Figure 3-9. a) Morphology of PSGM21 *ls* phase calculated using SCFT at $\chi_{AB}N = 105$, $\chi_{BC}N = 120$ and $\chi_{AC}N = 10.14$ and b) 1D composition profile along the dotted line in units of R_g calculated using $L = 2.5 R_g$ with a contour step of $\Delta s = 0.002$ and a space step of $\Delta r = 0.005 R_g$.¹¹

For the HEX case, where one χ is large, one is intermediate and χ_{AC} is small, the interfacial tension between B and C is larger than the LAM case, and so the chain stretching becomes less energetically favorable (Figure 3-3b). As a result, the local density of the mixed B/C phase near the interface increases as the B block relaxes and returns to its less stretched state near the interface. Since the local density on the B/C side of the interface is now higher than the A side (Figure 3-10), the interface will curve towards the A domain to maintain constant density resulting in cylinders as observed experimentally and theoretically.

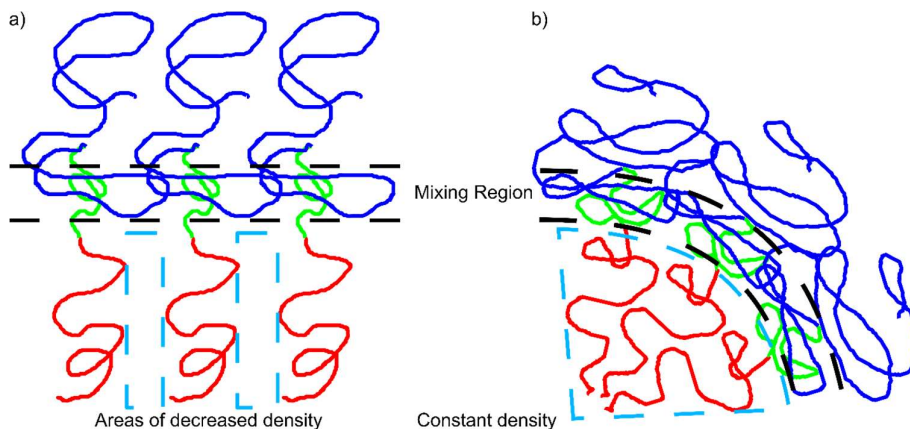


Figure 3-10. a) Illustration of a flat interface when the B block is located near the A/C interface. On the A block side there will be areas of decreased density. b) Illustration of a curved interface when the B block is located near the A/C interface. On the A block side, the density is constant throughout due to the interface curvature.

Next, we constructed the phase diagram for $\chi_{AC}N = 8.64$ corresponding to PSGM18 and found that the predicted morphologies were in agreement with the experimental results (Figure 3-11). Given the position of PSGM18_{OH} on the phase diagram near the boundary between the tetragonal A cylinders phase and the lamellar phase, we speculate that the broad peaks observed in Figure 3-4a indicate a mixed morphology that may be the result of a trapped non-equilibrium morphology because of the relatively high χN which reduces the rate of molecular diffusion

after the initial microphase segregation. This effect has previously been demonstrated to be significant for linear ABC triblock terpolymers using both experimental and theoretical studies.^{24–26} Previous reports have also shown that by changing the annealing conditions it is possible to change the self-assembled morphology of polymers near phase boundaries,^{27,28} so by lengthening the annealing time or increasing temperature to promote diffusion, we may be able to produce well-ordered structures in PSGM18_{OH}.

While the PSGM18 phase diagram is largely similar to that of PSGM21, a new phase similar to the so-called “tiling pattern” phase found previously for miktoarm arm star polymers,²⁹ consisting of HEX cylinders with B spheres spaced equidistantly, hereafter called *cs* (Figure 3-12a), is predicted. This phase differs dramatically from previously discovered triblock cylinder phases like core-shell cylinders, cylinder-sphere or cylinder-ring phases found previously.^{23,30–}
³² In this case, the B spheres are not found at the A/C interface of the cylinder surface, but are instead located within the surrounding matrix equidistant from neighboring cylinders (Figure 3-12a). It is clear that this arrangement must impose a strong entropic penalty due to chain stretching because the B domain is separated from the cylinder surface despite the covalent linkage as shown by the 1D composition profile (Figure 3-12b). However, since this phase is located only in regions of the phase diagram where $\chi_{AB}N$ and $\chi_{BC}N$ both exceed 60 but where one is at least 1.3 times larger than the other, we suggest that this entropic penalty is more than made up for by the decrease in enthalpy caused by eliminating the interface with the more strongly interacting phase and minimizing the interface with the matrix phase by forming distinct B spheres (i.e. if $\chi_{AB}N > \chi_{BC}N$, A will form cylinders in a C matrix with B spheres).

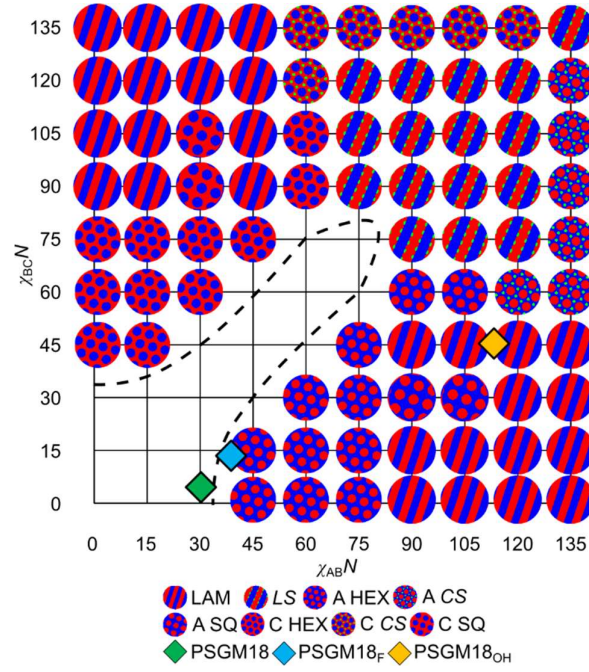


Figure 3-11. PSGM18 phase diagram calculated using SCFT at $\chi_{AC}N = 8.64$, $f_A = f_B = 0.45$, and $f_C = 0.10$ where each grid point represents a simulated result. Dashed lines indicating the extent of disordered region are meant solely as a visual aid.¹¹

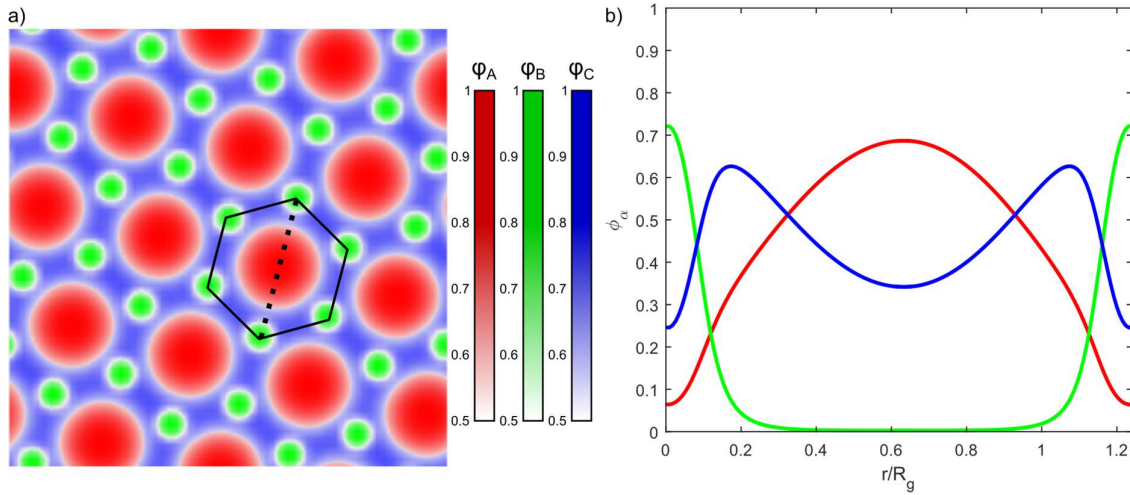


Figure 3-12. a) Morphology of PSGM18 cs phase calculated using SCFT at $\chi_{AB}N = 135$, $\chi_{BC}N = 90$ and $\chi_{AC}N = 8.64$ and b) 1D composition profile along the dotted line in units of R_g calculated using $L = 1.25 R_g$ with a contour step of $\Delta s = 0.002$ and a space step of $\Delta r = 0.005 R_g$.¹¹

As $\chi_{AC}N$ decreases further to 7.23 the phase diagram predicted using SCFT showed that there are much larger regions where the triBCP is predicted to be disordered (Figure 3-13). We also found that the tetragonal cylinders phase is larger, as is the complex *cs* phase. Since these samples have very similar physical properties barring their degrees of polymerization, it is clear that larger $\chi_{AC}N$ contributes to stabilizing the classical HEX, LAM and *ls* phases typically found in strongly-segregated triblock terpolymers.³⁰

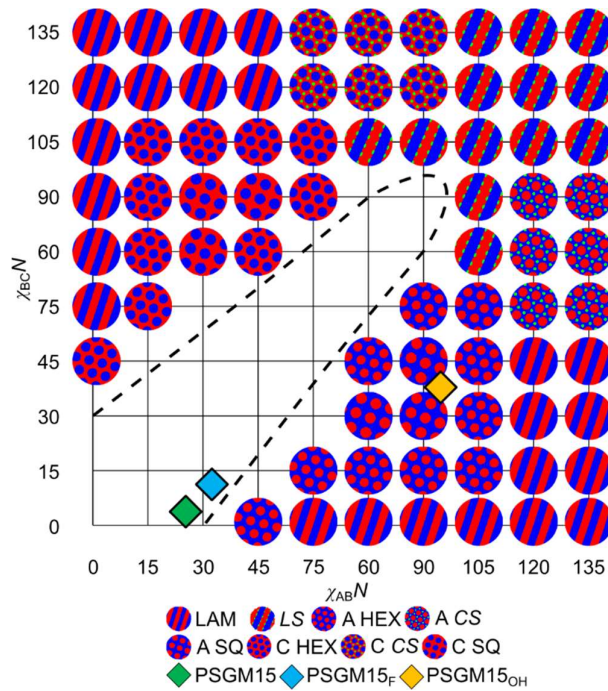


Figure 3-13. PSGM15 phase diagram calculated using SCFT at $\chi_{AC}N = 7.23$, $f_A = f_B = 0.45$, and $f_C = 0.10$ where each grid point represents a simulated result. Dashed lines indicating the extent of disordered region are meant solely as a visual aid.¹¹

Finally, the phase diagram for PSGM10 predicts that self-assembly will only occur when only one of $\chi_{AB}N$ or $\chi_{BC}N$ is very large, exceeding at least 90 (Figure 3-14). In these regions, the predicted phase is hexagonally packed (HEX) cylinders except at $\chi N = 135$ where the expected phase is lamellar. While it may seem counterintuitive that self-assembly should only

occur when only one of $\chi_{AB}N$ or $\chi_{BC}N$ is large, previous studies have shown that such an asymmetry between χ_{AB} and χ_{BC} can lower the $\chi_{AC}N$ necessary for spinodal decomposition in linear triblock terpolymers.¹⁹ With the continued pursuit of high- χ systems, we expect that these regions will eventually be able to be examined experimentally.

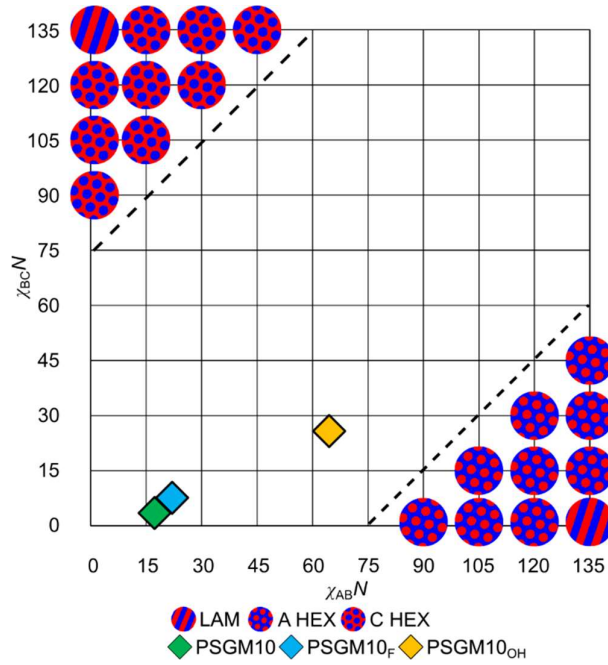


Figure 3-14. PSGM10 phase diagram calculated using SCFT at $\chi_{AC}N = 4.92$, $f_A = f_B = 0.475$, and $f_C = 0.05$ where each grid point represents a simulated result. Dashed lines indicating the extent of the disordered region are meant solely as a visual aid.¹¹

3.4 Conclusion

Using self-consistent field theory, we demonstrated that the predicted phases agree with our experimental results. Additionally, we have constructed the phase diagrams of four frustrated ABC linear triblock terpolymers using SCFT by systematically varying $\chi_{AB}N$ and $\chi_{BC}N$ at different values of $\chi_{AC}N$. These phase diagrams predicted the presence of a new *cs* phase when $\chi_{AB}N$ and $\chi_{BC}N$ are both large and asymmetric while $\chi_{AC}N$ remains much smaller. We expect that this approach which combines an arbitrarily customizable triblock terpolymer with theoretical predictions could act as a general platform to facilitate the discovery of new morphologies of linear triblock terpolymers.

3.5 References

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Chapter 4

Self-Assembly of Side-Chain Liquid Crystal Functionalized PS-*b*-PGMA-*b*-PMMA Triblock Terpolymers

4.1 Introduction

Liquid crystals (LCs) are a diverse type of molecule that exhibit both liquid-like and crystal-like behavior first discovered in 1888 by Reinitzer,¹ and today find use in diverse applications such as electro-optical displays, data storage, and separation membranes.² Liquid crystals can generally be classified into one of two types: lyotropic LCs where the behavior is influenced by the action of a solvent, and thermotropic LCs where the behavior is the result of heat.³ Under suitable conditions, these molecules will spontaneously self-assemble into ordered structures on the scale of 1-10 nm.

Liquid crystalline polymers (LCPs) can be categorized as either main-chain liquid crystal polymers (MCLCPs) where the liquid crystal mesogen is incorporated into the polymer chain, or side-chain liquid crystal polymers (SCLCPs) where the mesogen is attached to the main chain as a pendant side group. Depending on the length of the flexible spacer between the LC mesogen and the polymer backbone, the self-assembly behavior of the SCLCP can vary dramatically.^{4,5} By introducing LC mesogens therefore, the physical properties and nanoscale behavior of polymers can be greatly enriched.⁶⁻⁸

Block copolymers (BCPs) are widely studied due to their ability to self-assemble into periodic structures on the order of several to hundreds of nanometers.⁹ For a diblock copolymer, the classical self-assembled morphologies of lamellae, hexagonally packed cylinders, cubic packed spheres and the gyroid morphology have been demonstrated experimentally and theoretically.¹⁰⁻¹² Introducing LC mesogens to the diblock copolymer results in a complex interplay between different length scales of the LC ordering and the BCP

self-assembly with elements of anisotropy in a normally isotropic system.¹³ As a result, previous work using both MCLCPs and SCLCPs have demonstrated myriad phase separated structures not possible with a typical coil-coil BCPs including tetragonal cylinders,^{14,15} perforated lamellae,¹⁶ and zigzag lamellae among others.^{17,18}

Similarly, triblock terpolymers (triBCPs) have also been shown to exhibit interesting new morphologies not possible with diblock copolymers.^{19–21} As discussed previously in Chapters 2 and 3, this is a result of the much larger parameter space available to triBCPs which gives rise to a much richer phase diagram.

By introducing liquid crystal mesogens to a linear ABC triBCP, we expect that it could enrich the self-assembly behavior further still and may give rise to previously undiscovered morphologies of self-assembled materials. Using our previously synthesized poly(styrene-*b*-glycidyl methacrylate-*b*-methyl methacrylate) (PSGM) triblock copolymer with a reactive PGMA middle block, we were able to introduce liquid crystalline fluorinated alkyl chains via the thiol-epoxy reaction. This method allowed us to compare the effect of adding LC mesogens to the middle of a triBCP using small-angle x-ray scattering (SAXS) and transmission electron microscopy (TEM) to characterize the bulk morphology. We also analyzed the synthesized and analyzed a PGMA homopolymer and functionalized it in the same manner to investigate the LC behavior by differential scanning calorimetry (DSC), polarized optical microscopy (POM), and wide-angle x-ray diffraction (WAXD).

4.2 Experimental Section

4.2.1 Reagents

The polymers used in this study were prepared as described in Chapter 2. All other reagents and solvents were purchased from Kanto Chemical Co. Inc, Tokyo Chemical Industry or Sigma-Aldrich and used as received.

4.2.2 Synthesis of PSGM_{LC} via the Thiol-Epoxy Reaction

A general procedure for the functionalization of PSGM_{LC} is presented here.²² PSGM (147 mg, 7.0 μ mol) and 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol (PFDT) (44.6 mg, 93 μ mol) were dissolved in 1.2 ml THF. LiOH_{aq} (0.05 M, 0.07 ml, 3.5 μ mol) was then added to initiate the reaction. The resulting solution was stirred at 313 K for 3 h. The polymer was precipitated in 50 ml of cold hexane and filtered a minimum of three times to remove residual thiol. The resultant solid was dried under reduced pressure overnight at 313 K (0.1477 g, 90% yield). ¹H NMR (400 MHz, chloroform-*d*, δ , ppm): 7.22-6.85 (br, *m*-, *p*-aromatic), 6.82-6.25 (br, *o*-aromatic), 4.04 (m, -(C=O)O-CH₂-), 4.04 (m, -CH₂-CH(CH₂)-OH), 3.59 (s, -(C=O)O-CH₃), 2.81 (m, -CH(OH)-CH₂-S-), 2.71 (br -S-CH₂-CH₂-CF₂-), 2.39 (br, -S-CH₂-CH₂-CF₂-), 2.20-1.67 (br, -CH₂-CH-, -CH₂-C(CH₃)-, 1.54-1.22 (br, -CH₂-CH-), 1.05-0.75 (br, -CH₂-C(CH₃)-).

4.2.3 Characterization Methods

The ¹H nuclear magnetic resonance (NMR) spectra were recorded on a JEOL 400 MHz instrument using deuterated chloroform at ambient temperature. The number-average and weight-average molecular weights (M_n and M_w) were measured by size-exclusion chromatography (SEC) using a Shodex GPC-101 equipped with a refractive index detector and a LF-804 column (Showa Denko) with THF as the eluent at 313 K. Bulk samples were prepared by slow evaporation of chloroform solutions followed by thermal annealing at 453 K for 24 h. SAXS measurements were performed at the BL40B2 beamline of SPring-8 with a wavelength of 1.00 Å and a sample-to-detector distance of 2.0 m. SAXS thermal experiments were performed on a Bruker NanoSTAR (50 kV/ 50 mA) with a wavelength of 1.54 Å and a sample-to-detector distance of 1.0 m equipped with a TCPU-H heating stage and a Vântec-500 detector. Samples were placed in quartz glass capillaries (wall thickness 0.1 mm) for measurement. The SAXS profiles were collected using a cooling process beginning from 250 °C and cooled at a rate of 1 °C min⁻¹. At each measurement temperature, the sample was held

for 15 min and exposed to X-ray radiation for 15 min to collect the spectrum. Background spectra were collected for each sample by exposing an empty glass capillary for 15 min. Transmission electron microscopy (TEM) (H-7650 Hitachi High Tech) was used to examine ultrathin samples prepared by room temperature ultramicrotomy (Leica EM UC7) and stained by ruthenium tetroxide (RuO₄).

4.3 Results and Discussion

4.3.1 Synthesis of Side-Chain Liquid Crystal Containing PSGM

Several symmetric PSGM triBCPs were synthesized by sequential living anionic polymerization in the presence of excess LiCl under an inert atmosphere as described in Chapter 2.^{23–25} The characteristic data of the polymers can be found in Table 2-1. In this study, we used only PSGM21, PSGM18, and PSGM15 when introducing the SCLC PFDT. Using the same method as in Chapter 2, the PSGM triBCPs were functionalized by ring-opening the epoxide moieties using 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol (PFDT) in THF with LiOH as catalyst to yield PSGM_{LC} according to the procedure of Gadwal et al,^{22,26–28} with the only difference being the use of hexane to precipitate the polymer. PFDT was found to be insoluble in methanol, so it was unsuitable for removing any remaining unreacted thiol from the polymer. As before, the reaction was found to proceed quantitatively as determined by ¹H NMR where the five characteristic glycidyl peaks (4.28, 3.78, 3.59, 2.83, and 2.62 ppm) disappeared and were replaced by broad around 4.0, 2.8, 2.7, and 2.4 ppm (Figure 4-1). The density of the SCLC functionalized PGMA_{LC} was estimated using the group contribution method of Fedors and calculated to be 1.70 g cm⁻³.²⁹ The volume fractions of the functionalized polymers are summarized in Table 4-1.

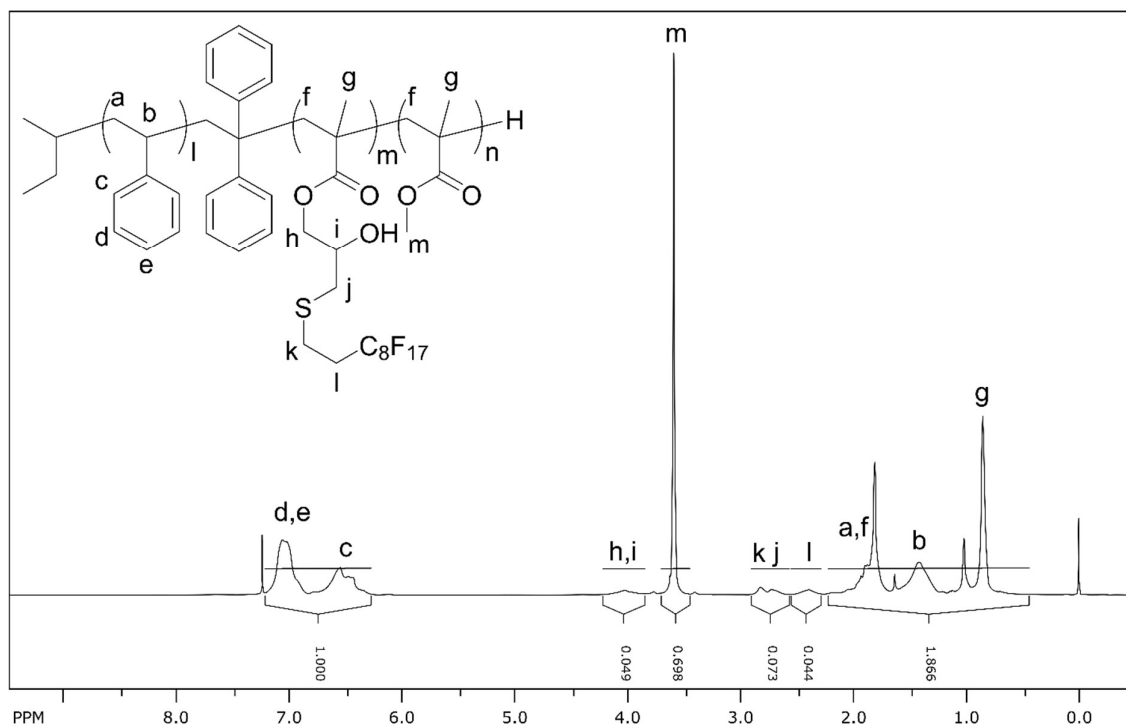


Figure 4-1. Representative ^1H NMR spectrum of PSGM_{LC} .

Table 4-1. Sample Characteristics of Functionalized PS-b-PGMALC-b-PMMA Triblock Terpolymers

Sample ^a	f_{PS}^b	f_{PGMA}^b	f_{PMMA}^b	Morphology ^c	d^d (nm)
PSGM21_{LC}	0.44	0.13	0.43	Double Tetragonal	25.0
PSGM18_{LC}	0.40	0.19	0.41	Double Tetragonal	18.7
PSGM15_{LC}	0.42	0.20	0.38	Unknown	18.4

^aNumbers indicate the molecular weights of the triBCPs; subscript LC indicates functionalization by PFDT

^bDetermined ^1H NMR analysis with densities calculated by the group contribution method²⁹

^cDetermined by SAXS peak ratios

^dDetermined by position of the primary scattering peak

Compared to the thiols used in Chapter 2, here, the volume fraction of the middle PGMA block increases significantly to between 0.13 and 0.20. This, along with the expected increase

in χ as well as the liquid crystal behavior of PFDT should result in markedly different self-assembly behavior than the previous study.

4.3.2 Estimation of Interaction Parameters

Using the same method as in Chapter 2, the two new binary interaction parameters ($\chi_{\text{PS-PGMALC}}$ and $\chi_{\text{PGMALC-PMMA}}$) were estimated using the random phase approximation (RPA).^{11,50,51} A low molecular weight diblock copolymer synthesized as described in Chapter 2 was functionalized with PFDT to measure the interaction parameter using SAXS over a range of temperatures and fitted using RPA analysis (Figure 4-2, Figure 4-3). The temperature dependence of each of the χ parameters, taking the form $\chi = \alpha T^{-1} + \beta$ where αT^{-1} is the enthalpic contribution and β is the entropic contribution, were determined. Each of the pairwise interaction parameters' coefficients are listed in Table 4-2 as well as the χ_{eff} at 453 K, the annealing temperature used in this study.

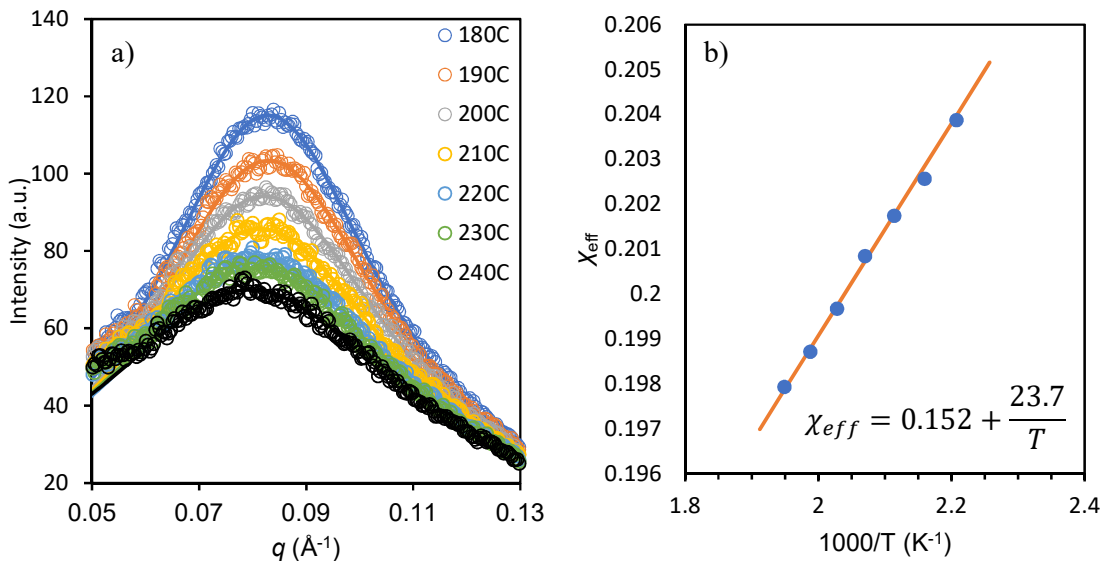


Figure 4-2. a) Fitting of PS-PGMALC using RPA and b) temperature dependence of $\chi_{\text{S-GMA-LC}}$.

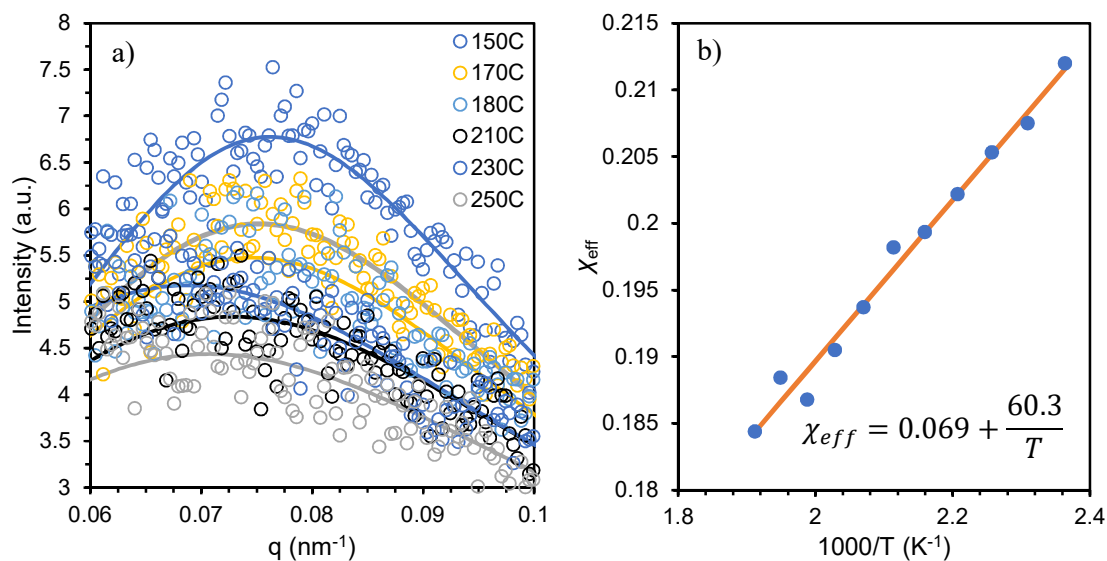


Figure 4-3. a) Fitting of PGMA_{LC}-PMMA using RPA and b) temperature dependence of $\chi_{\text{MMA-GMA-LC}}$.

Table 4-2. Summary of the Temperature Dependent Pairwise Interaction Parameters Estimated by RPA

Monomer Pair ^a	β	α	χ_{eff} at 453 K
S-MMA ^b	0.0282	4.46	0.0380
S-GMA ^c	0.098	16.0	0.133
MMA-GMA ^d	-0.015	19.0	0.0268
S-GMA _{LC} ^e	0.152	23.7	0.204
GMA _{LC} -MMA ^e	0.069	60.3	0.202

^aS = styrene, MMA = methyl methacrylate, GMA = glycidyl methacrylate, subscript LC indicates functionalization by PFDT

^bFrom Zhao et al.⁵²

^cFrom Yoshimura et al.⁴⁹

^dCalculated using a triblock terpolymer (see Chapter 2)

^eCalculated using a diblock copolymer

As expected, the functionalization of the PGMA block had a significant effect on the χ of each monomer pair with χ_{AB} changing from 0.133 (S-GMA) to 0.204 (S-GMA_{LC}) and χ_{BC}

changing from 0.0268 (GMA-MMA) to 0.202 (GMA_{LC}-MMA). χ_{AC} (S-MMA) remains the same for all samples since it was not modified. Interestingly, comparing the results in Table 4-2 with those in Table 2-5, the χ parameters for S-GMA_{LC} and GMA_{LC}-MMA are nearly identical instead of being much higher for S-GMA as was the case in Chapter 2. A closer look at the individual entropic (β) and enthalpic (α) contributions shows that for S-GMA_{LC} the values are similar to those of S-GMA_F suggesting that the driving force for phase separation should be similar, whereas the enthalpic contribution of GMA_{LC}-MMA is much higher than that of PGMA_F-PMMA. This suggests that even at elevated temperatures where PMMA and PGMA_F would normally mix to some extent, the interfacial tension between PMMA and PGMA_{LC} remains large and so promotes phase separation.

4.3.3 Liquid Crystal behavior of PGMA_{LC}

Previous studies have shown that long fluorinated alkyl chains exhibit liquid crystalline behavior, particularly when the number of perfluorinated carbons is eight or larger.³⁰ To confirm the liquid crystalline behavior in our particular case, we synthesized a PGMA homopolymer and functionalized it with PFDT to yield a PGMA_{LC} homopolymer. Then, using DSC, POM and WAXD, the liquid crystalline behavior of the polymer was characterized. From the DSC curve heating cycle, a sharp endothermic peak was observed at around 79 °C, which may be the result of an isotropic transition, along with the T_g at around 117 °C (Figure 4-4a). Another sharp exothermic peak was observed in the cooling cycle at around 70 °C. Observation of the sample by POM (Figure 4-4b,c) revealed clear crystallization behavior starting at around 80 °C when cooling from 150 °C which is in good agreement with the DSC results and supports the conclusion that the fluoroalkyl chain forms liquid crystalline domains.

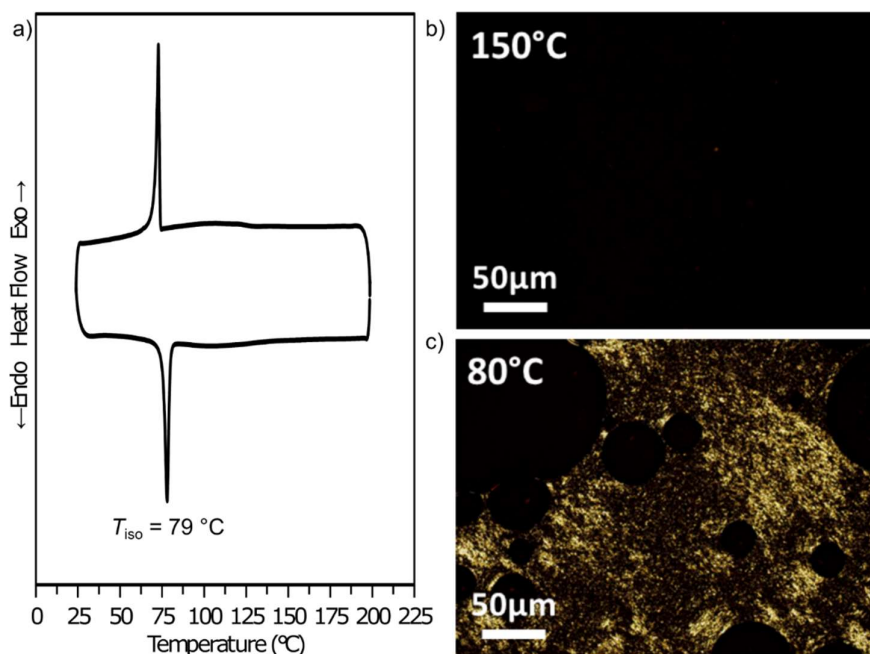


Figure 4-4. a) DSC measurement of PGMA_{LC} during the second cycle. b) POM images of PGMA_{LC} above and below T_{iso} determined by DSC.

Finally, to characterize the molecular spacing and ordering phase, we analyzed the sample using WAXD (Figure 4-5a). The spectrum shows three clear scattering peaks with the primary peak at $d = 3.4$ nm and higher ordering peaks consistent with a smectic stacking arrangement. Furthermore, a broad peak centered at $d = 0.5$ nm is consistent with hexagonal packing of the liquid crystalline molecules within the smectic layer structure and is consistent with previous studies of perfluorinated liquid crystals.³⁰ Comparing these results to a representative molecule simulated with Chem3D using MM2 force fields resulted in a head-to-tail length of about 1.6 nm which is approximately half the d spacing measured by WAXD (Figure 4-5a). Thus, we expect that the liquid crystalline domains are fully extended and packed head-to-head with little to no overlap resulting in smectic bilayers.

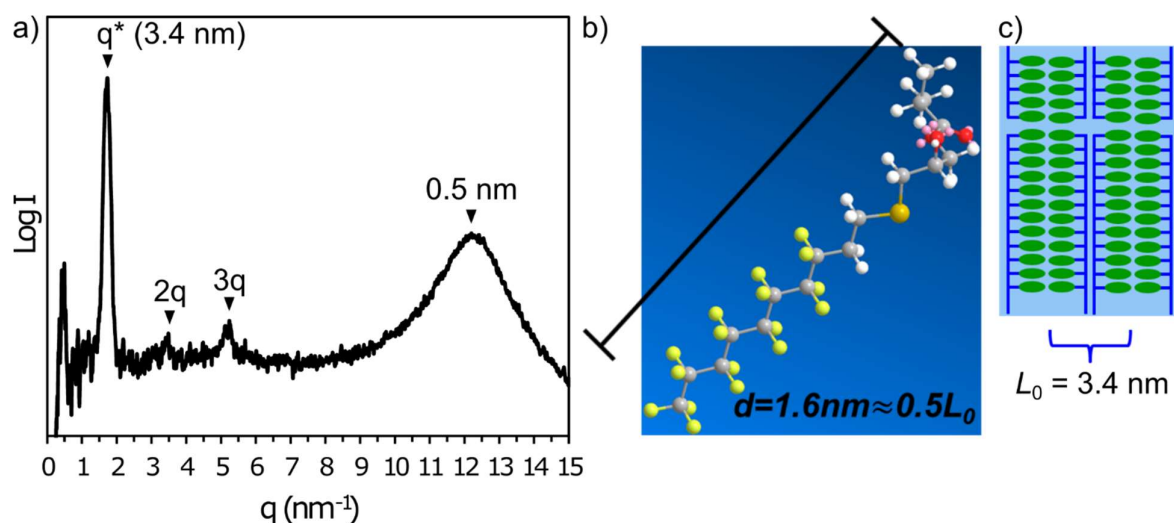


Figure 4-5. a) WAXD spectrum of PGMA_{LC}. b) MM2 simulation result of one PGMA_{LC} monomer in fully extended configuration. c) Illustration of potential molecular packing of PGMA_{LC}.

4.3.4 Bulk Morphology Characterization

Bulk samples for SAXS and TEM analysis were prepared by slow evaporation of solutions of the polymers in chloroform followed by thermal annealing under reduced pressure at 453 K for 24 h. 1D SAXS spectra were obtained by subtracting the background and azimuthally integrating the 2D scattering profiles taken at room temperature. The domain spacing (d) of each sample was determined by the position of the first-order scattering peak q^* ($d = 2\pi q^{*-1}$) and the morphologies by the ratio of q^* to the higher order peaks. The samples were also observed directly by TEM after microtoming and staining with RuO₄.

The self-assembly behavior of the unmodified triBCPs is shown below in Figure 4-6a where only PSGM21 self-assembles into lamellar (LAM) domains with $d = 19.3 \text{ nm}$ as determined previously in Chapter 2. After functionalizing with PFDT however, the SAXS profiles change significantly in all cases (Figure 4-6b). The observed scattering spectra of PSGM21_{LC} and PSGM18_{LC} showed several peaks with ratios consistent with tetragonal packing of cylinders

with $q^*:q$ of $1:\sqrt{2}:2:\sqrt{5}:\sqrt{8}:3:\sqrt{10}:\sqrt{13}:4$ and an additional broad peak at $q = 1.83 \text{ nm}^{-1}$ consistent with the liquid crystal ordering determined by WAXD. The position of the primary peak gives $d = 20.5 \text{ nm}$ for PSGM21_{LC}, similar to the domain spacing of the unmodified polymer, and $d = 18.8 \text{ nm}$ for PSGM18_{LC}. PSGM15_{LC} on the other hand, showed very broad peaks indicating poorly ordered structures, potentially hexagonally packed cylinders with peak ratios $1:\sqrt{3}:2$. However, the low- q shoulder at $0.85q^*$ does not match that of any known morphology.

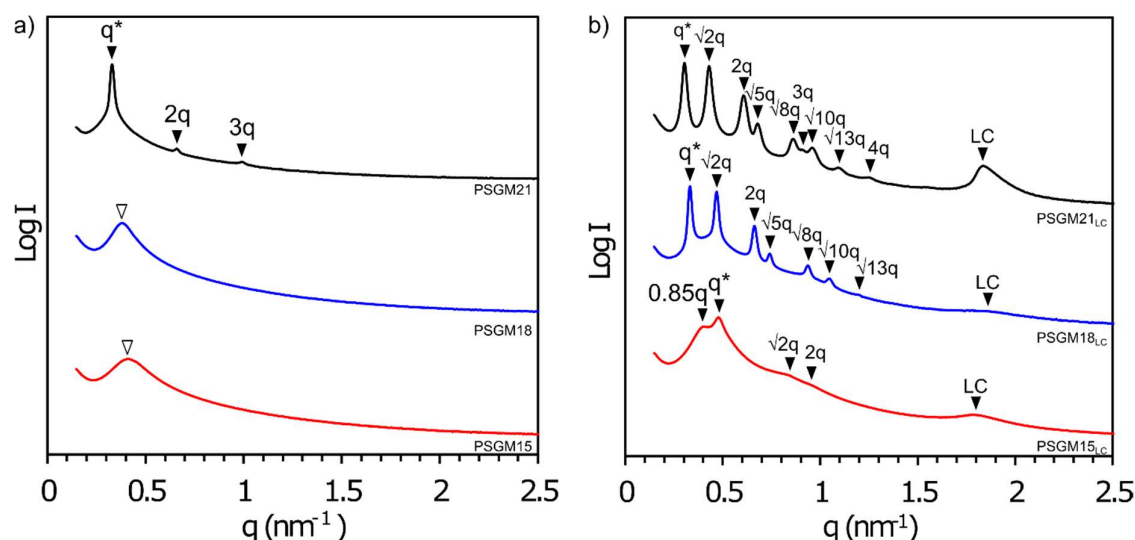


Figure 4-6. a) SAXS spectra of the PSGM triBCPs before functionalization and b) SAXS spectra of the PSGM_{LC} triBCPs after functionalization with PFDT. The SAXS spectra have been shifted vertically for clarity.

One interesting feature of the PSGM21_{LC} and PSGM18_{LC} SAXS spectra is the relative intensity of the first- and second-order scattering peaks which are nearly identical. In a typical sample exhibiting tetragonal packing, the peaks will decrease in intensity sharply after the first-order peak, as seen in Figure 2-7 and Figure 2-8 as well as in previous studies.^{14,31}

Inspection of the TEM images of PSGM21_{LC} and PSGM18_{LC} revealed that there appeared to be three distinct phases colored white, gray, and black due to the different degrees of staining

by RuO₄ (Figure 4-7). The TEM image of PSGM15_{LC} demonstrated that it is poorly ordered in what appears to be hexagonal cylinders (HEX), though there are large areas where contrast is low, likely due to weak phase separation.

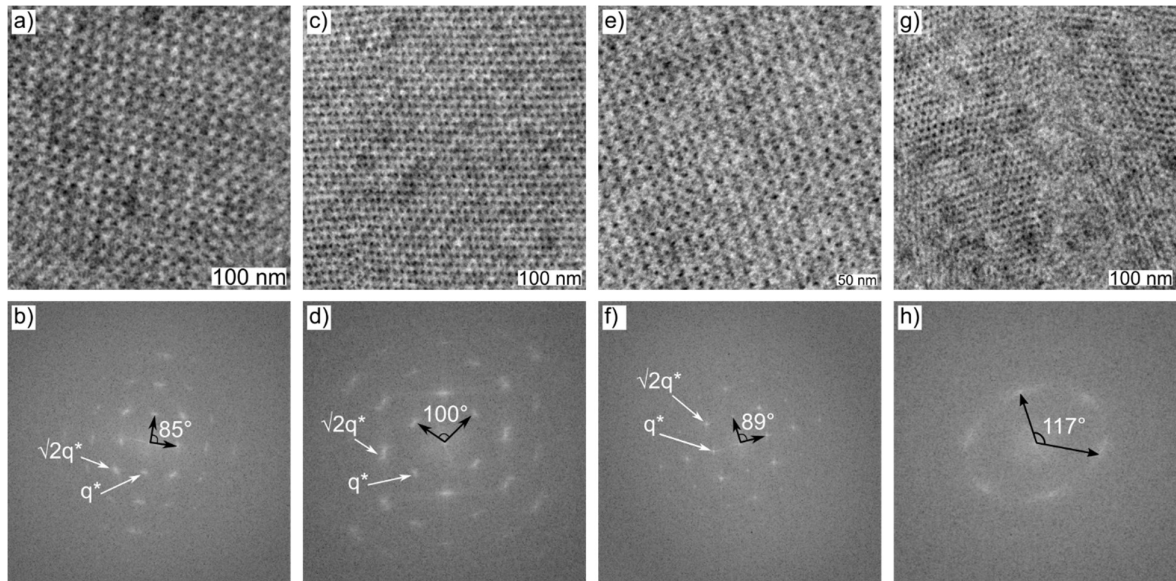


Figure 4-7 a) TEM image and b) Fourier transform of PSGM21_{LC}. c) TEM image and d) Fourier transform of PSGM21_{LC}. e) TEM image and f) Fourier transform of PSGM18_{LC}. g) TEM image and h) Fourier transform of PSGM21_{LC}.

As seen in Figure 4-7c for PSGM21_{LC}, depending on which area of the sample is imaged, the contrast between the 3 phases becomes weaker and they become more difficult to distinguish. Here, a tetragonal array of black dots can be seen which could account for the SAXS scattering peaks observed previously. However, by taking the FFT of the image we found that the domain spacing of the black dots is only about $d = 14$ nm which would not account for the q^* , $\sqrt{5}q$, $3q$, and $\sqrt{13}q$ peaks observed by SAXS. Instead, we propose that there are two offset tetragonal arrays of cylinders with one at $d = 20.5$ nm and the other at $d = 14.5$

nm. For PSGM18_{LC} the same observations hold true with $d = 18.8$ nm for the larger array and $d = 13.5$ nm for the smaller one.

In both cases, the PS is believed to form the black domains while the white and gray domains are formed by PMMA and PGMA_{LC} respectively. This speculation is primarily based on the RuO₄ staining behavior of each of the blocks. PS is known to be stained preferentially while PMMA is completely unstained resulting in dark and light domains respectively.³⁴ PGMA_{LC} on the other hand has one stainable hydroxyl group so appears gray. Based on the bulk characterization and the reasoning above, we proposed a unit cell (Figure 4-8) for PSGM21_{LC} and PSGM18_{LC} which differ only in their dimensions. While this structure has been reported previously by Hückstädt et al using miktoarm star polymers,³² and by Miyamori et al using linear ABAC tetrablock polymers,³³ to our knowledge it has never been reported for linear triblock terpolymers.

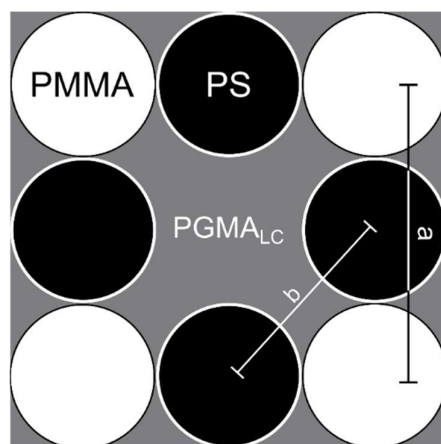


Figure 4-8. Proposed unit cell for PSGM21_{LC} ($a = 20.5$ nm, $b = 14.5$ nm) and PSGM18_{LC} ($a = 18.8$ nm, $b = 13.5$ nm).

Based on the unit cell shown above, we were able to calculate the expected SAXS peak positions and relative intensities of three different cases: Only one tetragonal array with $d =$

20.5 nm, only one with $d = 14.5$ nm, and a double offset tetragonal array combining both of these results assuming a cylinder radius of about 5 nm.^{31,35,36} The scattering intensity can be expressed as

$$I(q) \propto |F(q)|$$

where $F(q)$ is the structure factor

$$F(q) = \sum_j f_j e^{-iqr_j} \text{ and } f_j = \rho_{e,j} f'_j$$

where j is the number of a unique scattering element in the unit cell, r_j is the j th position of domain r , f'_j is the form factor, and $\rho_{e,j}$ is the electron density of the j th element.

The expression for the form factor of a cylinder of radius R and length L is

$$f'_j = \int_0^{\pi/2} \left\{ \left[\frac{2 J_1(qR \sin(\phi))}{qR \sin(\phi)} \right] \left[\frac{\sin\left(\frac{qL}{2} \cos \phi\right)}{\left(\frac{qL}{2}\right) \cos \phi} \right] \right\}^2 \sin \phi d\phi$$

where J_1 is the Bessel function of the first kind. ϕ is the angle between the cylinder's longitudinal axis and the scattering vector q , so the integral over ϕ results in an average of the form factor over all possible orientations. Using the proposed unit cell, for the triblock, the structure factor $F(q)$ becomes

$$F(q) = \sum f_{PS} e^{-iqr_{j,PS}} + \sum f_{PGMA} e^{-iqr_{j,PGMA}} + \sum f_{PMMA} e^{-iqr_{j,PMMA}}$$

If PGMA_{LC} is assumed to form the matrix, the above equation can be rewritten using the difference in electron densities relative to PGMA_{LC}.

$$\begin{aligned} F(q) = \rho_{e,PGMA} \left\{ f'_{PS} \sum e^{-iqr_{j,PS}} + f'_{PGMA} \sum e^{-iqr_{j,PGMA}} + f'_{PMMA} \sum e^{-iqr_{j,PMMA}} \right\} \\ + \Delta\rho_{e,PS-PGMA} f'_{PS} \sum e^{-iqr_{j,PGMA}} + \Delta\rho_{e,PGMA-PMMA} f'_{PMMA} \sum e^{-iqr_{j,PMMA}} \end{aligned}$$

where $\Delta\rho$ is the difference in electron density. The first term can be neglected since it describes the matrix with a uniform electron density $\rho_{e,PGMA}$. Converting the position r_j of each element to its Miller index (hkl) gives

$$F(hkl) = \Delta\rho_{e,PS-PGMA} f'_{PS} \sum e^{-2\pi i(x_{j,PS}h + y_{j,PS}k + z_{j,PS}l)} \\ + \Delta\rho_{e,PGMA-PMMA} f'_{PMMA} \sum e^{-2\pi i(x_{j,PMMA}h + y_{j,PMMA}k + z_{j,PMMA}l)}$$

where (x_j, y_j, z_j) are the coordinates of the j th element in the unit cell. Based on the unit cell given in Figure 4-8, the coordinates are as follows

$$(x_{j,PS}h + y_{j,PS}k + z_{j,PS}l) = \left(\frac{1}{2}h + 0k + 0l\right), \left(0h + \frac{1}{2}k + 0l\right)$$

and

$$(x_{j,PMMA}h + y_{j,PMMA}k + z_{j,PMMA}l) = (0h + 0k + 0l)$$

which when substituted into $F(hkl)$ gives

$$F(hkl) = \Delta\rho_{e,PS-PGMA} f'_{PS} \left(e^{-2\pi i \frac{1}{2}h} + e^{-2\pi i \frac{1}{2}k} \right) + \Delta\rho_{e,PGMA-PMMA} f'_{PMMA} (e^{-2\pi i(0)})$$

which becomes the following after applying Euler's identity

$$F(hkl) = \Delta\rho_{e,PS-PGMA} f'_{PS} ((-1)^h + (-1)^k) + \Delta\rho_{e,PGMA-PMMA} f'_{PMMA} (1)$$

The above equation can then be used to calculate the scattering peak position and relative intensity for each hkl using $\Delta\rho_{e,PS-PGMA} = 1.82 \times 10^{23} \text{ cm}^{-3}$ and $\Delta\rho_{e,PGMA-PMMA} = 1.39 \times 10^{23} \text{ cm}^{-3}$ and the results are shown below in Figure 4-9.

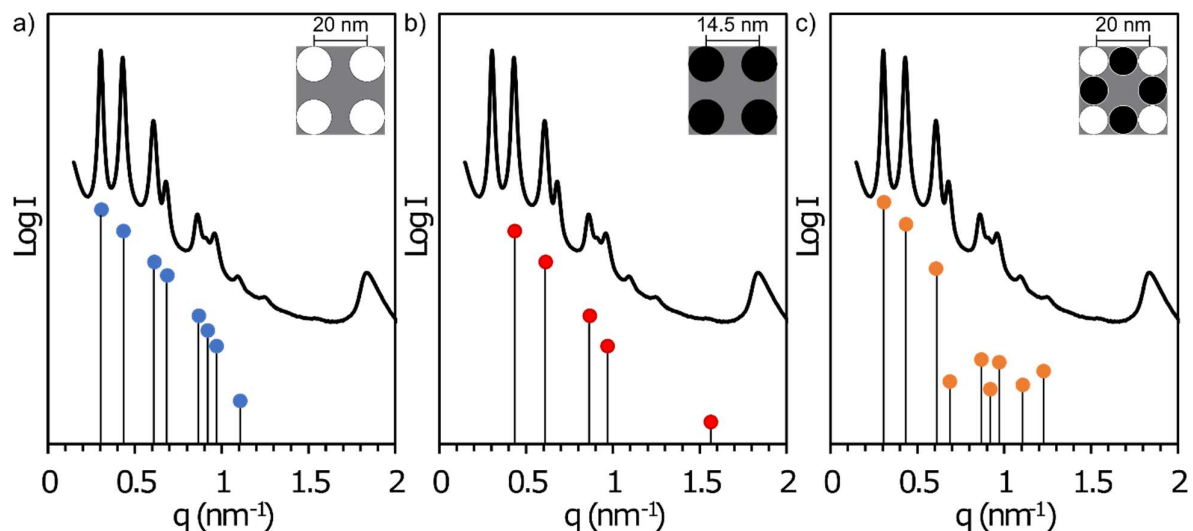


Figure 4-9. Comparison of PSGM21_{LC} SAXS spectrum to the simulated peaks for a) the $d = 20.5$ nm single tetragonal case (blue), b) the $d = 14.5$ nm single tetragonal case (red), and c) the $d = 20.5$ nm and $d = 14.5$ nm double tetragonal case (orange). Example unit cells are inset in each figure. Cylinders were assumed to be approximately 5 nm in diameter.

With only tetragonal cylinders at $d = 20.5$ nm, all the experimentally observed peaks are expected, however the relative intensities do not match, especially for the first and second scattering peaks since they decrease continuously as expected (Figure 4-9a). When only tetragonal cylinders at $d = 14.5$ nm are considered, neither the peak positions nor their relative intensities match the experimental spectrum (Figure 4-9b). Only in the case where both of these periodic structures are present in the arrangement suggested in Figure 4-8 do the peak positions and intensities match the experimental results (Figure 4-9c). Based on this analysis in addition to the apparent three-color staining seen in the TEM images, we believe that the self-assembled morphology shown by the unit cell in Figure 4-8 is the correct morphology.

4.4 Conclusion

Using a tailorable poly(styrene-*b*-glycidyl methacrylate-*b*-methyl methacrylate) linear triblock terpolymer containing a short, reactive middle block, we introduced a liquid crystalline mesogen to the middle of the polymer to investigate its effect on the self-assembly behavior. The perfluorinated liquid crystal mesogen not only increased $\chi_{\text{PS-PGMA}}$ and $\chi_{\text{PGMA-PMMA}}$, thereby augmenting the driving force for self-assembly, it also introduced a second length scale at which the polymers self-assembled. Using small-angle x-ray scattering and transmission electron microscopy, we analyzed the bulk morphology of the resultant modified triblock terpolymers and found that PSGM15_{LC} formed weakly-ordered periodic structures. On the other hand, PSGM18_{LC} and PSGM21_{LC} were found to have self-assembled into offset double tetragonal arrays of cylinders with d of 20.5 and 18.8 nm respectively which is the first report of this phase for linear ABC triblock copolymers.

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Chapter 5

Synthesis and Bulk Characteristics of Block Copolymers

Containing a Functional 1,1-Diphenylethylene Derivative

5.1 Introduction

Amidst the wide variety of diblock copolymers available, poly(styrene-*block*-methyl methacrylate) (PS-*b*-PMMA) is perhaps the most widely studied diblock copolymer because of the ease with which perpendicular structures can be formed during thermal annealing, a necessary aspect for nanopatterning applications.¹⁻³ However, PS-*b*-PMMA is limited by its low Flory-Huggins interaction parameter to feature sizes of about 10-11 nm resulting in a larger focus on high- χ BCPs for achieving ultrasmall patterns.⁴⁻⁸ Though these high- χ BCPs are able to achieve features less than 5 nm in the bulk, the large chemical difference between the blocks makes it difficult to achieve perpendicular orientation necessitating the use of solvent vapor annealing⁹⁻¹¹ or top-coats.^{12,13}

Recently however, several results have sought to expand the scope of usefulness of PS-*b*-PMMA by using it as a base polymer and modifying it through mid- or end-chain functionalization to decrease the smallest feature size while maintaining the beneficial properties of PS-*b*-PMMA.¹⁴ Woo et al. demonstrated that by introducing a strongly interacting small methacrylic acid block to conventional PS-*b*-PMMA, they were able to reduce the minimum feature size in the thin film regime to 17 nm.¹⁵ A study by Lee et al. investigated the effect of introducing a hydrogen bonding urea linker between PS and PMMA and found that the mixed region at the interface was significantly reduced.¹⁶ These reports along with theoretical work by Erukhimovich et al. have demonstrated that targeted functionalization of the block junction points have an outsized impact on the self-assembly behavior of diblock copolymers.¹⁷

However, many of the studies exploring this effect rely on a priori design of the block copolymer which involves guesswork and makes it difficult or impossible to compare results across samples. In Chapter 2, we introduced a newly designed poly(styrene-*b*-glycidyl methacrylate-*b*-methyl methacrylate) (PSGM) triblock terpolymer with a small, reactive middle block which allowed us to change the χ parameters between the middle and outer blocks at will. However, since the volume fraction of the middle block is significant, we expect that this would have a negative impact on self-assembly in the thin film regime by making it difficult to achieve perpendicular orientation.

Here we present another route towards tuning the self-assembly behavior of PS-*b*-PMMA by synthesizing several functional 1,1-diphenylethylene (DPE) derivatives and introducing exactly one DPE molecule to the block junction point via living anionic polymerization followed by post-polymerization functionalization. Therefore, in this chapter we are investigating the limiting case for triblocks where the degree of polymerization of the middle, reactive block goes to one. In doing so, we aim to investigate the effect of introducing strongly dissimilar molecules to the block interface on the self-assembled morphology in the bulk and particularly in the thin film regime. The method discussed herein has the distinct advantages of being able to compare the effect of the functionalization before and after as well as across different samples that are derived from the same functional parent polymer.

5.2 Experimental Section

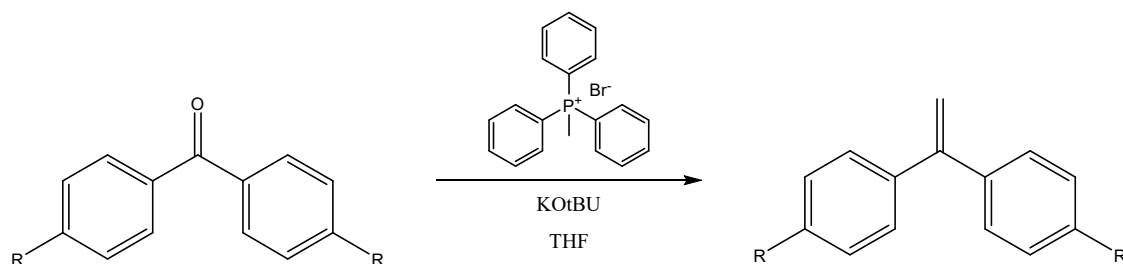
5.2.1 Reagents

Lithium chloride (LiCl) was purchased from Kanto Chemical Co. and dried by heating under reduced pressure immediately before use. Styrene, methyl methacrylate (MMA), and 2-hydroxyethyl methacrylate (HEMA) were purchased from Tokyo Chemical Industry. They were first distilled over calcium hydride (CaH_2) under reduced pressure and then distilled a second time over di-*n*-butylmagnesium for styrene, and trioctylaluminum for HEMA and MMA. Azobisisobutyronitrile (AIBN) was purchased from Tokyo Chemical Industry and recrystallized from methanol before use. All other reagents and solvents were purchased from Kanto Chemical Co. Inc, Tokyo Chemical Industry or Sigma-Aldrich and used as received.

5.2.2 Synthesis of 1,1-Diphenylethylene Derivatives via the Wittig Reaction

A general procedure for the synthesis of functional DPE derivatives starting from benzophenone (BP) precursors via the Wittig reaction is given here using 4-bromobenzophenone (BP-Br) as an example. Under an inert atmosphere, methyltriphenylphosphonium bromide (37.71 g, 106 mmol), 100.0 ml of THF, and potassium *tert*-butoxide (15.36 g, 137 mmol) were added to a round-bottom flask fitted with a reflux condenser and an addition funnel. The solution was bright yellow, indicating the ylide has formed. The flask was then cooled in an ice bath, followed by the slow addition of 4-bromobenzophenone (25.14 g, 96.3 mmol) dissolved in 55 ml of THF. The solution was stirred at 0 °C for one hour then allowed to warm to room temperature before continuing to stir overnight. The reaction was quenched by adding methanol, filtered to remove any precipitated triphenylphosphine oxide and the solvent was removed under reduced pressure. After dissolving in diethyl ether, the solution was washed with 1 M ammonium chloride solution followed by brine. The collected organic layer was dried over magnesium sulfate before being filtered. The solvent was removed under reduced pressure to obtain an off-white oil as crude

product. The crude product was purified using silica gel chromatography with hexane as the eluent. The title compound (DPE-Br) was obtained as a colorless oil (15.22 g, 61% yield) ^1H NMR (400 MHz, chloroform-*d*, δ , ppm): 7.47 (2H, d, Br-*o*-aromatic), 7.34 (5H, br, aromatic), 7.22 (2H, d, Br-*p*-aromatic), 5.49 (1H, d, C=CH), 5.47 (1H, d, C=CH).

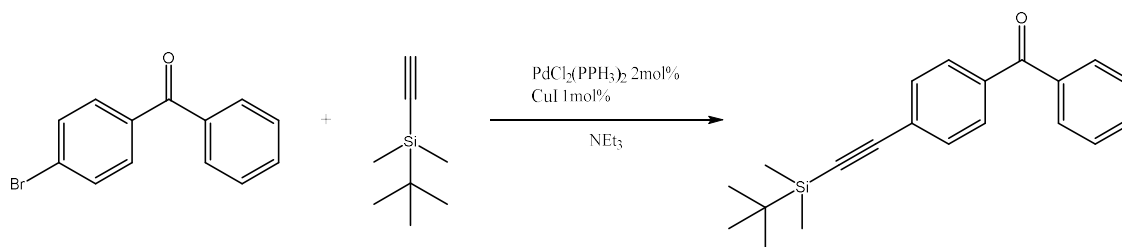


Scheme 5-1. General reaction scheme for the synthesis of DPE derivatives via the Wittig reaction.

5.2.3 Synthesis of (*tert*-Butyldimethylsilyl)acetylene Derivatives

tert-Butyldimethylsilyl (TBDMS) protected ethynyl benzophenone derivatives with one (BP-yneTBDMS) or two (BP-2yneTBDMS) were synthesized via the Sonogashira coupling reaction. An example of the synthesis of BP-yneTBDMS is given here. Copper(I) iodide (22 mg, 0.12 mmol), bis(triphenylphosphine)palladium chloride ($\text{PdCl}_2(\text{PPh}_3)_2$) (146 mg, 0.21 mmol), triethylamine (40.0 ml, 287 mmol), and 4-bromobenzophenone (BP-Br) (2.633 g, 101 mmol) were added to a round bottom flask equipped with a condenser and an addition funnel under an inert gas atmosphere. (*tert*-Butyldimethylsilyl)acetylene (yneTBDMS) (1.690 g, 12.0 mmol) was then slowly added turning the solution from yellow to orange. The reaction mixture was stirred overnight at room temperature followed by removal of the solvent under reduced pressure. The residue was extracted with diethyl ether, washed with water and brine, dried over magnesium sulfate and filtered. The solvent was removed under reduced pressure to yield the crude product as brown solid. The crude product was then purified by silica gel

chromatography using hexane: ethyl acetate (20:1) as the eluent to yield the product as an off-white solid (3.23 g, >95% yield). ^1H NMR (400 MHz, chloroform-*d*, δ , ppm): 7.75 (2H, t, *o*-aromatic), 7.56 (2H, t, *m*-aromatic), 7.47 (1H, t, *p*-aromatic), 1.00 (9H, s, Si-C-(CH₃)₃), 0.19 (6H, s, Si-(CH₂)₂).

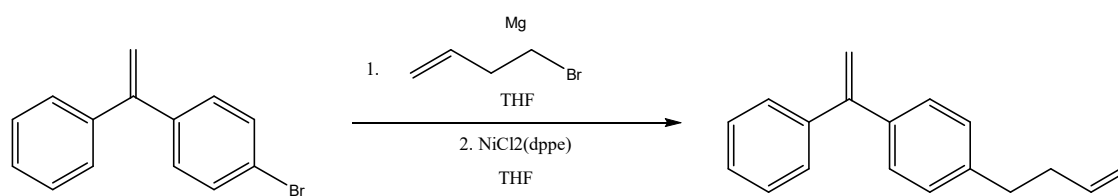


Scheme 5-2. Example synthesis of a (tert-Butyldimethylsilyl)acetylene DPE derivative using the Sonogashira coupling reaction.

5.2.4 Synthesis of 1-(3-Butenyl)-4-(1-phenylvinyl)benzene

1-(3-butenyl)-4-(1-phenylvinyl)benzene (DPE-C4) was synthesized via the Kumada Coupling reaction. Magnesium shavings (0.64 g, 26 mmol) was added to a round bottom flask equipped with a reflux condenser and an addition funnel under an inert gas atmosphere. Diethyl ether (7.5 ml) was then added to make a suspension followed by the slow addition of 4-bromo-1-butene (Br-C4) (3.37 g, 25 mmol) in 7.5 ml of diethyl ether. During addition, the solution began to boil as the Grignard reagent was formed. After complete addition, the solution was stirred for one hour. DPE-Br (2.59 g, 10 mmol) and dichloro(1,2-bis(diphenylphosphino)ethane)nickel (NiCl₂(dppe)) (0.13 g, 0.25 mmol) were added to a separate round-bottom flask equipped with a reflux condenser and an addition funnel under an inert gas atmosphere. The Grignard reagent solution was transferred to the second addition funnel via cannula and slowly added to the DPE-Br solution at 0 °C, turning the solution from cloudy red to clear brown. The reaction was then allowed to continue at room temperature

overnight after which it was quenched by the slow addition of dilute hydrochloric acid. The reaction solution was then extracted with fresh diethyl ether, washed with 1 M ammonium chloride and brine before being dried over magnesium sulfate and filtered. The organic solvent was removed under reduced pressure to yield the crude product as an off-white oil. The crude product was purified by silica gel chromatography using hexane as the eluent. The title compound was recovered as a colorless oil (1.14 g, 49% yield). ^1H NMR (400 MHz, chloroform-*d*, δ , ppm): 7.36 (5H, br, aromatic), 7.23 (2H, d, C4-*p*-aromatic), 7.18 (2H, d, C4-*o*-aromatic), 5.90 (1H, m, $\text{CH}=\text{CH}_2$), 5.45 (2H, dd, Ph-C(=CH)-Ph), 5.05 (2H, dd, $-\text{CH}=\text{CH}_2$), 2.75 (2H, t, phenyl- CH_2-), 2.42 (2H, q, $-\text{CH}_2-\text{CH}_2-\text{CH}=\text{}$).

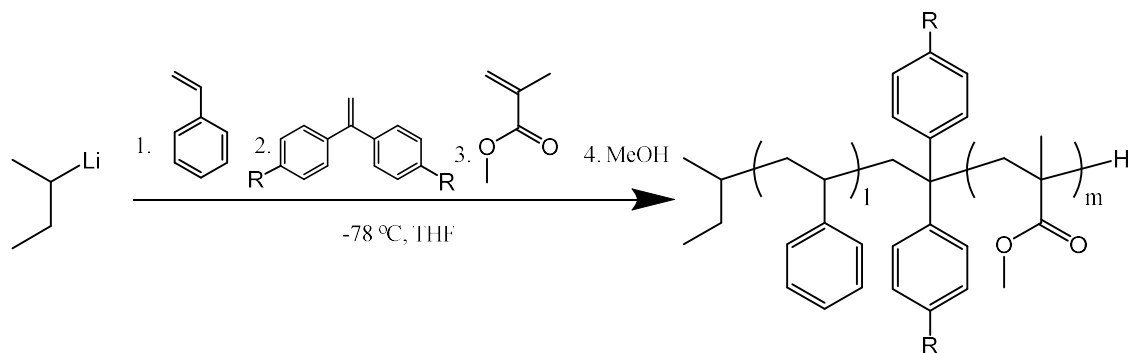


Scheme 5-3. Synthesis of DPE-C4 via nickel-catalyzed Kumada coupling.

5.2.5 Synthesis of PS-*b*-PMMA Containing Functional DPE Derivatives via Anionic Polymerization

To an oven-dried flask under argon gas were added LiCl (9.7 mg, 0.215 mmol) and 25 ml of THF. The flask was cooled to 195 K and *sec*-BuLi (0.99 M in hexanes) was added until a yellow color remained indicating the endpoint of impurity titration. The flask was removed from the cold bath and allowed to slowly warm to room temperature at which point the yellow color disappeared. The flask was once again cooled to 195 K and *sec*-BuLi (43 μl , 0.043 mmol) was added followed immediately by styrene (1.10 ml, 9.60 mmol) resulting in an orange color and stirred for 30 min. A DPE derivative (0.150 ml, 0.165 mmol) was then added, changing the color to dark red, and stirred for 30 min. Finally, MMA (1.20 ml, 11.3 mmol) was added

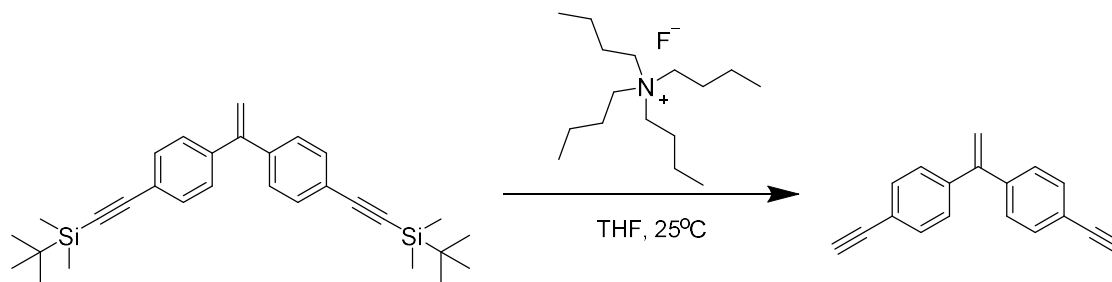
and stirred for 30 min before being terminated by the addition of degassed methanol. The polymer was precipitated in 500 ml of cold methanol and collected by filtration. The collected solid was dried under reduced pressure overnight at 313 K (1.86 g, 87% yield). ^1H NMR (400 MHz, chloroform- d , δ , ppm): 7.22-6.85 (br, m -, p -aromatic), 6.82-6.25 (br, o -aromatic), 3.59 (s, $-(\text{C}=\text{O})\text{O}-\text{CH}_3$), 2.20-1.67 (br, $-\text{CH}_2-\text{CH}-$, $-\text{CH}_2-\text{C}(\text{CH}_3)-$), 1.54-1.22 (br, $-\text{CH}_2-\text{CH}-$), 1.05-0.75 (br, $-\text{CH}_2-\text{C}(\text{CH}_3)-$).



Scheme 5-4. Synthesis of PS-*b*-PMMA containing functional DPE derivatives.

5.2.7 Deprotection of TBDMS-containing PS-*b*-PMMA

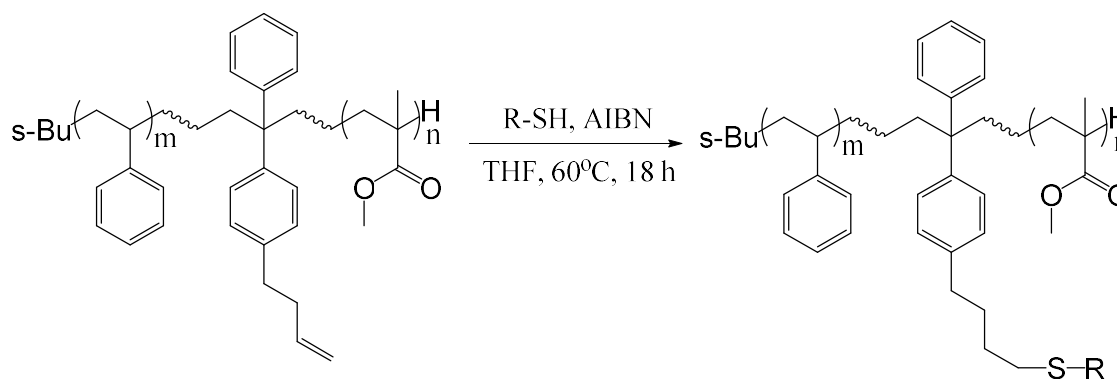
A general procedure for the deprotection of yneTBDMS-containing PS-*b*-PMMA is given here. PS-*b*-PMMA (1.313 g, 0.077 mmol) is dissolved in 15 ml of THF. Tetrabutylammonium fluoride (TBAF) (1 M in THF, 0.15 ml, 0.15 mmol) is then added slowly. The reaction mixture is stirred for one hour at room temperature before being precipitated in 100 ml of cold methanol and collected by filtration. The collected white solid was dried under reduced pressure overnight at 313 K (1.29 g, >95% yield).



Scheme 5-5. Deprotection of the TBDMS moiety using TBAF.

5.2.8 Post-Functionalization of PS-*b*-PMMA via the Thiol-Ene Reaction

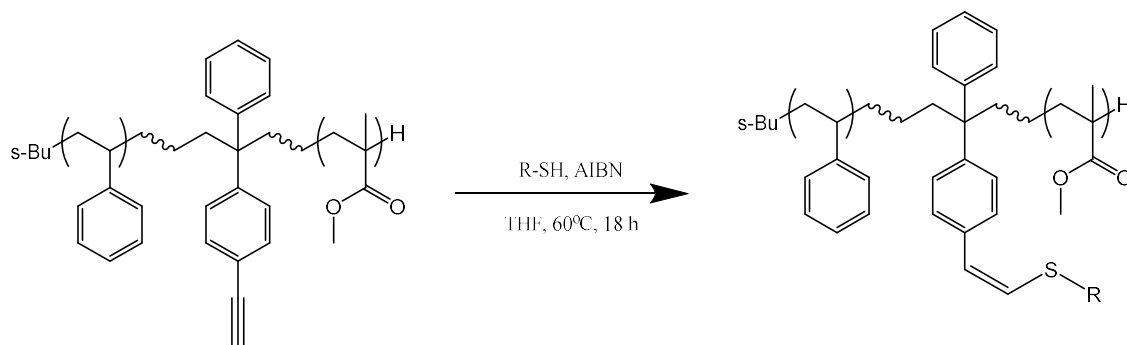
A general procedure for the post-polymerization functionalization of DPE-C4 containing PS-*b*-PMMA is given here. PS-*b*-PMMA (0.1924 g, 5.0 μmol), mercaptopropyl isobutyl POSS (POSS-SH) (0.0255 g, 32.3 μmol), and AIBN (0.001 g, 6.1 μmol) were dissolved in THF (1 ml) in a Schlenk tube. The reaction mixture was degassed by three cycles of freeze-pump-thaw using liquid nitrogen to freeze the solution, exposing the flask to vacuum, resealing the flask and thawing the solution in a bath of methanol. After the third cycle, the tube was backfilled using nitrogen gas and heated to 60 $^{\circ}\text{C}$ to initiate the reaction. The reaction was allowed to proceed for 18 h then precipitated from cold methanol and filtered to collect the product. The collected white solid was dried under reduced pressure overnight at 313 K (0.160 g, 81% yield).



Scheme 5-6. Post-polymerization functionalization of PS-*b*-PMMA containing DPE-C4 using the thiol-ene reaction.

5.2.9 Post-Functionalization of PS-*b*-PMMA via the Thiol-Yne Reaction

A general procedure for the post-polymerization functionalization of DPE-yne or DPE-2yne containing PS-*b*-PMMA is given here. PS-*b*-PMMA (0.1392 g, 5.3 μmol), mercaptopropyl isobutyl POSS (POSS-SH) (0.0388 g, 43.5 μmol), and AIBN (0.001 g, 6.1 μmol) were dissolved in THF (1 ml) in a Schlenk tube. The reaction mixture was degassed by three cycles of freeze-pump-thaw using liquid nitrogen to freeze the solution, exposing the flask to vacuum, resealing the flask and thawing the solution in a bath of methanol. After the third cycle, the tube was backfilled using nitrogen gas and heated to 60 °C to initiate the reaction. The reaction was allowed to proceed for 18 h then precipitated from cold methanol and filtered to collect the product. The collected white solid was dried under reduced pressure overnight at 313 K (0.133 g, 92% yield).

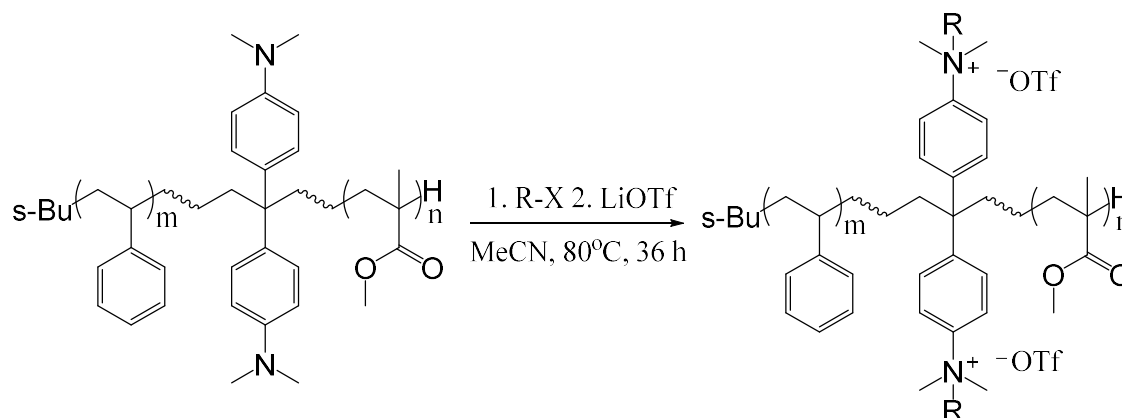


Scheme 5-7. Post-polymerization functionalization of PS-*b*-PMMA containing DPE-yne via the Thiol-Yne reaction.

5.2.10 Post-Functionalization of PS-*b*-PMMA by Amine Quaternization

A general procedure for the post-polymerization functionalization of DPE-2N containing PS-*b*-PMMA is given here. PS-*b*-PMMA (0.1369 g, 5.6 μmol) and methyl iodide (MeI) (0.0182 g, 128 μmol) were dissolved in acetonitrile (1 ml) in a Schlenk tube. The reaction mixture was degassed by three cycles of freeze-pump-thaw using liquid nitrogen to freeze the solution, exposing the flask to vacuum, resealing the flask and thawing the solution in a bath of methanol.

After the third cycle, the tube was backfilled using nitrogen gas and heated to 80 °C. The reaction was allowed to proceed for 18 h after which time lithium triflate (LiOTf) (0.0030 g, 20.2 μ mol) was added. The reaction was stirred for a further 18 h then precipitated from cold methanol and filtered to collect the product. The collected white solid was dried under reduced pressure overnight at 313 K (0.088 g, 64% yield).



Scheme 5-8. Post-polymerization functionalization of PS-*b*-PMMA containing DPE-2N by amine quaternization.

5.2.11 Poly(styrene-*r*-methyl methacrylate-*r*-2-hydroxyethyl methacrylate) via Free Radical Polymerization

Poly(styrene-*r*-methyl methacrylate-*r*-2-hydroxyethyl methacrylate) (PSMH) random copolymers were synthesized via free radical polymerization initiated thermally by AIBN. Styrene (1.77 ml, 15.5 mmol), MMA (2.43 ml, 22.8 mmol), HEMA (0.05 ml, 0.39 mmol), and toluene (8 ml) were added to a Schlenk tube and degassed by purging with N₂ for 15 min. AIBN (57.8 mg, 0.35 mmol) was then added followed by heating to 60 °C to initiate the reaction. The reaction was terminated after 12 h, precipitated in cold methanol, and collected by filtration. The collected solid was dried under reduced pressure overnight at 313 K (3.72 g, 93% yield). ¹H NMR (400 MHz, chloroform-*d*, δ , ppm): 7.22-6.85 (br, *m*-, *p*-aromatic), 6.82-6.25 (br, *o*-aromatic), 4.05 (s, -CH₂-OH), 3.74 (s, -(C=O)O-CH₂-), 3.59 (s, -(C=O)O-CH₃),

2.20-1.67 (br, $-\text{CH}_2\text{-CH-}$, $-\text{CH}_2\text{-C}(\text{CH}_3)\text{-}$), 1.54-1.22 (br, $-\text{CH}_2\text{-CH-}$), 1.05-0.75 (br, $-\text{CH}_2\text{-C}(\text{CH}_3)\text{-}$).

5.2.12 Preparation of Thin Film Samples

All thin film samples were prepared following this general procedure. Silicon wafers were cut into small ($1\text{-}2\text{ cm}^2$) sections using a diamond cutting tool, washed with water then cleaned using a piranha solution at $80\text{ }^\circ\text{C}$ for 60 minutes (**CAUTION! Piranha solution can cause explosions if prepared incorrectly or exposed to excess organic material**). The wafers were rinsed with deionized water, followed by acetone then methanol and dried under a flow of N_2 . PSMH random copolymers were then deposited on the wafers by spin-coating a 1 wt% solution in toluene at 5000 rpm for 30 s and baked at $180\text{ }^\circ\text{C}$ for 18 h. The wafers were then sonicated in toluene to remove ungrafted PSMH before spin-coating the block copolymer using 1 wt% solutions at 5000 rpm for 30 s. The BCP thin films were then baked at $250\text{ }^\circ\text{C}$ for 10 min after which they were quickly quenched to room temperature.

5.2.13 Characterization Methods

The ^1H nuclear magnetic resonance (NMR) spectra were recorded on a JEOL 400 MHz instrument using deuterated chloroform at ambient temperature. The number-average and weight-average molecular weights (M_n and M_w) were measured by size-exclusion chromatography (SEC) using a Shodex GPC-101 equipped with a refractive index detector and a LF-804 column (Showa Denko) with THF as the eluent at 313 K. Bulk samples were prepared by slow evaporation of chloroform solutions followed by thermal annealing at 453 K for 24 h. Bulk SAXS measurements were performed using a Bruker NanoSTAR (50 kV/ 50 mA) with a wavelength of $1.54\text{ \AA}$ and a sample-to-detector distance of 1.0 m equipped with a Vantec-500 detector. AFM images were obtained using a JPK Instruments NanoWizard Ultra Speed AFM in AC mode.

5.3 Results and Discussion

5.3.1 Synthesis of Functional 1,1-Diphenylethylene Derivatives

Four different 1,1-diphenylethylene derivatives were synthesized using the Wittig reaction starting from benzophenone precursors which are inexpensive and readily available. In this study, we selected 3 different reactive functional groups that could be used for post-polymerization functionalization of a BCP: a double bond for the thiol-ene reaction, a triple bond for the thiol-yne or copper-catalyzed azide-alkyne cycloaddition (CuAAC) “click” reaction, and a tertiary amine that can be quaternized by organohalide compounds.

The double bond containing derivative (DPE-C4) was synthesized in a two step process beginning with the Wittig reaction (Scheme 5-1) to convert the ketone group to a double bond, followed by a Kumada coupling reaction using $\text{NiCl}_2(\text{dppe})$ as a catalyst (Scheme 5-3). This two-step process had an overall yield of 30% but resulted in a very pure product as determined by ^1H NMR where the characteristic peaks of the phenylethylene protons can be clearly seen at 5.45 ppm and those of the butenyl group can be clearly seen at 5.91, 5.05, 2.75, and 2.42 ppm (Figure 5-1). The vinyl bond of the 3-butenyl moiety of DPE-C4 has been previously shown to be able to undergo anionic polymerization without any side-reactions.¹⁸

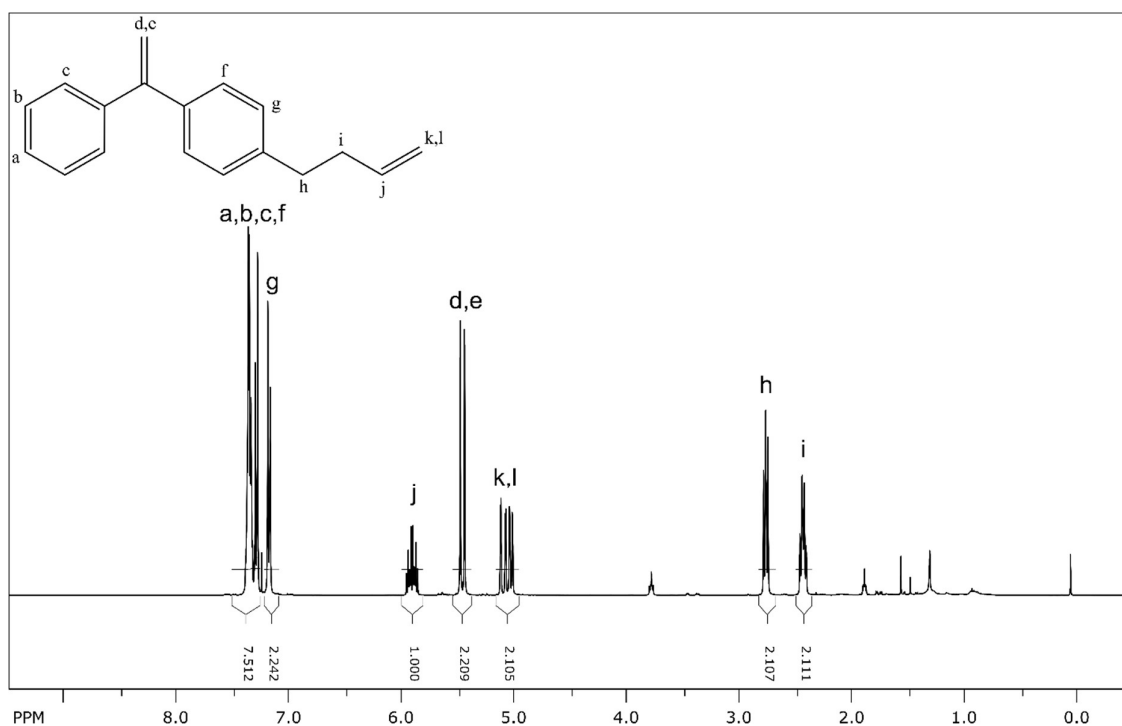


Figure 5-1. ^1H NMR spectra of DPE-C4

Because of the strict requirement of no acidic protons during anionic polymerization, TBDMS-protected acetylene was used to synthesize both the single alkyne derivative (DPE-yneTBDMS) and the double alkyne derivative (DPE-2yneTBDMS). This two-step reaction sequence consisted of a palladium-catalyzed Sonogashira reaction using (*tert*-butyldimethylsilyl)acetylene (Scheme 5-2) followed by the general Wittig reaction (Scheme 5-1). Similar to DPE-C4, the ^1H NMR spectra of DPE-yneTBDMS shows the phenylethylene protons at 5.49 ppm and those of the TBDMS group at 1.00 and 0.19 ppm (Figure 5-2). Likewise, the ^1H NMR spectrum of DPE-2yneTBDMS shows the phenylethylene protons at 5.47 ppm and those of the TBDMS groups at 1.00 ppm and 0.19 ppm (Figure 5-3).

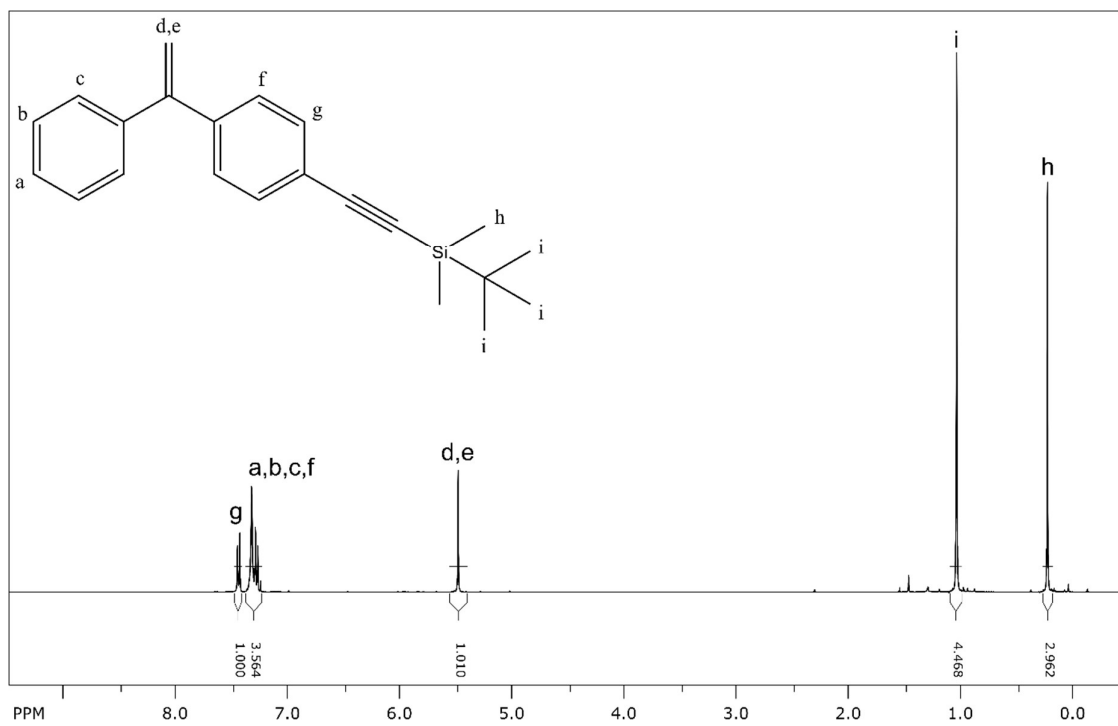


Figure 5-2. ^1H NMR spectra of DPE-yneTBDMS.

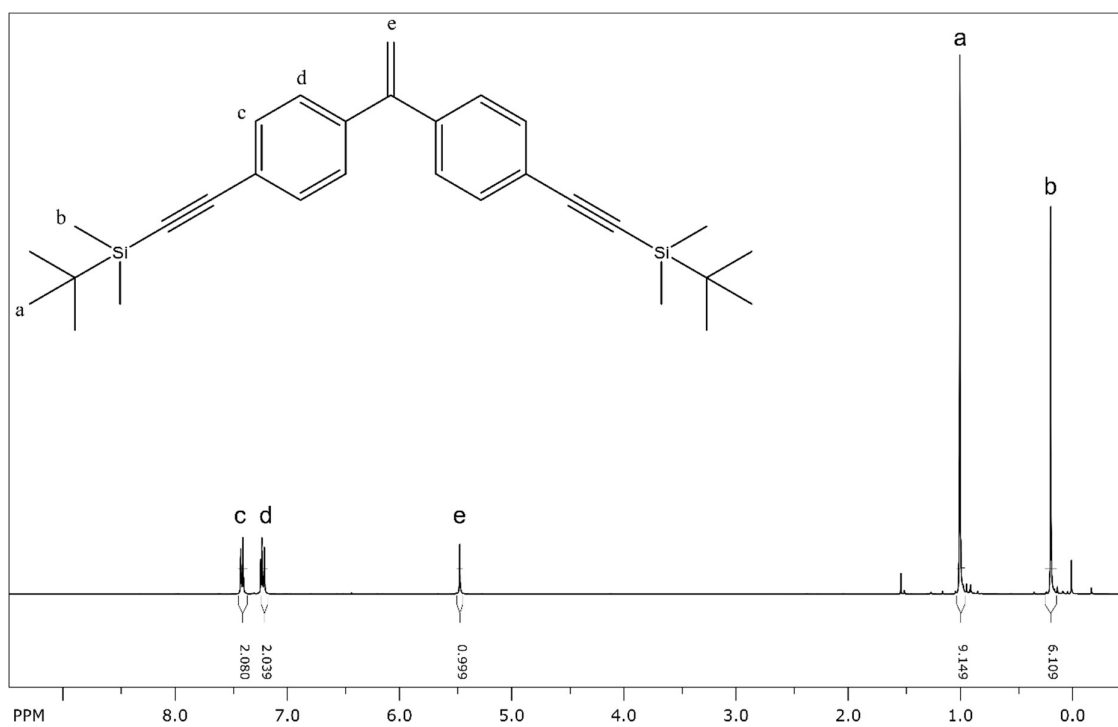


Figure 5-3. ^1H NMR spectra of DPE-2yneTBDMS.

1,1-bis(N,N-4-dimethylaminophenyl)ethylene (DPE-2N) on the other hand could be synthesized directly in a one-step process consisting solely of the Wittig reaction because it lacks any acidic protons. The ^1H NMR spectrum of DPE-2N shows the clear appearance of the vinyl peaks at 5.18 ppm along with a clear upfield shift of the aromatic peaks (Figure 5-4).

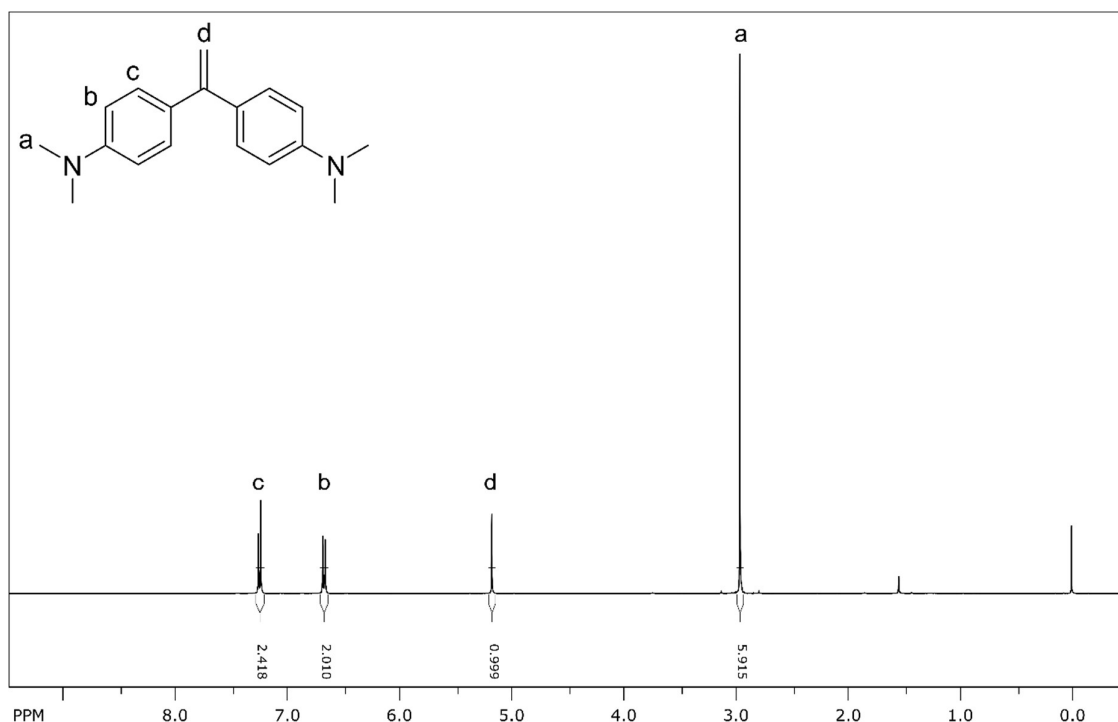


Figure 5-4. ^1H NMR spectra of DPE-2N.

5.3.2 Synthesis and Post-Functionalization of PS-*b*-PMMA Diblock Copolymers with a Functionalized DPE Derivative

While the four DPE derivatives were obtained with high purity, they were still unsuitable for direct use in anionic polymerization. To remove any trace impurities, they were titrated immediately before use using *sec*-BuLi under an inert argon atmosphere until a color persisted, indicating the presence of living anions. This active solution was then introduced directly into the polymerization reaction without quenching resulting in narrow dispersity BCPs.

Several PS-*b*-PMMA BCPs containing a single functionalized DPE molecule at the block junction was synthesized by living anionic polymerization in the presence of excess LiCl under an inert atmosphere.¹⁹ The number-average molecular weight and dispersity of the polymers were determined by SEC at 313 K using THF as the eluent and calibrated with PS standards. The volume fraction of each block was calculated by integrating the ¹H NMR peaks and using the densities of 1.05 and 1.18 g cm⁻³ for PS and PMMA respectively.²⁰ Because only one DPE molecule was incorporated into each BCP, we were unable to confirm its presence using ¹H NMR due small number of protons relative to the molecule as a whole. However, we can infer that each block copolymer will have exactly one DPE derivative incorporated precisely at the block junction because DPE does not homopolymerize and without a DPE-terminated living polymer, MMA will not be polymerized due to side-reactions.²¹ The BCPs investigated in this study had molecular weights ranging from 19.9 kg mol⁻¹ to 38.7 kg mol⁻¹ and had one of four different functional DPE derivatives located at the block junction point (Table 5-1). In all cases, the volume fractions of each block were controlled to be near symmetric (i.e. $f_{PS} \approx f_{PMMA} \approx 0.5$).

Table 5-1. Sample Characteristics of Parent PS-DPE-X-PMMA Diblock Copolymers

DPE Derivative	Sample Number	M_n^a (kg mol ⁻¹)	$\bar{D}^a$	f_{PS}^b	f_{PMMA}^b
DPE-C4	C4-20K	19.9	1.17	0.54	0.46
	C4-25K	24.9	1.13	0.58	0.42
	C4-29K	29.4	1.13	0.52	0.48
	C4-39K	38.7	1.11	0.56	0.44
DPE-yne	yne-26K	26.1	1.11	0.55	0.45
DPE-2yne	2yne-23K	23.1	1.12	0.56	0.44
DPE-2N	2N-24K	24.3	1.13	0.55	0.45

^aDetermined by SEC in THF using PS standards^bDetermined by ¹H NMR analysis^cDetermined by SAXS peak ratios^dDetermined by position of primary scattering peak

Post-functionalization of each of the PS-*b*-PMMA BCPs was carried out using the thiol-ene reaction, the thiol-yne reaction, and amine quaternization for DPE-C4, DPE-yne and -2yne, and DPE-2N respectively. Before the thiol-yne reaction was carried out however, the TBDMS group was quantitatively removed by TBAF in THF as confirmed by ¹H NMR. Because the reaction efficacy could not be measured directly by ¹H NMR due to the number of protons in the BCP relative to the DPE derivative, a model reaction was carried out using a low molecular weight PS homopolymer terminated with DPE-C4 ($M_n = 5.0$ kg mol⁻¹). Using the bulky and proton-rich 3-mercaptopropyl isobutyl POSS (POSS-SH) as a test compound, the thiol-ene reaction was performed using AIBN as the initiator at 60 °C. Analysis of the resultant functionalized homopolymer by SEC showed a clear increase in peak molecular weight to 5.7 kg mol⁻¹ while the ¹H NMR spectrum showed the disappearance of the vinyl peaks located at 5.8 and 5.0 ppm along with the appearance of the peaks at 1.0 and 0.6 ppm corresponding to the isobutyl alkyl protons (Figure 5-5). Based on these results, we assumed that the post-

functionalization of the high molecular weight BCPs would also proceed to near-quantitative conversion.

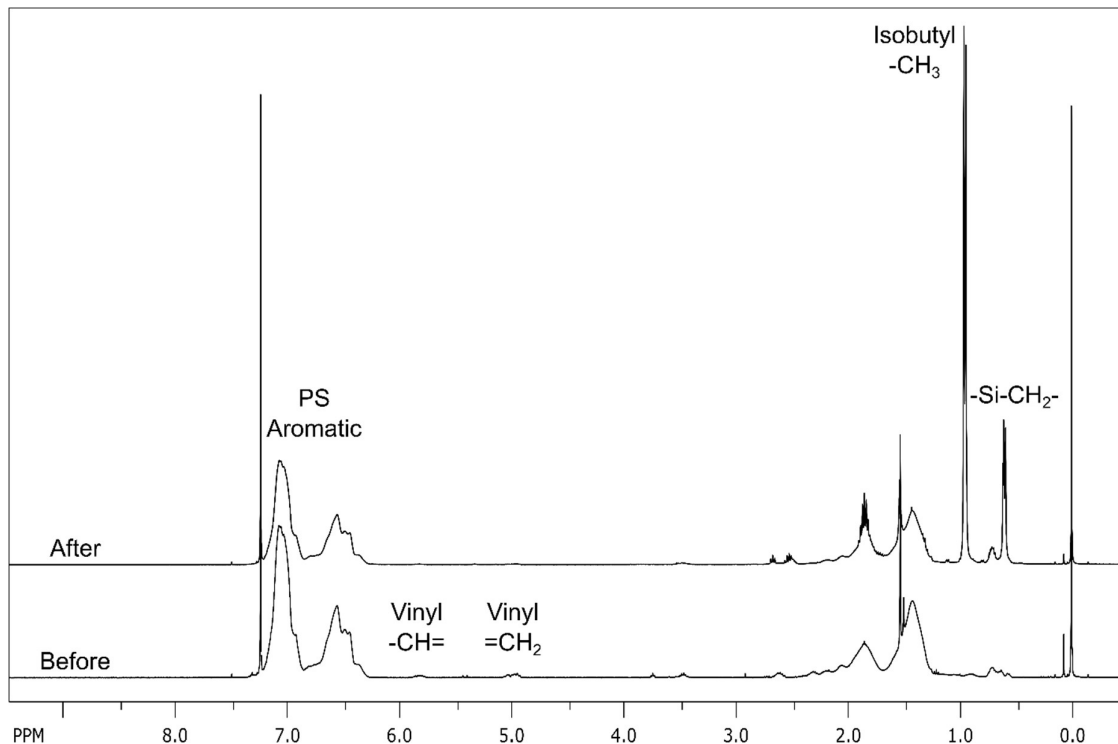
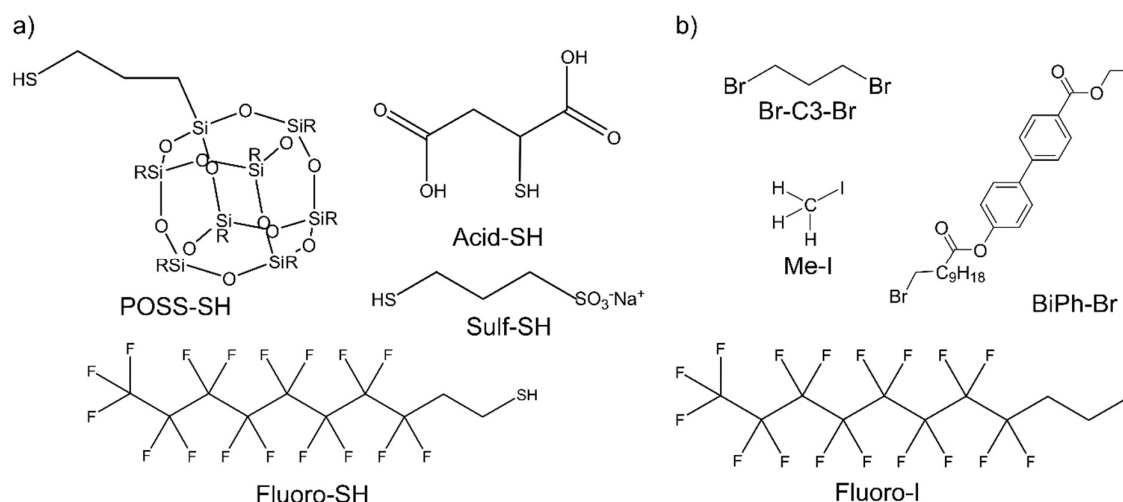


Figure 5-5. Comparison of ^1H NMR spectra of a low molecular weight PS homopolymer before and after functionalization with POSS-SH via the thiol-ene reaction.

For the DPE-C4, DPE-yne, and DPE-2yne BCPs, post-functionalization was performed using four different thiols that were chosen due to their strong dissimilarity to both PS and PMMA, which should in turn have the strongest effect on self-assembly behavior.^{17,22} The four thiols used in this study were the following: 3-mercaptopropyl isobutyl POSS (POSS-SH), 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol (Fluoro-SH), mercaptosuccinic acid (Acid-SH), and sodium 3-mercaptopropanesulfonate (Sulf-SH) (Scheme 5-9a). Using AIBN as a radical initiator, one, two, or four of each of the thiols could be added to DPE-C4, DPE-yne, and DPE-2yne respectively. For the DPE-2N BCPs, post-functionalization was performed using four

different organohalides: methyl iodide (Me-I), 1-iodo-1*H*,1*H*,2*H*,2*H*-perfluorodecane (Fluoro-I), ethyl 4'-((11-bromoundecanoyl)oxy)-[1,1'-biphenyl]-4-carboxylate (BiPh-Br), and 1,3-dibromopropane (Br-C3-Br) (Scheme 5-9b). The amine quaternization was performed by simple mixing of the DPE-2N containing BCP with the target halide at 80 °C for several hours. However, previous reports have shown that for small-molecule quaternary ions such as Me-I, the I⁻ anion should be exchanged with the bulky trifluoromethanesulfonate (OTf) anion to avoid de-quaternization when annealing samples at elevated temperatures.²³



Scheme 5-9. a) Thiols used in this study. b) Halides used in this study.

Thus, using one of a few functional DPE derivatives inserted precisely at the block junction, we were able to produce several well-characterized functionalizable BCPs by living anionic polymerization. The main advantages to this technique are twofold. The first is that it allows for the direct comparison between the pre- and post-functionalized BCPs because the molecular weight and volume fractions do not significantly change. The second is that it uses a general strategy for post-functionalization that permits any thiol or organohalide to be introduced which in turn permits the direct comparison of the effect of different functional groups.

5.3.3 Bulk Morphology Characterization

Bulk samples for SAXS were prepared by slow evaporation of solutions of the polymers in chloroform followed by thermal annealing under reduced pressure at 453 K for 24 h. 1D SAXS spectra were obtained by subtracting the background and azimuthally integrating the 2D scattering profiles taken at room temperature. The domain spacing (d) of each sample was determined by the position of the first-order scattering peak q^* ($d = 2\pi q^{*-1}$) and the morphologies by the ratio of q^* to the higher order peaks.

Unfunctionalized DPE-C4 BCPs C4-39K, C4-29K, and C4-25K were found to self-assemble into a lamellar (LAM) morphology with peak ratios of 1:2:3 while C4-20K was found to be disordered as indicated by the single broad scattering peak (Figure 5-6). As expected, the domain spacing of the self-assembled samples increases with N and varied from 21.1 nm for C4-25K to 29.0 nm for C4-39K (Table 5-2). These results are in broad agreement with previous studies which demonstrated that a molar mass of around 22 kg mol⁻¹ for symmetric PS-*b*-PMMA is the lower limit for self-assembly of symmetric BCPs.^{4,5}

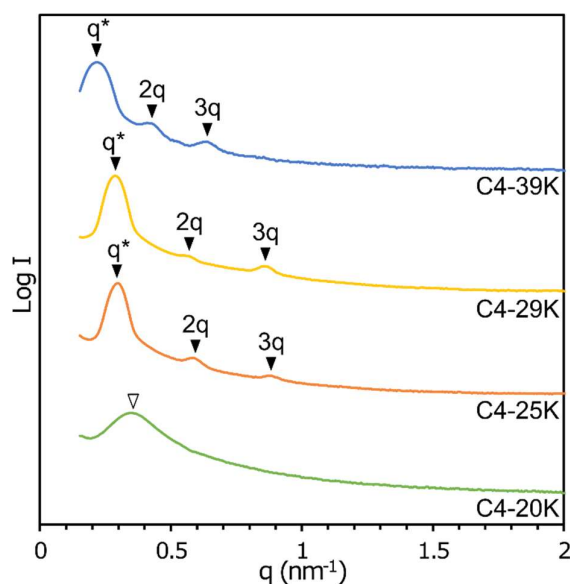


Figure 5-6. SAXS spectra of unmodified DPE-C4 BCPs. The spectra have been shifted vertically for clarity.

Table 5-2. Self-assembled morphology characteristics of DPE-C4 BCPs determined by SAXS.

Sample	M_n^a (kg mol ⁻¹)	d^b (nm)	Peak Ratios	Morphology ^c
C4-20K	19.9	-	None	Disordered
C4-25K	24.9	21.1	1:2:3	LAM
C4-29K	29.4	21.9	1:2:3	LAM
C4-39K	38.7	29.0	1:2:3:4	LAM

^aDetermined by SEC in THF using PS standards^bDetermined by position of primary scattering peak^cDetermined by SAXS peak ratios

Beginning with the largest molecular weight, after functionalization of the C4-39K BCP via the thiol-ene reaction, the self-assembled morphology remains unchanged with peak ratios of $q^*:q$ of 1:2:3 indicating a lamellar morphology (Figure 5-7a). However, the peaks have all shifted to higher q relative to the unmodified BCP which indicates a decrease in d . This is a counterintuitive result, since by introducing strongly dissimilar molecules, we expected χ_{eff} of the BCP to increase which in turn should increase d because it scales as $d \propto \chi^{1/6} N^{2/3}$ in the strong segregation regime.^{24,25} Since the opposite effect was observed, there must therefore be another mechanism in action.

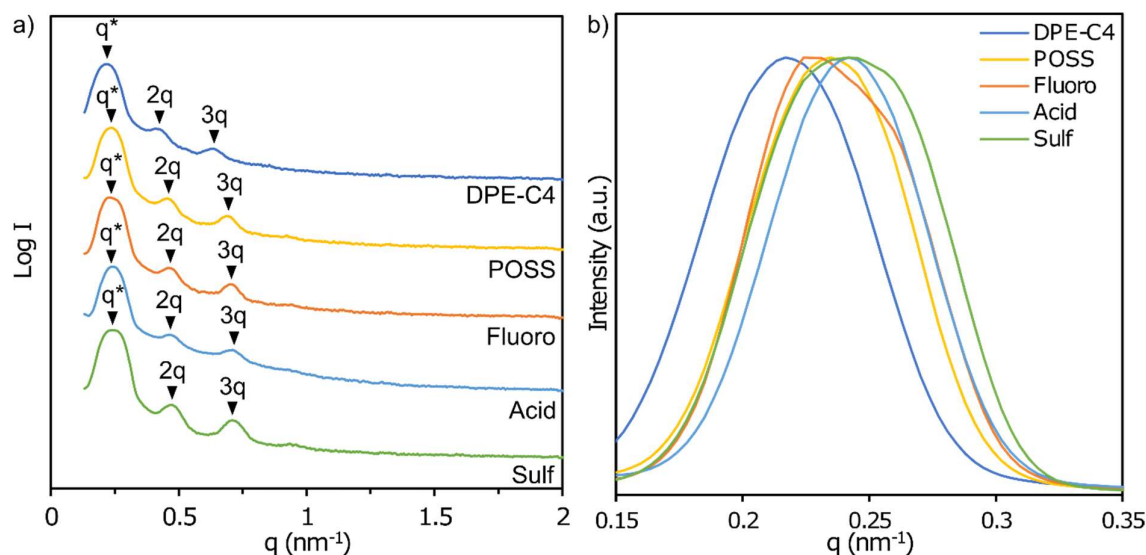


Figure 5-7. a) SAXS spectra of C4-39K BCPs after functionalization via the thiol-ene reaction. The spectra have been shifted vertically for clarity. b) Enlarged view of the region near the first order peak.

Upon closer inspection of the primary peak positions (Figure 5-7b), it is clear that the largest change was seen in the samples modified with Sulf-SH and Acid-SH where d had shrunk to 26.0 nm (Table 5-3). Both thiols possess some type of self-interaction in the form of ionic interactions for Sulf-SH and hydrogen bonding for Acid-SH which may have a strong effect on the interface between the PS and PMMA domains. A previous study by Lee et al. showed that PS-*b*-PMMA has an interfacially mixed region around 5 nm wide, but by addition of a hydrogen bonding urethane unit at the interface, they were able to reduce this mixed region by about 25%.¹⁶ However, this was accompanied with an increase in d as a result of the increased χ_{eff} which does not match the phenomenon seen in this work.

Table 5-3. Self-assembled morphology characteristics of functionalized DPE-C4 BCPs determined by SAXS.

Sample	Domain spacing, d^a (nm)				
	DPE-C4	POSS	Fluoro	Acid	Sulf
C4-20K	-	-	-	-	-
C4-25K	21.0	20.9	21.3	20.9	21.1
C4-29K	21.8	22.2	21.8	22.1	22.1
C4-39K	29.0	26.8	27.6	26.0	26.0

^aDetermined by position of primary scattering peak

For the lower molecular weight C4 BCPs, C4-29K and C4-25K, the effect of the functionalization was much less clear, with some samples showing a small increase in d and others a small decrease in d but overall, the domain size can not be said to have changed significantly like the case of C4-39K (Figure 5-8, Table 5-3). This would seem to indicate a dependence of the effect seen here on molecular weight. Interestingly, the segregation strength of C4-25K, measured as the product of χN where $\chi = 0.0380$ at 453 K,⁵ is about 12 which is considered the upper limit for the weak segregation regime. In this regime, the domain spacing d scales as $N^{0.5}$ only, with no dependence on χ .^{25,26} Since the primary effect of the functionalization would be a change in χ with no significant change in N , the fact that the observed d for C4-25K does not change significantly is in agreement with the scaling law in the weak segregation regime. C4-29K, which has a χN of about 14 is only just outside of the limit, so it is reasonable to infer that changes in χ should still have only a small effect.

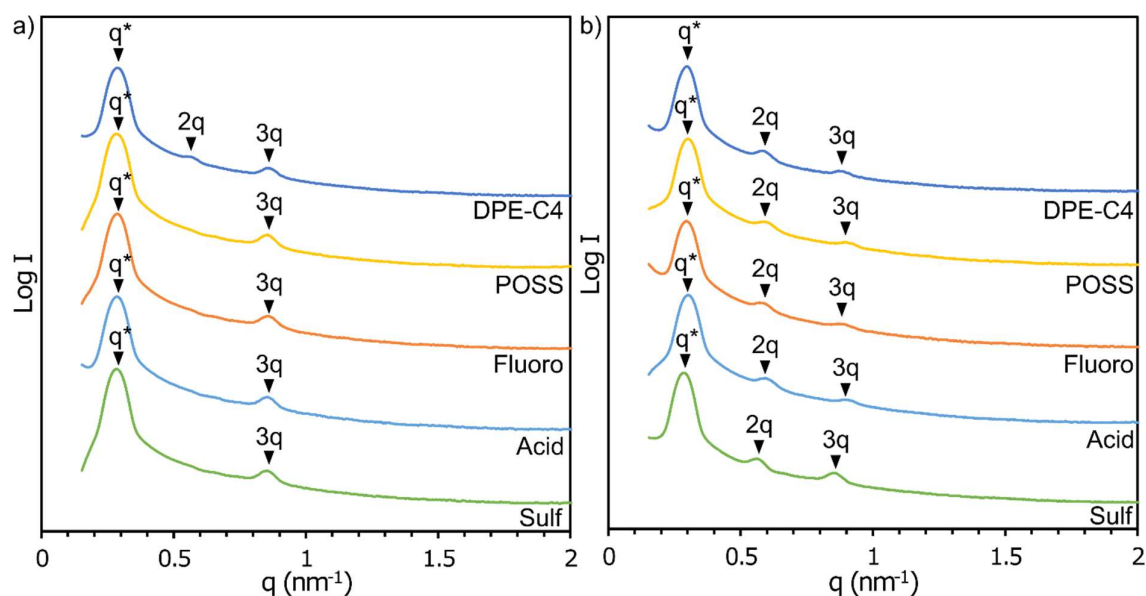


Figure 5-8. SAXS spectra of a) C4-29K BCPs and b) C4-25K BCPs after functionalization via the thiol-ene reaction. The spectra have been shifted vertically for clarity.

Finally, C4-20K was observed to be disordered for all functionalized BCPs. With a χN of only about 9.6, which is lower than the critical value of 10.5 necessary for self-assembly, this result was expected.

One polymer containing DPE-yne, yne-26K, and one polymer containing DPE-2yne, 2yne-23K were also synthesized with molecular weights of 26.1 and 23.1 kg mol⁻¹ respectively (Table 5-1). Instead of the double bond used in DPE-C4, these DPE derivatives contained a triple bond which can be functionalized via the thiol-yne reaction or the CuAAC “click” reaction. It should be noted here that while the product of the thiol-yne reaction is in fact a double bond which can normally be used again in the thiol-ene reaction, when immediately adjacent to an aromatic ring as is the case here, previous studies have shown that due to steric hindrance and energetic effects, this double bond will remain unreacted.²⁷ So in our case, DPE-yne should yield a monofunctional BCP and DPE-2yne should yield a difunctional BCP. The SAXS spectrum for yne-26K shows a lamellar morphology with peak ratios of 1:2:3 with $d =$

19.2 nm which is smaller than that of C4-25K despite the larger molecular weight. Similar to C4-25K, functionalization with each of the four thiols yields little change in d and no visible trend like that of C4-39K (Figure 5-9a). The SAXS spectrum for 2yne-23K on the other hand indicates that all samples are likely disordered or very weakly ordered. Introduction of the different thiols also had no effect in this case (Figure 5-9b).

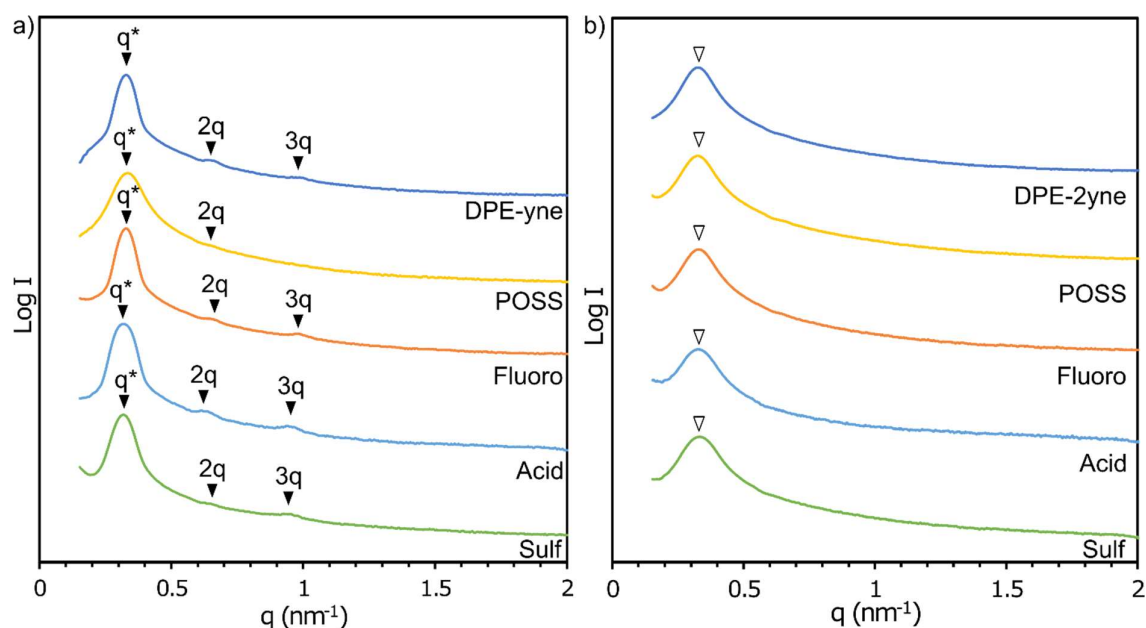


Figure 5-9. SAXS spectra of a) yne-26K BCPs and b) 2yne-23K BCPs after functionalization via the thiol-yne reaction. The spectra have been shifted vertically for clarity.

Finally, one polymer containing DPE-2N, 2N-24K was also synthesized and functionalized by quaternizing the tertiary amines present at the block junction. The unmodified polymer was found to have self-assembled into a lamellar morphology with peak ratios 1:2:3 and $d = 19.8$ nm (Figure 5-10a). Using the method of Luo et al.,²³ the low-molecular weight halide was exchanged with the heavy and bulky triflate anion to prevent de-quaternization during thermal annealing. However, the SAXS results of the Me-I, Fluoro-I, and BiPh-Br modified 2N-24K

show no change in d which suggests that the quaternization reaction was unsuccessful or that they had decomposed during thermal annealing.

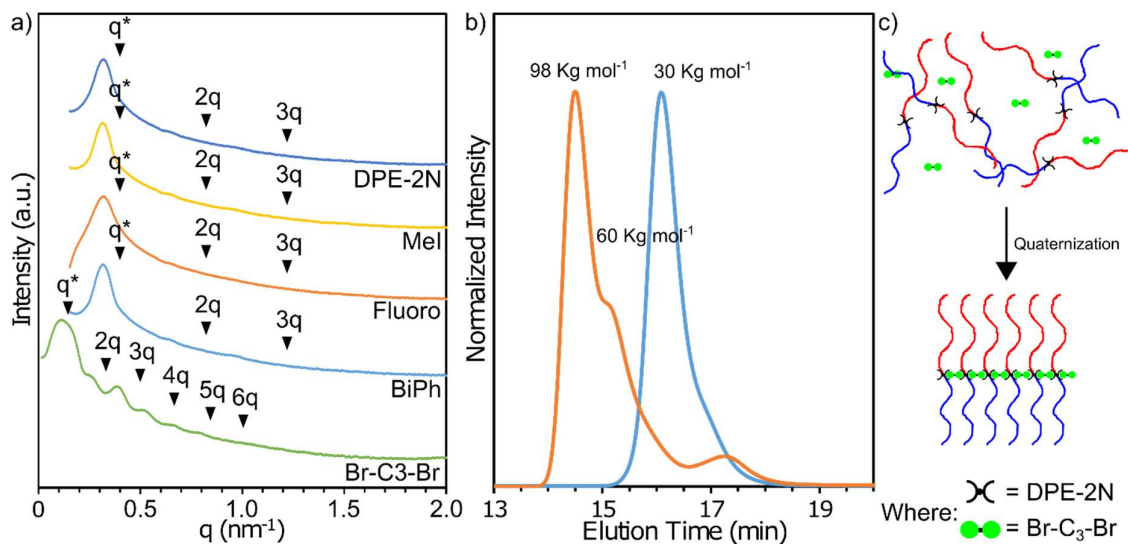


Figure 5-10. a) SAXS spectra of 2N-24K BCPs after functionalization via amine quaternization. The SAXS spectra have been shifted vertically for clarity. b) SEC trace of 2N-24K before (blue) and after (orange) reaction with Br-C3-Br. c) Illustration of grafting-through polymerization of 2N-24k with Br-C3-Br.

Quaternizing the difunctional DPE-2N with a difunctional organohalide, however, produced a very noticeable change in the self-assembled morphology. The primary scattering peak was seen to have shifted significantly to the left, indicating a large increase in d to 48.4 nm, more than double the unmodified 2N-24K d of 19.8 nm, while the morphology appears to have remained lamellar with peak ratios of 1:2:3:4:5:6. Analysis of this polymer by SEC demonstrated that the elution time had shifted significantly earlier, indicating an increase in M_n . While the SEC trace shows a clear shoulder on the low molecular weight side indicating a relatively uncontrolled reaction, the peak molecular weight (M_p) of the main peak is about triple that of 2N-24K while the M_p of the shoulder is about double that of 2N-24K (Figure 5-10b).

Thus, the resultant polymer should be a blend of the trimer and dimer of 2N-24K, effectively making it a blend of A_3B_3 and A_2B_2 miktoarm star polymers (Figure 5-10c). Previous experimental and theoretical studies have shown that a change in the chain topology from linear to star polymers causes a significant increase in the segregation strength of the polymer as seen here.^{28–30}

5.3.4 Thin-Film Morphology Characterization

Because one of the more useful properties of PS-*b*-PMMA is its ability to easily form structures perpendicular to the substrate, the self-assembly behavior of the C4-39K BCPs was also investigated in thin films to test whether functionalization of the block junction had any effect on this property. The thin films were deposited on chemically neutral substrates to induce perpendicular orientation of the lamellae^{31,32} with a film thickness approximately equal to d and annealed at 250 °C for 10 min to achieve thermodynamic equilibrium. Height and phase images of each of the five unetched samples were taken simultaneously by AFM.

Unmodified C4-39K was found to self-assemble into perpendicular lamellae with $d = 27.7$ nm, similar to the domain spacing determined for the bulk phase as expected. Functionalization with POSS-SH and Fluoro-SH decreased d to 27.3 and 26.7 nm respectively, while functionalization with Acid-SH and Sulf-SH decreased d yet further to 26.0 nm in both cases. The thin film results therefore follow the same trend as the bulk morphology, where the two thiols with some type of self-interaction cause the largest decrease in d , though not as pronounced as the bulk case.

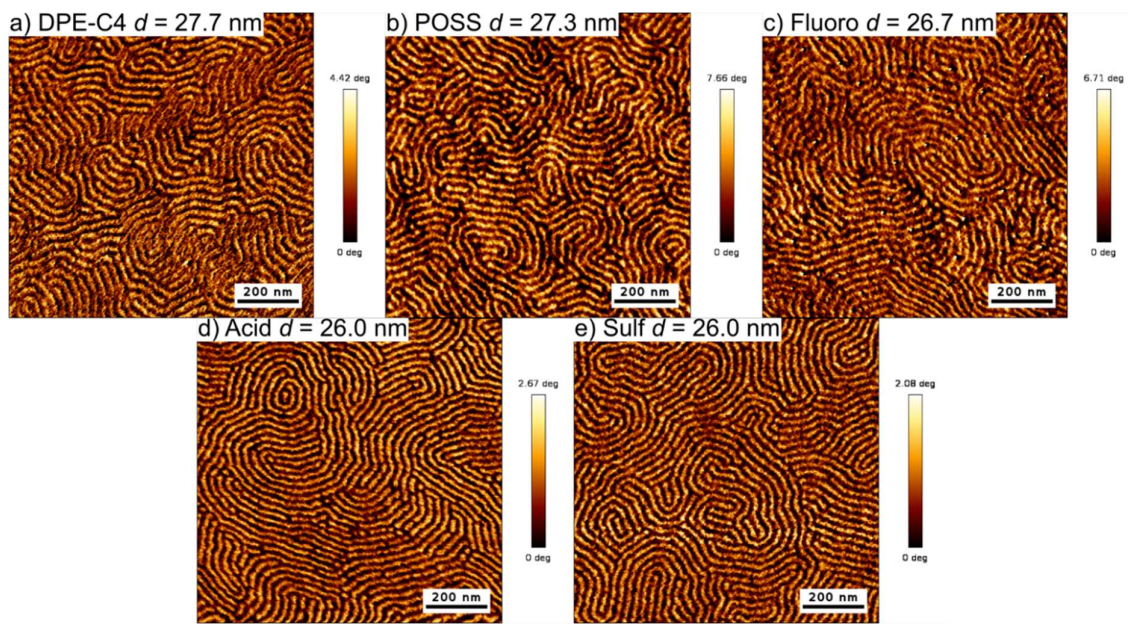


Figure 5-11. AFM phase image of unetched a) C4-39K, b) C4-39K-POSS, c) C4-39K-Fluoro, d) C4-39K-Acid, and e) C4-39K-Sulf.

Though the domain spacing changed as a result of the functionalization, the perpendicular orientation behavior was not significantly affected. As a result, this technique could prove useful for introduction of functional molecules at the domain interface in thin films.

5.4 Conclusion

By synthesizing several different functional 1,1-diphenylethylene derivatives and placing them exactly at the block junction point of PS-*b*-PMMA during anionic polymerization followed by post-polymerization functionalization using either the thiol-ene reaction, thiol-yne reaction, or amine quaternization, we were able to produce several well characterized polymers with a precisely known number of functional groups at the block interface. Thus, we were able to investigate the effect of functionalization on self-assembly when the middle block has a degree of polymerization of exactly one.

Though this led to some changes in the self-assembled morphology as characterized by small-angle x-ray scattering, in general the effect, if any, was too small to be measured. Only

C4-39K showed any noticeable change in d , especially when functionalized with either of the self-interacting small molecules. However, the mechanism driving this phenomenon is not yet understood. This trend was also observed in the thin film samples of C4-39K investigated by atomic force microscopy. The thin film results, however, are promising in that they demonstrated the functionalized PS-*b*-PMMA can still be orientated perpendicular to the substrate. Additionally, the difunctional DPE-2yne and DPE-2N derivatives allow for the grafting-through polymerization of the parent diblock copolymer to produce star polymers or block bottlebrush polymers.

5.5 References

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Chapter 6

General Conclusion

The self-assembly behavior of block copolymers is a widely investigated topic, particularly for the simplest case of diblock copolymers where the phase behavior is very well understood. However, as the number of blocks increases, so too does the number of experimental variables that must be understood and controlled to be able to control the self-assembled morphology and repeatability of results. The interaction parameters between each of the blocks are a particularly interesting area of study because they are habitually determined simply by the monomers chosen, so few studies have been performed that explore how changes in these parameters affect the self-assembly behavior of triblock polymers because few reactive monomer systems have been developed to date. While simulation using self-consistent field theory has proven to be an invaluable tool for the discovery of new phases and the exploration of the triblock copolymer phase diagram, it has customarily focused on how changes in volume fractions affect the morphology at set degrees of separation.

In this thesis, a new molecular design was presented that allows for the tailoring of the self-assembly behavior of block copolymers by functionalizing the interface block interface.

In Chapter 1, this thesis was placed in the context of the existing body of literature and the contents were summarized.

In Chapter 2, a newly designed poly(styrene-*b*-glycidyl methacrylate-*b*-methyl methacrylate) triblock terpolymer with a short, reactive middle block was presented. Using strongly dissimilar small molecules, the middle block was functionalized, thereby tuning the interaction parameters between the middle and outer blocks independently of the other parameters affecting self-assembly. It was shown that changes in the interaction parameters alone had a significant effect on the self-assembled morphology of the triblock terpolymer. A variety of

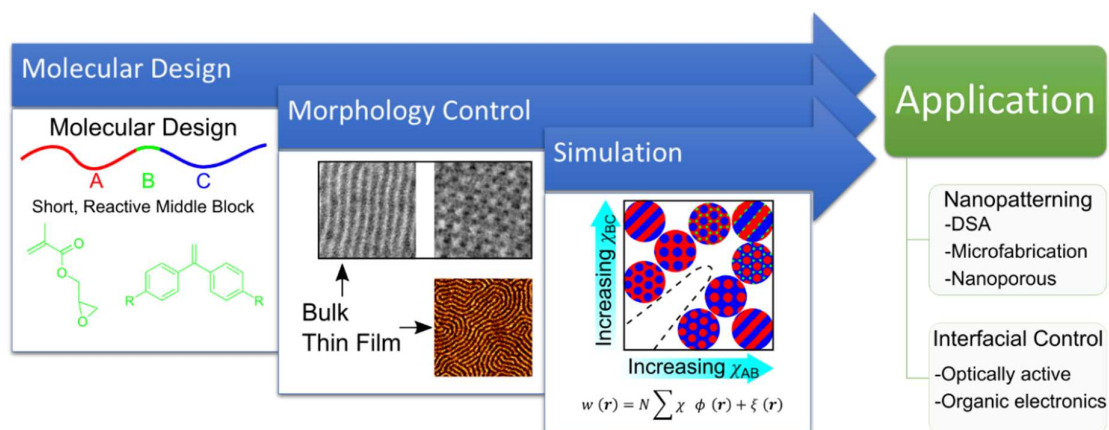
morphologies were obtained including lamellae and hexagonally packed cylinders as well as tetragonally packed cylinders.

In Chapter 3, self-consistent field theory was used to deepen the understanding of the effect changes in the interaction parameters has on self-assembly. The simulated morphologies were found to match closely to the experimental ones, so the approach was extended to over four hundred simulations to construct phase diagrams for the triblock terpolymers studied. In doing so, a new phase was discovered and it was shown that both the magnitude and the relationship between the three interaction parameters is crucial to understanding the self-assembly behavior of linear triblock terpolymers.

In Chapter 4, liquid-crystal side-chains were introduced to the reactive middle block of the previously studied triblock terpolymer and were found to have a substantial effect on the self-assembled morphology of the terpolymers. Careful analysis of the resultant morphologies found that two of the three terpolymers studied had self-assembled into an offset double-tetragonal array of cylinders with two different characteristic lengths scales while the third went from the disordered state to a weakly ordered morphology of hexagonally packed cylinders.

Finally, in Chapter 5 a series of poly(styrene-*block*-methyl methacrylate) diblock copolymers containing exactly one functional 1,1-diphenylethylene (DPE) derivative at the block interface were synthesized and functionalized using different strongly interacting molecules. This case is analogous to the limiting triblock terpolymer case as the reactive middle block goes to a degree of polymerization of 1. We demonstrated that in this regime, the effect of tailoring the block interface is minimal, with only one copolymer demonstrating any significant change. However, thin films of perpendicularly oriented lamellae were achieved for many of the functionalized block copolymers, meaning that this approach could find application in areas where it is necessary to place a target molecule precisely at the block junction.

Expanding upon the conclusions presented in this thesis, a more complete understanding of the effect of χ on self-assembly should be undertaken, particularly to try to investigate experimentally the new cylinder-and-sphere phase predicted by simulation. Because the two functional monomers studied at present were designed and chosen specifically for their ability to react with a wide range of molecules such as thiols and amines which are readily available, offering nearly limitless tunability of the self-assembly behavior. In the short term, this should involve extending the precise control of the triblock self-assembled morphologies studied here into the thin film regime where they can be used alongside directed self-assembly for applications ranging from nanopatterning and microelectronics to nanoporous materials. Challenges in this area would involve the balancing of the interfacial energies to achieve orientation control along with repeatability and minimization of defects.



The molecular design presented here is not only limited to the basic study of the self-assembly behavior of tri- and diblock copolymers. The polymers developed in this thesis could be used for applications where specific target molecules are desired precisely at the interface between two blocks. One such example is the introduction of photoluminescent molecules at the block interface to study the kinetics of self-assembly or to transmit light or information

across distances by combining polymer directed self-assembly with organic semiconductors. Combined with self-consistent field theory to model the expected phase behavior, this approach can act as a general platform for the study and development of self-assembled polymeric materials.

List of Publications and Presentations

Publications Related to this Dissertation

- (1) Modifying the Interaction Parameters of a Linear ABC Triblock Terpolymer by Functionalizing the Short Reactive Middle Block to Induce Morphological Change.
Kevin Wylie, Lei Dong, Alvin Chandra, Yuta Nabae, and Teruaki Hayakawa, *Macromolecules*, 2020, <https://doi.org/10.1021/acs.macromol.9b02567>
<https://pubs.acs.org/articlesonrequest/AOR-Mnsi6yNH7dJHREWWn3AB>
- (2) Altering the Self-Assembly of Poly(styrene-*block*-methyl methacrylate) by Introduction of Strongly Dissimilar Molecules at the Block Interface.
Kevin Wylie, Yuta Nabae, and Teruaki Hayakawa, *J. Photopolym. Sci. Technol.*, 2019, 32, (3) 395-400, <https://doi.org/10.2494/photopolymer.32.395>

List of Presentations

- (1) Enhanced Self-Assembly of Poly(Styrene-*block*-Methyl Methacrylate) by Introducing a Short Functional Middle Block.
Kevin Wylie, Lei Dong, Yuta Nabae, and Teruaki Hayakawa, 68th SPSJ Symposium on Macromolecules, Fukui, Japan, September 2019 (Oral).
- (2) Tailored microphase separation of poly(styrene)-*b*-poly(methyl methacrylate) by introducing a functional middle block.
Kevin Wylie, Lei Dong, Yuta Nabae, and Teruaki Hayakawa, Korea-Japan Joint Symposium on Polymer Science 2019, Seoul, South Korea, September 2019 (Poster).
- (3) Chemical Modification of Poly(Styrene-*block*-Methyl Methacrylate) for Increased Self-Assembly Performance in Thin Films.

Kevin Wylie, Lei Dong, Yuta Nabae, and Teruaki Hayakawa, The 36th International Conference of Photopolymer Science and Technology, Chiba, Japan, June 2019 (Oral).

- (4) Self-Assembly Behavior of Mid-Chain Functionalized Poly(Styrene)-b-Poly(Methyl Methacrylate) using a Monofunctional 1,1-Diphenylethylene Derivative.

Kevin Wylie, Yuta Nabae, and Teruaki Hayakawa, Japan-Korea Joint Symposium on Polymer Science 2018, Hokkaido, Japan, July 2018 (Poster).

- (5) Synthesis and Self-Assembly of In-Chain Functionalized Poly(Styrene)-b-Poly(Methyl Methacrylate) using 1,1-Diphenylethylene Derivatives.

Kevin Wylie, Yuta Nabae, and Teruaki Hayakawa, 67th SPSJ Annual Meeting, Aichi, Japan, May 2018 (Oral).

- (6) In-Chain Functionalized Poly(Styrene)-b-Poly(Methyl Methacrylate) using 1,1-Diphenylethylene Derivatives.

Kevin Wylie, Yuta Nabae, and Teruaki Hayakawa, Research Group on Precisely Designed Network Polymers, Tokyo, Japan, March 2018 (Poster).

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I would first like to convey my utmost thanks to Professor Teruaki Hayakawa for his guidance throughout my studies at the Tokyo Institute of Technology. I would also like to extend my sincere gratitude to Assistant Professor Yuta Nabae for all his suggestions and help. I would like to thank Associate Professor Tomoyasu Hirai of the Osaka Institute of Technology for his aid with the synchrotron radiation experiments which were performed at beamline BL40B2 of Spring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal no. 2019A1173). I would also like to thank Professor Hiroshi Jinnai of Tohoku University and the members of his group for their aid and expertise with the characterization of the liquid-crystalline polymer samples by transmission electron microscopy and discussion related to TEM analysis of block copolymers.

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Kevin Wylie

February 2020