Chapter 3

SELF-ASSEMBLY OF COIL-LIQUID CRYSTALLINE DIBLOCK COPOLYMERS IN A SOLVENT OF "SWITCHABLE" QUALITY: STRUCTURE AND INTERACTIONS MEASURED BY SANS AND RHEOMETRY

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Rafael Verduzco contributed to the experiments discussed in this chapter. He synthesized and characterized the side-on polymers (names ending with "BB"). He and I traveled together to Argonne National Lab where we shared the responsibility of performing the neutron scattering experiments. He also performed rheometry on solutions of side-on polymers. Zuleikha Kurji assisted us in performing neutron scattering experiments. We are grateful to the Macromolecular Complex Systems group at Oak Ridge National Laboratory's Center for Nanophase Material Sciences (CNMS), especially David Uhrig, for synthesizing some of our diblock prepolymers. We also thank Jyotsana Lal and Ed Lang at Argonne's Intense Pulsed Neutron Source for their help with neutron scattering experiments.

3.1 Introduction

Microphase separation in diblock copolymer melts is a well-understood phenomenon that allows access to a wide range of morphologies that find application in nanotechnologies, as reviewed by Park, Yoon, and Thomas.^[1] The symmetry and length scale of the ordered state are controlled by selection of the chemical structure, connectivity, and relative lengths of the component blocks.^[2] Binary thermodynamic interactions between the polymer blocks ultimately determine the block copolymer's nanostructure in the melt. In solution, thermodynamic interactions with a third component modulate the self-assembled structure: a fixed block copolymer at a fixed concentration can adopt various morphologies depending on the solvent.^[3-10] Block copolymers in selective solvents are used as rheology modifiers and drug delivery systems, for example, and are also of fundamental interest because of the rich thermodynamics governing their self-assembly.

The choice of solvent heavily influences the equilibrium microstructure of AB diblock copolymer micelles.^[3, 5-8] Partitioning of the solvent between the microdomains rich in block A and those rich in block B is referred to as the solvent's "selectivity" and is determined by thermodynamic interaction parameters between the solvent (S) and each polymer, χ_{AS} and χ_{BS} .^[11-15] In the limit of strong selectivity towards A ($\chi_{BS} \gg \chi_{AS}$), diblock copolymers form micelles with cores composed of B almost completely devoid of solvent. In contrast, a neutral, or non-selective, solvent partitions between core and corona. In the former case, dense-core micelles are formed having stronger inter-micelle interaction potentials than the highly swollen, soft micelles afforded in the latter case.^[16, 17]

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When the solvent is a small-molecule thermotropic liquid crystal (LC) the phase behavior of a dissolved block copolymer is enriched by the discontinuous change in quality at the LC phase transitions. The simplest example is the transition from the nematic to the isotropic phase. The orientational order of the LC in the nematic phase presents a large entropic penalty to solvation of a random coil polymer, but in the isotropic phase the solvent's spherical symmetry imposes no such solubility constraints.^[18, 19] In contrast to a random coil polymer, a side-group liquid crystalline polymer (SGLCP) can undergo the change in orientational order with the LC solvent, making it soluble in both the nematic and isotropic phases. A coil-SGLCP block copolymer in a LC solvent can switch from being dissolved in a strongly selective solvent to being dissolved in a good solvent for both blocks when the first-order transition from the nematic to isotropic phase takes place. Such abrupt changes in solvent quality do not occur in non-LC solvents, and we term the phenomenon "switchable solvent quality." We demonstrate that the jump in solvent quality indeed produces an abrupt change in the self-assembly of block copolymers, specifically a change in micelle structure of coil-SGLCP diblocks in solution. We infer the driving force for block copolymer self-assembly from the phase behavior of ternary homopolymer solutions and further demonstrate that exceptional sensitivity to temperature and concentration allows the dominant driving force for block copolymer self-assembly to be modulated with small changes to these parameters.

3.2 Experimental

3.2.1 Materials

A series of diblock copolymers was synthesized having a random coil polymer block (polystyrene, PS) and a side-group liquid crystal polymer (SGLCP) block (Figure 3.1). Starting with poly[styrene-*b*-1,2-butadiene], the reactive 1,2-butadiene monomers were functionalized with cyanobiphenyl-based mesogenic side groups by methods described in Appendix A. These polymers are referred to as "end-on" SGLCPs because the mesogenic group is attached along its long axis, perpendicular to the polymer backbone. Their properties are summarized in Table 3.1 and details of their characterization are given in

Appendix A. Using the same set of PS-PB prepolymers (Appendix A), a series of SGLCPs bearing "side-on" mesogens, attached with the long axis parallel to the polymer backbone, was synthesized by Rafael Verduzco.^[20]

Prepolymers were obtained from two different sources; the details of characterization are given in Appendix A. A series of four PS-PB diblock copolymers having approximately equally sized PB blocks and variably sized PS blocks were synthesized via living anionic polymerization by David Uhrig at Oak Ridge National Laboratory's Center for Nanophase Material Sciences (CNMS). The molecular weight (M_n) of the PB block is approximately 55 kg/mol and the molecular weight of the PS block ranges from 40 to 120 kg/mol. The PB block contains greater than 95 mol % 1,2-butadiene monomers, the remainder being unreactive 1,4-butadiene. These prepolymers were used to synthesize the first four polymers listed in Table 3.1. Other PS-PB prepolymers were purchased from Polymer Source (Montreal, Quebec) and used to synthesize the remaining three polymers listed in Table 3.1. These diblocks are also synthesized by living anionic polymerization and the PB block is composed of 10 - 20 mol % 1,4-butadiene monomers.

The sizes of the PS and PB blocks were chosen to yield a series of PS-SGLCP diblock copolymers that would access a variety of polymer compositions and overall molecular weights, changing only one variable at a time (Figure 3.4). The four polymers synthesized at the CNMS give a series of variable composition, but approximately equal molecular weight. Two of the polymers purchased from Polymer Source closely match the composition of the largest CNMS polymer, giving a series of different molecular weights.

In addition to PS-SGLCP diblock copolymers, end-on and side-on SGLCP homopolymers (Figure 3.2) were synthesized from an anionically polymerized PB prepolymer purchased from Polymer Source. The prepolymer has $M_n = 47.5$ kg/mol and the properties of the resulting SGLCPs are summarized in Table 3.2. Finally, a coil-SGLCP diblock copolymer with a poly(methyl methacrylate) (PMMA) coil block (Figure 3.3) was synthesized, starting from a poly[(methyl methacrylate)-*b*-1,2-butadiene] prepolymer. This prepolymer was also purchased from Polymer Source and the properties of the PMMA-SGLCP diblock

are summarized in Table 3.3. A PS-SGLCP diblock with similar coil block content and total molecular weight was synthesized from a PS-PB prepolymer also purchased from Polymer Source. The details of the characterization of all these polymers and their precursors are given in Appendix A.

Solutions of SGLCP homopolymers and diblock copolymers in liquid crystal solvent were prepared by dissolving a polymer together with the nematic LC 4-pentyl-4'-cyanobiphenyl (5CB) in dichloromethane, then evaporating the dichloromethane under a stream of air followed by drying in vacuum for at least 18 hours.

3.2.2 Methods

Small-angle neutron scattering (SANS) experiments were performed on the Small-Angle Scattering Instrument (SASI) at Argonne National Laboratory's Intense Pulsed Neutron Source (IPNS). The instrument records the intensity of neutrons scattered from a sample at various scattering vectors, $q = 4\pi/\lambda \sin(\theta/2)$, between approximately 0.007 and 2 Å⁻¹. Neutrons at the IPNS are generated by spallation and are therefore polychromatic. The wavelength, λ , is calculated from a neutron's time of flight to a detector at an angle, θ , to the sample. The raw intensity scattered onto a two-dimensional array of detectors is converted to the two-dimensional scattered intensity in *q*-space by computers at the IPNS. An advantage of time-of-flight SANS at a spallation source is that the instrument's entire *q* range is accessed in a single experiment without having to change the sample-detector distance.

Samples were prepared by dissolving diblock copolymers in a perdeuterated liquid crystal solvent. Since the coherent neutron scattering length of hydrogen ($b_H = -3.74 \times 10^{-5} \text{ Å}$) is very different from that of deuterium ($b_D = 6.67 \times 10^{-5} \text{ Å}$), the perdeuterated solvent provides scattering contrast without significantly altering the solvent's other physical properties. Perdeuterated 4-penyl-4'-cyanobiphenyl ($d_{19}5CB$) was synthesized according to methods described in Appendix B. The nematic-isotropic transition temperature (T_{NI}) of $d_{19}5CB$ is approximately 3 °C lower than that of hydrogenated 5CB.^[21]

Diblock copolymer solutions were contained in cells consisting of circular quartz windows spaced apart by a metal or quartz ring either 0.5 or 1.0 mm thick. In most cases the samples were simply loaded in the polydomain state; no effort was made to achieve uniform alignment of the liquid crystal director. During the scattering experiments the cells were held in a heated aluminum block where the temperature was stable within approximately 0.1 °C. At least fifteen minutes of temperature equilibration was allowed prior to collecting data. Samples were typically irradiated for one hour and the two-dimensional scattering pattern was circularly averaged to yield data in the form of intensity versus q.

Rheometry was performed on solutions of diblock copolymers dissolved in 5CB using a TA Instruments ARES-RFS fluids rheometer with a dynamic range of 0.001 to 200 rad/s. Approximately 200 mg of solution was held in a titanium cone-and-plate tool 25 mm in diameter. The temperature was controlled with the rheometer's built-in Peltier plate and was stable to within 0.1 °C. Frequency sweeps were performed in the linear regime at temperatures ranging from 25 °C to at least 60 °C, traversing small temperature increments near the isotropization point. Temperature ramps between 25 and 60 °C were performed in the linear regime at heating/cooling rates of 1, 5, and 10 °C/min. Prior to beginning each experiment, the sample's thermal history was erased by heating it to 60 °C for at least 5 minutes, then annealing at the desired temperature for at least 5 minutes.

The transition temperatures of diblock copolymer solutions were measured by polarized optical microscopy (POM). A drop of solution was placed on a microscope slide and observed between crossed polarizers in a Zeiss Universal stereomicroscope with temperature controlled by a Mettler FP82 hot stage. The temperature at which the colorful, birefringence texture began to disappear was recorded as the isotropization point (T_{NI}). Two temperatures were recorded for samples that became biphasic during the transition: the temperature at which the first black spots appear marks the beginning of the biphasic region and the temperature at which the last colorful spots disappear marks the end.

3.3 Results

3.3.1 Neutron Scattering at High q

The scattering patterns from diblock copolymer solutions all have a few basic features in common (Figure 3.5 and Figure 3.6). The scattered intensity is highest at low q and drops precipitously as q increases, until it merges with I(q) of the equivalent SGLCP homopolymer for q > ~0.06 Å⁻¹. At large q, q-independent, incoherent background scattering becomes dominant beyond $q \approx 0.3 - 0.5$ Å⁻¹. The magnitude of the scattered intensity at low q is highly sensitive to changes in temperature (Figure 3.5). For example, the maximum intensity, I_{max} , for a 5 wt % 320(120)ABSiCB4 solution drops an order of magnitude as the temperature is raised from 25 °C to 40 °C (Figure 3.5a). A similar decrease of I_{max} is observed as 10 wt % 320(120)ABSiCB4 is heated from 25 °C to 50 °C and then drops down to the level seen for the equivalent SGLCP homopolymer as T increases to 60 °C (Figure 3.5b). At high q (q > ~0.06 Å⁻¹), however, I(q) is insensitive to temperature (Figure 3.5). The high-q scattering is also unaffected by changing the size of the polystyrene block (Figure 3.6). Scattering patterns from 40 to 120 kg/mol all overlap at q greater than approximately 0.06 Å⁻¹ (Figure 3.6).

Since the high-q scattering is completely described by the scattering of SGLCP homopolymers (Figure 3.5 and Figure 3.6), this portion of the SANS patterns is attributed to the monomer-level structure of SGLCP chains. At low values of q the self-assembled structure dominates the scattering and from here on the presentation of SANS patterns will be limited to this regime.

3.3.2 Effects of PS Block Size on Structure: Temperature Dependence of SANS and Rheometry

The diblock copolymers 470(40)ABSiCB4, 390(60)ABSiCB4, 420(80)ABSiCB4, and 320(120)ABSiCB4 comprise a series with approximately constant total molecular weight (440 - 510 kg/mol) having increasing PS content from 8 and 23 wt % (Figure 3.4). The changes in the SANS patterns from these diblock solutions with temperature (Figure 3.7a-

Figure 3.14a) are correlated with the temperature dependence of the storage modulus, G' (Figure 3.7b-Figure 3.14b). The SANS patterns from 5 wt % solutions of all four polymers change shape within a small temperature window near T_{NI} , and three out of the four polymers have a large change in the maximum scattered intensity, I_{max} , near T_{NI} (Figure 3.7a-Figure 3.10a, inset). The storage modulus of each of these solutions drops from $G' \sim O(10^0 \text{ Pa})$ to $G' \sim O(10^{-2} \text{ Pa})$ within, at most, 5 °C of T_{NI} (Figure 3.7b-Figure 3.10b). The correlated changes in SANS and G' are similar to those observed at the order-disorder or order-order transition temperatures of non-LC diblock copolymers in isotropic solvents^[3, 8].

The temperature at which the low q scattering decreases to the level seen in an analogous homopolymer solution increases with increasing PS block length, M_{PS} . In the case of the smallest PS block ($M_{PS} = 40$ kg/mol) this temperature is below T_{NI} (Figure 3.7a); for the next in the series ($M_{PS} = 60$ kg/mol), it is above T_{NI} (at 40 °C, I(q) is similar to that of a homopolymer solution) (Figure 3.8a). Block copolymer segregation persists up to 40 °C for the case of PS block lengths greater than 60 kg/mol and the resulting scattering that remains at 40 °C is of higher intensity for the polymer with $M_{PS} = 120$ kg/mol (Figure 3.10a) than for the polymer with $M_{PS} = 80$ kg/mol (Figure 3.9a).

Similarly, the temperature at which *G'* drops below 1 Pa increases with increasing PS block length. For the diblock with $M_{PS} = 40$ kg/mol, *G'* falls to 1 Pa at $T_{NI} - 0.4$ °C (the subsequent rise and fall of *G'* results from the narrow biphasic temperature range of 5 wt % 470(40)ABSiCB4) (Figure 3.7b). When $M_{PS} = 60$ or 80 kg/mol, *G'* falls to 1 Pa at the end of the nematic-isotropic phase transition (35.4 and 36.6 °C, respectively) (Figure 3.8b and Figure 3.9b). For the longest PS block in the series ($M_{PS} = 120$ kg/mol), the decrease in *G'* with increasing temperature beyond T_{NI} is relatively gradual, reaching 1 Pa at a temperature distinctly greater than T_{NI} (Figure 3.10b). Within the nematic phase, increasing PS block length causes the temperature dependence of *G'* to change from softening ($M_{PS} = 40$ kg/mol) to stiffening ($M_{PS} = 60$, 80, and 120 kg/mol), and the steepness of stiffening with increasing temperature increases as the size of the PS block increases from 60 to 120 kg/mol (Figure 3.7b-Figure 3.10b).

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Solutions of 10 wt % diblock copolymer (Figure 3.11-Figure 3.14) exhibit similar trends in SANS and rheology as the 5 wt % solutions. At high *q*, the scattered intensity is approximately two times greater in the 10 wt % as in their 5 wt % counterparts, as it should be for scattering arising from approximately the monomer-level structure. Interestingly, at small *q*, the 10 wt % solutions with $M_{PS} \le 60$ kg/mol do *not* have greater intensity; indeed, when normalized by concentration, I_{max} / c is greater for the 5 wt % solutions in each pair. When $M_{PS} \ge 80$ kg/mol, I_{max} / c is approximately the same for 5 and 10 wt % solutions, as expected. The storage modulus of a 10 wt % solution is approximately ten times greater than its 5 wt % counterpart. Similar to 5 wt % solutions, *G'* increases with temperature in the nematic phase (except for the diblock with $M_{PS} = 40$ kg/mol) and decreases with temperature above T_{NI} . However, for $M_{PS} \ge 60$ kg/mol the decay of *G'* in the isotropic phase is much more gradual for 10 wt % solutions. Whereas *G'* of 5 wt % solutions fell approximately tenfold at T_{NI} for diblocks with $M_{PS} = 60$ or 80 kg/mol, the corresponding drop requires T > T_{NI} for the 10 wt % solutions (Figure 3.12b and Figure 3.13b). The largest PS block delays a comparable drop in *G'* to $T_{NI} + 10$ °C (Figure 3.14b).

3.3.3 Effects of Total Molecular Weight on Structure: Temperature Dependence of SANS and Rheometry

Together with 320(120)ABSiCB4, the diblock copolymers 210(60)ABSiCB4 and 580(190)ABSiCB4, synthesized from prepolymers purchased from Polymer Source, comprise a series with approximately constant PS content (~24 wt %) having total molecular weights of 270, 440, and 780 kg/mol (Figure 3.4). Similar to 5 wt % 320(120)ABSiCB4 (Figure 3.10a), scattering patterns from 5 wt % 210(60)ABSiCB4 (Figure 3.15a) change shape at T_{NI} ; however, unlike 5 wt % 320(120)ABSiCB4 and solutions of other polymers derived from prepolymers provided by the CNMS, their maximum scattered intensities are insensitive to temperature. For the longest polymer in this series, neither the shape nor intensity change across T_{NI} . The magnitude of the storage modulus in the nematic phase increases with increasing molecular weight from $G' \sim O(10^{0} Pa)$ (Figure 3.10b and Figure 3.15b) to $G' \sim O(10^{2} Pa)$ (Figure 3.16b). The decay of G' above T_{NI} becomes increasingly gradual as the polymer molecular weight is increased. For the smallest polymer, 210(60)ABSiCB4, G' decays tenfold at T_{NI} (Figure 3.15b).

Increasing the molecular weight causes the tenfold decay of *G*' to shift to T_{NI} + 2.5 °C (Figure 3.10b), and for the largest polymer, 580(190)ABSiCB4, *G*' does not decay tenfold until T_{NI} + 16 °C (Figure 3.16b).

The same trends are observed in 10 wt % solutions (Figure 3.17, Figure 3.14, and Figure 3.18). The effect of increasing concentration on G' is similar to what was observed for diblocks with a series of different PS contents; doubling the concentration increases G' approximately tenfold and the decay of G' in the isotropic phase becomes more gradual. In the case of the largest polymer, G' decays so slowly that it changes less than four-fold over the entire temperature range (Figure 3.18b). When the concentration of 210(60)ABSiCB4 or 580(190)ABSiCB4 is increased to 20 wt % (Figure 3.19 and Figure 3.20), the storage modulus remains relatively constant throughout the entire temperature range studied (Figure 3.19b and Figure 3.20b). The value of I_{max} / c in 20 wt % solutions (Figure 3.19a and Figure 3.20a, inset) is lower than that of their 5 or 10 wt % counterparts. The shapes of the scattering patterns from 20 wt % 210(60)ABSiCB4 (Figure 3.19a) are also qualitatively different than those of its 5 and 10 wt % counterparts.

3.3.4 Effects of PS Block Size on Dynamics: Frequency Dependent Rheology

Frequency dependent rheology of diblock solutions exposes their dynamics as a function of temperature. The magnitude of the complex viscosity, $|\eta^*|$, is normalized by the bulk viscosity of 5CB, η_{5CB} , at the same temperature to remove the solvent's temperature dependence. Solutions of 5 wt % diblock copolymers having varied PS block sizes are viscoelastic fluids in the nematic phase: the reduced viscosity slopes upward at low frequency (Figure 3.21). In the isotropic phase, the three diblocks with $M_{PS} < 120$ kg/mol remain viscoelastic fluids right after T_{NI} and at T \geq 40 °C the reduced viscosity becomes frequency-independent, characteristic of a viscous fluid (Figure 3.21a,b,c). The polymer with the largest PS block remains a viscoelastic fluid for temperatures less than 50 °C and is a viscous fluid at T \geq 50 °C (Figure 3.21d).

When the polymer concentration is increased to 10 wt % the solutions become room-temperature gels: $|\eta^*| / \eta_{5CB} \sim \omega^1$ at 25 °C, corresponding to nearly constant storage

modulus, $G'(\omega)$, and $G'(\omega) >> G''(\omega)$ (Figure 3.22)[†]. When these solutions are heated above T_{NI} they immediately cease to be gels. When $M_{PS} = 40$ kg/mol the solution transitions directly to a viscous fluid at T_{NI} (Figure 3.22a), but when $M_{PS} \ge 60$ kg/mol the solutions are viscous fluids only at T ≥ 50 °C (Figure 3.22b,c,d). Within the nematic phase, the size of the PS block is correlated to deviations from $|\eta^*| / \eta_{5CB} \sim \omega^1$. Solutions of diblocks with $M_{PS} \ge 80$ kg/mol retain this scaling throughout the dynamic range at all temperatures in the nematic phase (Figure 3.22c and d). When the PS block is decreased to $M_{PS} = 60$ kg/mol, deviations are observed at 35 °C (Figure 3.22b). The viscosity of 10 wt % 470(40)ABSiCB4 begins to deviate from $|\eta^*| / \eta_{5CB} \sim \omega^1$ at T = 32 °C, and the frequency range over which the scaling is valid shrinks as temperature is increased (Figure 3.22a).

3.3.5 Effects of Total Molecular Weight on Dynamics: Frequency Dependent Rheology

The frequency dependent rheology of solutions of 210(60)ABSiCB4 and 580(190)ABSiCB4 was measured at concentrations of 2, 5, 10, and 20 wt %. Solutions of 210(60)ABSiCB4 are room-temperature gels only at concentrations of 10 and 20 wt %; lower concentration solutions are fluids. At 2 wt % the solution is a viscous fluid both above and below T_{NI} (Figure 3.23a). Increasing the concentration to 5 wt % results in a solution that is a viscoelastic fluid in the nematic phase and a viscous fluid at $T \ge 40$ °C (Figure 3.23b). The 10 wt % solution is a gel in the nematic phase and the viscosity deviates from $|\eta^*| / \eta_{5CB} \sim \omega^1$ when T = 35 °C. At $T \ge 50$ °C the solution is a viscous fluid (Figure 3.23c). When the polymer concentration is 20 wt % the solution is a gel throughout the entire temperature range (Figure 3.23d).

Increasing the molecular weight of the diblock results in solutions that are nematic gels at all four concentrations (Figure 3.24). The most dilute solution, 2 wt % 580(190)ABSiCB4, transitions to a viscoelastic fluid at T_{NI} and becomes a viscous fluid at $T \ge 50$ °C (Figure 3.24a). The other three solutions remain gels after the nematic-isotropic transition (Figure 4.24a).

[†] Detailed plots of $G'(\omega)$ and $G''(\omega)$ are located in Appendix E.

3.24b,c,d). The 5 and 10 wt % solutions become viscoelastic fluids at 50 and 60 °C, respectively (Figure 3.24b,c). The 5 wt % solution becomes a viscous fluid at 60 °C (Figure 3.24b), but the 10 wt % solution remains a viscoelastic fluid over the entire temperature range (Figure 3.24c). The 20 wt % solution remains a gel up to at least 100 °C (Figure 3.24d).

3.3.6 Frequency Dependent Rheology: Changing the Identity of the Coil Block

Comparing solutions of 700(70)ABSiCB4 and 950(70)BdMMASiCB4 allows the effects of changing the identity of the coil block to be investigated in polymers having similar composition (~9 and 7 wt % coil block, respectively) and molecular weight (770 and 1,050 kg/mol, respectively). At low concentration (2 wt % polymer) solutions of both PS- and PMMA-containing diblocks are viscoelastic fluids in the nematic phase and transition to viscous fluids above T_{NI} (Figure 3.25a and Figure 3.26a). Data are not available for 5 wt % 700(70)ABSiCB4, but a 10 wt % solution is a gel in the nematic phase, transitioning to a viscoelastic fluid at T_{NI} and at T \geq 50 °C the solution is a viscous fluid (Figure 3.25b). Deviation from $|\eta^*| / \eta_{5CB} \sim \omega^{-1}$ is never seen in 10 wt % 700(70)ABSiCB4. The 10 wt % solution of PMMA-based polymer behaves similarly in that it is a gel in the nematic phase, transitioning to a viscoelastic fluid in the temperature range between T_{NI} and 40 °C (Figure 3.26c). However, in contrast to its PS-based counterpart, the reduced viscosity shows strong low-frequency deviations $|\eta^*| / \eta_{5CB} \sim \omega^1$ at temperatures between 30 °C and T_{NI} . The frequency range over which deviations from this scaling occur expands as temperature When the concentration is increased to 20 wt % polymer, both is increased. 700(70)ABSiCB4 and 950(70)ABSiCB4 behave similarly (Figure 3.25c and Figure 3.26d); the reduced viscosity scales with ω^1 throughout the nematic phase and at temperatures just above T_{NI} . In the isotropic phase the solutions are viscoelastic fluids with the PS-based diblock transitioning to a viscous fluid at 80 °C.

3.4 Discussion

3.4.1 Background: Connecting SANS and Rheology to Self-Assembled Particle Structure

Dissolving a coil-SGLCP diblock copolymer in a small-molecule LC solvent causes the polymer to self-assemble into a core-shell type structure where the LC-phobic coil block is segregated into the core and surrounded by a corona rich in the SGLCP block. SANS and rheometry provide complimentary means to understand both the structure of self-assembled micelles and the interactions between them.

Within a given polymer solution, changes in I_{max} that occur with changing temperature can be related to changes in the number of polymer chains participating in one micelle (the aggregation number, N_{agg}). Regardless of whether any self-assembled structure exists, the monomer-level scattering (at large q) of solutions of diblock copolymers resembles that of homopolymer solutions (Figure 3.5 and Figure 3.6). Excess scattering at low q, however, is from the structure of the self-assembled micelles. The differential scattering crosssection for a solution of N_p particles (here, micelles) of volume V_P and overall neutron scattering contrast $(\Delta \rho)^2$ is

$$\frac{\partial \Sigma}{\partial \Omega}(q) = N_p V_p^2 (\Delta \rho)^2 P(q) S(q), \qquad (3.1)$$

where P(q) is the form factor describing the shape of the particle and S(q) is the structure factor describing interparticle correlations.^[22] In the limit of vanishing q, P(q) = 1 and in the absence of long-range correlations, S(q) = 1. The differential scattering cross-section of uncorrelated particles at q = 0 is, therefore

$$\frac{\partial \Sigma}{\partial \Omega} (q=0) = N_p V_p^2 (\Delta \rho)^2.$$
(3.2)

Equation 3.2 is valid for any solution of uncorrelated particles; it assumes nothing about the shape or constitution of the scatterers. The scattering length density (ρ_p) of a micellar particle swollen with solvent, such that the overall volume fraction of polymer in the particle is ϕ_A , may be calculated from the scattering length densities of the polymer (ρ_A) and solvent (ρ_B):

$$\rho_p = \phi_A \rho_A + (1 - \phi_A) \rho_B, \qquad (3.3)$$

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so that the contrast between the micelle and a pure solvent background is

$$(\Delta \rho)^2 = \phi_A^2 (\rho_A - \rho_B)^2 .$$
 (3.4)

The volume of a solvent-swollen micelle is

$$V_p = \frac{N_{agg}v}{\phi_A},\tag{3.5}$$

where *v* is the volume of a single polymer chain, and the number of particles in a volume of solution, V_S , is

$$N_p = \frac{V_s c}{V_p \phi_A},\tag{3.6}$$

where *c* is the volume fraction of "dry" polymer. Combining Equations 3.2, 3.4, 3.5, and 3.6 gives the differential scattering cross-section in terms of fixed solution properties (V_S , *c*, v, ρ_A , ρ_B) and only one structural property, N_{agg} :

$$\frac{\partial \Sigma}{\partial \Omega} (q=0) = V_S c v (\rho_A - \rho_B)^2 N_{agg}. \qquad (3.7)$$

Equation 3.7 is valid for any solution of arbitrarily shaped, uncorrelated micelles, provided every polymer chain participates in a micelle and the matrix surrounding the micelles is composed of pure solvent. In the case of overlapping micelles, the scattering length density of the surrounding matrix, ρ_M , is unknown and the contrast becomes

$$(\Delta \rho)^{2} = [\phi_{A}(\rho_{A} - \rho_{B}) + \rho_{B} - \rho_{M}]^{2}.$$
(3.8)

The differential scattering cross-section will depend on both N_{agg} and ϕ_A , but Equation 3.7 may still be a valid approximation if the matrix is composed of a dilute polymer solution $(\rho_M \approx \rho_B)$.

Zero-angle scattering is not accessible in these experiments, but the relative changes in I_{max} for a given polymer solution at different temperatures still reflect changes in N_{agg} according to Equation 3.7, provided the form factor is not drastically different from one temperature to the next. For example, if the size of the particles increases, the form factor may shift within the window of observation to decrease the maximum measured intensity (Figure 3.27). Nevertheless, in many data sets (e.g., 10 wt % 390(60)ABSiCB4, Figure

25 - 32 °C) indicating that P(q) is not responsible for the observed drop in I_{max} .

Micellar dispersions studied here are all within the "liquid-like" or "gas-like" concentration regime. In both cases, micelles lack long-range order, but micelles in a liquid-like dispersion remain correlated with one another, while in a gas-like dispersion they are non-interacting.^[3] The "solid-like" regime is ruled out because SANS patterns do not exhibit structure factor peaks resulting from inter-micelle interference,^[3, 8] nor do they exhibit diffraction peaks characteristic of well-ordered micellar lattices.^[23, 24] Inter-micellar correlations are, however, clearly demonstrated by rheology, and result in viscoelasticity or gelation. In general, the more strongly the micelles interact with one another, the higher *G'* becomes. The most likely mechanism for inter-micellar interactions is the overlap of adjacent coronas or, equivalently, correlation of chain conformations in neighboring coronas in order to satisfy the osmotic requirement of minimum concentration variation in the matrix surrounding the micellar cores.^[24-26] SANS on SGLCP homopolymer solutions demonstrated that 5 wt % solutions are in the semidilute regime (Chapter 2), suggesting that diblock solutions of equal or greater concentration must also have corona chains that overlap one another, if only at the outermost edge of the micelle.

The time-scale for relaxation in a micellar solution, indicated by the transition to frequency-independent viscosity, indicates the strength of the coil block's segregation and may be qualitatively linked to how "hard" or "soft" are the micelle cores. When the reduced viscosity deviates from $|\eta^*| / \eta_{5CB} \sim \omega^1$ it indicates that the micelle-micelle interactions have dissipated on the time-scale where the viscosity is frequency-independent, and this time-scale may be attributed to the lifetime of a micelle (the time required for all the participating polymer chains to disengage from the core). Micelles have longer lifetimes as the free energy cost of chain dissociation (the strength of segregation) increases.^[27, 28] Micelles with short lifetimes have "soft" cores; mechanical interactions are weak because stress is relieved by the dissociation of the polymer chains.

3.4.2 Implications of "Switchable" Solvent Quality

The thermodynamic driving forces for self-assembly of coil-SGLCP diblock copolymers may be inferred from the phase behavior of PS and SGLCP homopolymers in 5CB discussed in Chapter 3. In the nematic phase, the entropic cost of dissolving PS in an ordered solvent makes it insoluble in 5CB. When the entropic penalty disappears in the isotropic phase, 5CB and PS become miscible. On the other hand, the covalent attachment of chemically similar, mesogenic units to the polymer backbone makes the SGLCP miscible with 5CB both above and below T_{NI} . Self-assembly of coil-SGLCP diblock copolymers below T_{NI} is intuitively understood as being driven by the solvent's strong selectivity for the SGLCP block. In the isotropic phase, where the solvent is reasonably good for both blocks, self-assembly is driven by a combination of unfavorable interactions between the polymer blocks and by the asymmetric solvent effect; the solvent's slight thermodynamic preference for the SGLCP block can drive self-assembly of a diblock copolymer in the same way that macroscopic phase separation is driven in ternary PS-SGLCP-5CB blends. At low polymer concentration, polymer-polymer interactions are screened by solvent, but as concentration is increased they dominate the system's thermodynamics.

Heating samples through the nematic-isotropic phase transition often has a profound and sudden effect on micellar structure and micelle-micelle interactions as a result of the discontinuous change in solvent quality that takes place at T_{NI} . In contrast to conventional solvents, whose quality changes continuously with temperature, the unique ability of the LC solvent to undergo a first-order phase transition between two distinct fluid phases allows the regimes of strong selectivity^[5, 7, 9] and slight selectivity^[3, 6, 8] to be accessed with small changes in temperature. Depending on the copolymer's composition and molecular weight, the temperature at which the micelles disassemble to become free chains (the microphase separation temperature, MST) can be below, above, or coincident with T_{NI} .

3.4.3 Influence of PS Content on the Driving Force for Self-Assembly

Just as the upper critical solution temperature of ternary homopolymer solutions is highly sensitive to changes in the relative concentrations of the two polymers, the MST of diblock

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solutions gets progressively higher as the copolymers' PS content is increased. At fixed total polymer concentration and molecular weight, increasing M_{PS} serves to increase the total volume fraction of PS and decrease the volume fraction of SGLCP. Interestingly, at low PS content, the covalent bonding between PS and SGLCP serves to draw the PS block into solution even when the solvent quality for PS is poor; the MST of these solutions (both 5 and 10 wt %) is less than T_{NI} . When M_{PS} is small, the free energy cost of mixing PS with a blend of nematic 5CB and SGLCP is not large enough to outweigh the entropic penalty of organizing the SGLCP into micelles. Increasing the size of the PS block to $M_{PS} = 120$ kg/mol shifts the MST of diblock solutions to be greater than T_{NI} , indicating that the asymmetric solvent effect together with unfavorable polymer-polymer interactions is sufficiently strong to overcome the favorable free energy of mixing the individual blocks with isotropic 5CB.

The aggregation number appears to increase with the size of the PS block, as predicted for solutions of associating polymers.^[27, 29, 30] Comparing the data from 5 or 10 wt % solutions at 25 °C, the increase in *G'* that takes place with increasing PS content indicates greater overlap between micelle coronas or, equivalently, an increase in the size of the micelle. The thickness of the micelle corona should be much larger than the radius of the core (a "hairy" micelle) by virtue of the SGLCP block's substantially larger volume fraction in the bulk polymer ($V_{SGLCP} / V_{PS} \ge 3$ for all polymers studied). At fixed N_{agg} , the size of a hairy micelle is insensitive to changes in the size of the core block because the dimensions of the corona chains dictate those of the micelle. Increasing N_{agg} , however, causes increased stretching of the corona chains due to greater crowding at the core-corona interface,^[30] and results in larger micelles with a greater degree of corona-corona overlap. In accord with the rheological data, I_{max} / c at 25 °C also increases with PS content in both 5 and 10 wt % solutions, implying an increase in N_{agg} . However, I_{max} / c cannot necessarily be compared from sample to sample because of possible differences in the form factor.

In a given diblock copolymer solution the temperature dependence of G' in the nematic phase is primarily due to changes in the aggregation number. In solutions of all but the diblock with $M_{PS} = 40$ kg/mol, G' increases with temperature in the nematic phase and is

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accompanied by a decrease in N_{agg} indicated by the decrease in I_{max} / c (except in 5 wt % 320(120)ABSiCB4 where I_{max} / c increases slightly between 25 and 32 °C). The order parameter of 5CB gets smaller with temperature, lessening the entropic penalty to dissolution of PS and allowing the solvent to penetrate the core. This decreases the energy per unit area of the core-corona interface and results in a decrease in N_{agg} . Consequently, the solution contains more micelles, each with fewer polymer chains. Swelling increases the volume fraction of micelles, pushes them closer together, and causes them to interact more strongly. The temperature-dependence of G' is stronger in diblocks with higher PS content because the swelling of the cores affects a larger volume fraction of the overall sample.

For samples that have a substantial *G'* above T_{NI} (Figure 3.10b, Figure 3.12b, Figure 3.13b), and Figure 3.14b), the temperature-dependence falls into two categories: *G'* rapidly decreases at T_{NI} (Figure 3.10b, Figure 3.12b, and Figure 3.13b), or *G'* decreases gradually at first, then rapidly decays after some $T > T_{NI}$ (Figure 3.14b). The former is characteristic of composition fluctuations that decay above the MST in conventional micellar solutions,^[3, 8] and the latter indicates that distinct micelles continue to exist in a range of $T_{NI} < T <$ MST, then decay with similar composition fluctuations. These observations are in accord with the scattering patterns that clearly demonstrate the existence of micelles in the temperature range where *G'* is gradually decreasing (Figure 3.14), but only show diffuse excess scattering in the range where *G'* is falling rapidly (Figure 3.10, Figure 3.12, Figure 3.13, Figure 3.14). The aggregation number of the isotropic micelles decreases with temperature, but the inter-micellar interactions decrease because the cores become very soft; frequency-dependent rheology shows that the fluid's relaxation time is fast (~ O(10² s) or greater) in this temperature range (Figure 3.22d).

3.4.4 Influence of Molecular Weight on the Driving Force for Self-Assembly

At fixed PS content, increasing the molecular weight of a coil-SGLCP diblock copolymer increases the driving force for self-assembly in 5CB; the MST of both 5 and 10 wt % solutions increases from being coincident with T_{NI} at low molecular weight (Figure 3.15 and Figure 3.17) to being much higher than T_{NI} at high molecular weight (Figure 3.16 and

Similar to what was observed as a function of PS content in the previous series of diblocks, increasing the total molecular weight causes the temperature dependence of G' in the isotropic phase to shift from being a steep decay reflecting composition fluctuations above the MST (Figure 3.10b and Figure 3.17b) to a gradual decay between T_{NI} and the MST characteristic of persisting micellization (Figure 3.14b, Figure 3.16b, and Figure 3.18b). However, the corroborating evidence from SANS is unclear in solutions of 210(60)ABSiCB4 and 580(190)ABSiCB4. Scattering patterns at high temperature do not resemble the diffuse excess scattering observed in solutions of 320(120)ABSiCB4; a highintensity upturn at low q is observed at all temperatures. The explanation for these anomalous scattering patterns is unclear, but may be related to the high content of 1,4butadiene in the SGLCP block. Perhaps there is some clustering among short domains of 1,4-polybutadiene driven by poor solubility in the strongly dipolar solvent that gives rise to low-q scattering, similar to clustering between hydrocarbon end-groups and polymer backbones in solutions of poly(ethylene oxide) in water.^[31] The ambiguity in interpreting the high-temperature SANS patterns makes it impossible to draw conclusions about changes in N_{agg} that take place with increasing temperature; I_{max} / c is virtually constant in these samples.

As predicted by theory,^[27, 28, 30] both the strength of coil-block associations and N_{agg} increase with molecular weight. Comparing samples at the same concentration, increase in segregation strength is evidenced by the slowing of the solution's relaxation time (Figure 3.22b, Figure 3.23c, and Figure 3.24c). The increase in N_{agg} with increasing molecular weight results in a transition from viscoelastic fluid to gel in 5 wt % solutions below T_{NI} . At higher concentration, the increased N_{agg} causes isotropic solutions of high molecular weight polymer to be gels (Figure 3.24c) while their low molecular counterparts form viscous liquid solutions (Figure 3.22b, Figure 3.23c).

3.4.5 Influence of Polymer Concentration on the Driving Force for Self-Assembly

In dilute solution, the relatively weak asymmetric solvent effect is the dominant thermodynamic driving force for self-assembly. The unfavorable interactions between the polymer blocks become increasingly important with concentration as they are less effectively screened by solvent. As a result, the segregation strength and, consequently, the MST increase with concentration. This is demonstrated most clearly in solutions of 210(60)ABSiCB4 and 580(190)ABSiCB4 because frequency-dependent rheometry was performed over the concentration range of 2 to 20 wt % polymer (Figure 3.23 and Figure 3.24). The increase in segregation strength is best illustrated by comparing 10 and 20 wt % solutions. The micelle lifetime in 10 wt % solutions of both polymers lies within the dynamic range at a few temperatures, but at 20 wt % deviations from $|\eta^*| / \eta_{5CB} \sim \omega^{-1}$ are never observed. The increase in the MST is also evident because the temperature required to achieve viscous liquid behavior increases with concentration. Similarly, SANS and rheology of the most concentrated samples (Figure 3.19 and Figure 3.20) show that polymers remain self-assembled throughout the entire temperature range of 25 to 60 °C, which is not the case in 5 wt % solutions (Figure 3.15 and Figure 3.16).

Similar trends are also observed in solutions of diblocks from the variable PS content series, though these were only studied at two concentrations (5 and 10 wt %). The observation that I_{max} / c decreased as the concentration of 470(40)ABSiCB4 or 390(60)ABSiCB4 was increased from 5 to 10 wt % is probably the result of a change in what constitutes the matrix surrounding the micelles. If the background matrix is pure solvent, the micelle's scattering contrast is maximized (Equation 3.4), but if the volume fraction of micelles increases to the point they are space-filling, the effective matrix becomes a solution of SGLCP chains in 5CB and the scattering contrast is lowered (Equation 3.8). The perceived scattering may then be from an effective corona composed of a dense layer of SGLCP adjacent to the core surface.^[32]

3.4.6 Influence of the Coil Block Identity on the Driving Force for Self-Assembly

Though the entropy of mixing is probably comparable, the enthalpy of mixing PMMA with 5CB is greater than that of PS with 5CB and the PMMA-SGLCP diblock is, therefore, less

strongly associated. Studies of the phase behavior of polyacrylates with cyanobiphenyl LCs shows them to be slightly more miscible with one another than PS and 5CB.^[33-36] The improved miscibility decreases the segregation strength so that the lifetime of a PMMA-based micelle is evident within the dynamic range of rheometry (Figure 3.26), while that of an equivalent PS-based micelle is not (Figure 3.25). Otherwise, solutions of the PMMA-based behave very similarly to their PS-based counterparts; the MST is comparable for solutions having the same polymer concentration.

3.5 Conclusions

Solutions of coil-SGLCP diblock copolymers in small-molecule LC solvent are unique in that two distinct regimes of solvent selectivity can be accessed in a single solution, simply by heating the solution through its nematic-to-isotropic phase transition. In the nematic phase, the solvent is strongly selective for the SGLCP block, but in the isotropic phase it is a reasonably good solvent for both blocks. The change in solvent quality often triggers the transition from self-assembled micelles to a solution of free chains, but by tailoring the composition and molecular weight of the block copolymer, the MST can be adjusted to be above or below the T_{NI} . These conclusions are summarized in Figure 3.28, where the structure and interactions between diblock copolymer micelles in 5 wt % PS-SGLCP solutions are superimposed over the phase diagram of PS content versus total molecular weight over a temperature range from well below to well above T_{NI} .

In the context of the literature on block copolymers in isotropic solvents, the results presented here imply that new juxtapositions of ordered phases can be introduced into their phase diagrams. The progression of ordered phases that would conventionally be observed in two separate solvents of different quality (strongly selective^[5, 7, 9] versus slightly selective ^[3, 6, 8]) can now be combined into the single phase diagram of a given block copolymer in a single LC solvent. Small temperature changes could switch the system between the two regimes of ordered phases. The present systems switch from a disordered micelle phase that is relatively rigid and has a low volume fraction of the PS-rich domains to a different disordered micelle phase that is much softer and has a substantial volume

fraction of the PS-rich domains. This suggests that for other relative block lengths and concentrations, the system could jump between ordered phases (e.g., FCC and BCC) very abruptly with temperature.

3.6 Tables

Table 3.1 Molecular weight, conversion, and polydispersity of the end-on side-group liquid crystal diblock copolymers with coil block composed of polystyrene (PS). Details of characterization are presented in Appendix A.

	PS	SGLCP Block				
Name	BIOCK M _n [kg/mol]	M _n [kg/mol]	Mole Fraction 1,2 PB	Mole Fraction 1,4 PB	Mole Fraction LC	PDI ^a
470(40)ABSiCB4	43	472	0	0.01	0.99	1.19
390(60)ABSiCB4	59	388	0.15	0.03	0.85	1.11
420(80)ABSiCB4	83	422	0.05	0.05	0.90	1.07
320(120)ABSiCB4	121	323	0.22	0.01	0.77	1.05
700(70)ABSiCB4	70	700	0	0.11	0.89	1.50
210(60)ABSiCB4	63.5	205	0.13	0.15	0.72	1.22
580(190)ABSiCB4	191	577	0.09	0.23	0.68	1.56

^aPDI = Polydispersity Index (M_w/M_n)

Name	M _n [kg/mol]	Mole Fraction 1,2 PB	Mole Fraction 1,4 PB	Mole Fraction LC	PDI ^a
350HSiCB4	347	0	0.11	0.89	1.27
		(8.4.)			

Table 3.2 Molecular weight, conversion, and polydispersity of end-on and side-on sidegroup liquid crystal homopolymers. Details of characterization are presented in Appendix A.

^aPDI = Polydispersity Index (M_w/M_n)

Table 3.3 Molecular weight, conversion, and polydispersity of the side-group liquid crystal diblock copolymer with coil block composed of poly(methyl methacrylate) (PMMA). Details of characterization are presented in Appendix A.

	PMMA	SGLCP Block				
Name	Biock M _n [kg/mol]	M _n [kg/mol]	Mole Fraction 1,2 PB	Mole Fraction 1,4 PB	Mole Fraction LC	PDI ^a
950(70)BdMMASiCB4	68	954	0.07	0.13	0.80	1.11
a DDI – Dolydioporaity Inday (M (M)						

^aPDI = Polydispersity Index (M_w/M_n)

3.7 Figures



Figure 3.1 Chemical structures of end-on side-group liquid crystal diblock copolymers having a coil block composed of polystyrene. The polymers' names are derived from the molecular weights of the liquid crystal polymer block (X) and the coil block (Y) in units of kg/mol, the letters "AB" to indicate a diblock copolymer, and "SiCB4" to indicate end-on, cyanobiphenyl-based mesogens. In addition to monomers having an attached mesogen, the polymer also contains some residual 1,2- and 1,4-butadiene monomers. Compositions, expressed as the mole fractions x,y, and z, are given in Table 3.1 and details of characterization are given in Appendix A.



Figure 3.2 Chemical structures of end-on side-group liquid crystal homopolymers. The polymers' names are derived from the polymer's molecular weight in units of kg/mol, the letter "H" to indicate a homopolymer, and "SiCB4" to indicate end-on, cyanobiphenyl-based mesogens. In addition to monomers having an attached mesogen, the polymer also contains some residual 1,2- and 1,4-butadiene monomers. Compositions, expressed as the mole fractions x,y, and z, are given in Table 3.2 and details of characterization are given in Appendix A.



Figure 3.3 Chemical structures of end-on side-group liquid crystal diblock copolymers having a coil block composed of poly(methyl methacrylate) (PMMA). The polymer's name is derived from the molecular weights of the liquid crystal polymer block (X) and the coil block (Y) in units of kg/mol, the letters "BdMMA" to indicate a diblock copolymer with PMMA coil block, and "SiCB4" to indicate end-on, cyanobiphenyl-based mesogens. In addition to monomers having an attached mesogen, the polymer also contains some residual 1,2- and 1,4-butadiene monomers. Compositions, expressed as the mole fractions x,y, and z, are given in Table 3.3 and details of characterization are given in Appendix A.



Figure 3.4 Diagram illustrating the relative lengths and compositions of PS-SGLCP diblock copolymers described in Table 3.1. The polymers derived from prepolymers synthesized at the Center for Nanophase Material Sciences (CNMS) comprise a series of almost equal total molecular weight (440 - 510 kg/mol) having PS block lengths between 40 and 120 kg/mol. Diblocks derived from prepolymers purchased from Polymer Source, together with the CNMS polymer having the largest PS block, comprise a series in which the PS content is almost constant (~ 24 wt %), but the total molecular weight varies between 270 and 770 kg/mol.



Figure 3.5 SANS patterns from solutions of (a) 5 wt % and (b) 10 wt % 320(120)ABSiCB4 at a variety of temperatures as compared to patterns from homopolymer solutions collected at 50 °C. The low *q* scattering of the diblock solutions is shown in detail in Figure 3.10a and Figure 3.14a.



Figure 3.6 Small-angle neutron scattering patterns from solutions of side-group liquid crystalline diblock copolymers and homopolymers at concentrations of (a) 5 wt % and (b) 10 wt % polymer. The scattering patterns from diblock solutions were collected at 25 °C and the patterns from homopolymer solutions were collected at 50 °C. The low q scattering of the diblock solutions is shown in detail in Figure 3.7a-Figure 3.14a.



Figure 3.7 SANS and rheology of 5 wt % 470(40)ABSiCB4. (a) The low *q* portions of SANS patterns collected at different temperatures in the nematic phase (open symbols) and in the isotropic phase (filled symbols). The intensities at temperatures less than 40 °C are successively shifted upwards by powers of three for clarity. The inset shows the maximum scattered intensity normalized by the solution concentration (I_{max} / c) as a function of reduced temperature ($T - T_{NI}$). (b) The storage modulus (G') at $\omega = 10$ rad/s as a function of temperature. Triangles are positioned at the same reduced temperatures where SANS patterns were collected. The solution is biphasic between 35.4 and 38.0 °C.



Figure 3.8 SANS and rheology of 5 wt % 390(60)ABSiCB4. (a) The low *q* portions of SANS patterns collected at different temperatures in the nematic phase (open symbols) and in the isotropic phase (filled symbols). The intensities at temperatures less than 40 °C are successively shifted upwards by powers of three for clarity. The inset shows the maximum scattered intensity normalized by the solution concentration (I_{max} / c) as a function of reduced temperature ($T - T_{NI}$). (b) The storage modulus (G') at $\omega = 10$ rad/s as a function of temperature. Triangles are positioned at the same reduced temperatures where SANS patterns were collected.



Figure 3.9 SANS and rheology of 5 wt % 420(80)ABSiCB4. (a) The low *q* portions of SANS patterns collected at different temperatures in the nematic phase (open symbols) and in the isotropic phase (filled symbols). The intensities at temperatures less than 40 °C are successively shifted upwards by powers of three for clarity. The inset shows the maximum scattered intensity normalized by the solution concentration (I_{max} / c) as a function of reduced temperature. Triangles are positioned at the same reduced temperatures where SANS patterns were collected. The solution is biphasic between 35.4 and 38.0 °C.



Figure 3.10 SANS and rheology of 5 wt % 320(120)ABSiCB4. (a) The low *q* portions of SANS patterns collected at different temperatures in the nematic phase (open symbols) and in the isotropic phase (filled symbols). The intensities at temperatures less than 40 °C are successively shifted upwards by powers of three for clarity. The inset shows the maximum scattered intensity normalized by the solution concentration (I_{max} / c) as a function of reduced temperature. Triangles are positioned at the same reduced temperatures where SANS patterns were collected.



Figure 3.11 SANS and rheology of 10 wt % 470(40)ABSiCB4. (a) The low *q* portions of SANS patterns collected at different temperatures in the nematic phase (open symbols) and in the isotropic phase (filled symbols). The intensities at temperatures less than 40 °C are successively shifted upwards by powers of three for clarity. The inset shows the maximum scattered intensity normalized by the solution concentration (I_{max} / c) as a function of reduced temperature. Triangles are positioned at the same reduced temperatures where SANS patterns were collected. The solution is biphasic between 37.3 and 37.7 °C.



Figure 3.12 SANS and rheology of 10 wt % 390(60)ABSiCB4. (a) The low *q* portions of SANS patterns collected at different temperatures in the nematic phase (open symbols) and in the isotropic phase (filled symbols). The intensities at temperatures less than 40 °C are successively shifted upwards by powers of three for clarity. The inset shows the maximum scattered intensity normalized by the solution concentration (I_{max} / c) as a function of reduced temperature ($T - T_{NI}$). (b) The storage modulus (G') at $\omega = 10$ rad/s as a function of temperature. Triangles are positioned at the same reduced temperatures where SANS patterns were collected.



Figure 3.13 SANS and rheology of 10 wt % 420(80)ABSiCB4. (a) The low *q* portions of SANS patterns collected at different temperatures in the nematic phase (open symbols) and in the isotropic phase (filled symbols). The intensities at temperatures less than 40 °C are successively shifted upwards by powers of three for clarity. The inset shows the maximum scattered intensity normalized by the solution concentration (I_{max} / c) as a function of reduced temperature ($T - T_{NI}$). (b) The storage modulus (G') at $\omega = 10$ rad/s as a function of temperature. Triangles are positioned at the same reduced temperatures where SANS patterns were collected. The solution is biphasic between 36.4 and 36.6 °C.



Figure 3.14 SANS and rheology of 10 wt % 320(120)ABSiCB4. (a) The low *q* portions of SANS patterns collected at different temperatures in the nematic phase (open symbols) and in the isotropic phase (filled symbols). The intensities at temperatures less than 40 °C are successively shifted upwards by powers of three for clarity. The inset shows the maximum scattered intensity normalized by the solution concentration (I_{max} / c) as a function of reduced temperature ($T - T_{NI}$). (b) The storage modulus (G') at $\omega = 10$ rad/s as a function of temperature. Triangles are positioned at the same reduced temperatures where SANS patterns were collected.



Figure 3.15 SANS and rheology of 5 wt % 210(60)ABSiCB4. (a) The low *q* portions of SANS patterns collected at different temperatures in the nematic phase (open symbols) and in the isotropic phase (filled symbols). The intensities at temperatures less than 40 °C are successively shifted upwards by powers of three for clarity. The inset shows the maximum scattered intensity normalized by the solution concentration (I_{max} / c) as a function of reduced temperature ($T - T_{NI}$). (b) The storage modulus (G') at $\omega = 10$ rad/s as a function of temperature. Triangles are positioned at the same reduced temperatures where SANS patterns were collected.



Figure 3.16 SANS and rheology of 5 wt % 580(190)ABSiCB4. (a) The low *q* portions of SANS patterns collected at different temperatures in the nematic phase (open symbols) and in the isotropic phase (filled symbols). The intensities at temperatures less than 40 °C are successively shifted upwards by powers of three for clarity. The inset shows the maximum scattered intensity normalized by the solution concentration (I_{max} / c) as a function of reduced temperature ($T - T_{NI}$). (b) The storage modulus (G') at $\omega = 10$ rad/s as a function of temperature. Triangles are positioned at the same reduced temperatures where SANS patterns were collected.



Figure 3.17 SANS and rheology of 10 wt % 210(60)ABSiCB4. (a) The low *q* portions of SANS patterns collected at different temperatures in the nematic phase (open symbols) and in the isotropic phase (filled symbols). The intensities at temperatures less than 40 °C are successively shifted upwards by powers of three for clarity. The inset shows the maximum scattered intensity normalized by the solution concentration (I_{max} / c) as a function of reduced temperature. Triangles are positioned at the same reduced temperatures where SANS patterns were collected.



Figure 3.18 SANS and rheology of 10 wt % 580(190)ABSiCB4. (a) The low *q* portions of SANS patterns collected at different temperatures in the nematic phase (open symbols) and in the isotropic phase (filled symbols). The intensities at temperatures less than 40 °C are successively shifted upwards by powers of three for clarity. The inset shows the maximum scattered intensity normalized by the solution concentration (I_{max} / c) as a function of reduced temperature. Triangles are positioned at the same reduced temperatures where SANS patterns were collected.



Figure 3.19 SANS and rheology of 20 wt % 210(60)ABSiCB4. (a) The low *q* portions of SANS patterns collected at different temperatures in the nematic phase (open symbols) and in the isotropic phase (filled symbols). The intensities at temperatures less than 40 °C are successively shifted upwards by powers of three for clarity. The inset shows the maximum scattered intensity normalized by the solution concentration (I_{max} / c) as a function of reduced temperature. Triangles are positioned at the same reduced temperatures where SANS patterns were collected.



Figure 3.20 SANS and rheology of 20 wt % 580(190)ABSiCB4. (a) The low *q* portions of SANS patterns collected at different temperatures in the nematic phase (open symbols) and in the isotropic phase (filled symbols). The intensities at temperatures less than 40 °C are successively shifted upwards by powers of three for clarity. The inset shows the maximum scattered intensity normalized by the solution concentration (I_{max} / c) as a function of reduced temperature ($T - T_{NI}$). (b) The storage modulus (G') at $\omega = 10$ rad/s as a function of temperature. Triangles are positioned at the same reduced temperatures where SANS patterns were collected.



Figure 3.21 Frequency (ω) dependence of the magnitude of the complex viscosity ($|\eta^*|$) of 5 wt % solutions of PS-SGLCP diblock copolymers having similar total molecular weights (440 - 510 kg/mol) and PS block sizes of (a) 40 kg/mol, (b) 60 kg/mol, (c) 80 kg/mol, and (d) 120 kg/mol. The complex viscosity is reduced by the bulk viscosity of 5CB (η_{5CB}) at the same temperature. In the nematic phase, data are represented by open symbols. In the isotropic phase, half-filled symbols indicate a viscoelastic solution and filled symbols are used in the terminal regime where solutions behave as viscous fluids.



Figure 3.22 Frequency (ω) dependence of the magnitude of the complex viscosity ($|\eta^*|$) of 10 wt % solutions of PS-SGLCP diblock copolymers having similar total molecular weights (440 - 510 kg/mol) and PS block sizes of (a) 40 kg/mol, (b) 60 kg/mol, (c) 80 kg/mol, and (d) 120 kg/mol. The complex viscosity is reduced by the bulk viscosity of 5CB (η_{5CB}) at the same temperature. In the nematic phase, data are represented by open symbols. In the isotropic phase, half-filled symbols indicate a viscoelastic solution and filled symbols are used in the terminal regime where solutions behave as viscous fluids.



Figure 3.23 Frequency (ω) dependence of the magnitude of the complex viscosity ($|\eta^*|$) of solutions of PS-SGLCP diblock copolymer 210(60)ABSiCB4 at concentrations of (a) 2 wt %, (b) 5 wt %, (c) 10 wt %, and (d) 20 wt %. The complex viscosity is reduced by the bulk viscosity of 5CB (η_{5CB}) at the same temperature. In the nematic phase, data are represented by open symbols. In the isotropic phase, half-filled symbols indicate a viscoelastic solution and filled symbols are used in the terminal regime where solutions behave as viscous fluids.



Figure 3.24 Frequency (ω) dependence of the magnitude of the complex viscosity ($|\eta^*|$) of solutions of PS-SGLCP diblock copolymer 580(190)ABSiCB4 at concentrations of (a) 2 wt %, (b) 5 wt %, (c) 10 wt %, and (d) 20 wt %. The complex viscosity is reduced by the bulk viscosity of 5CB (η_{5CB}) at the same temperature. In the nematic phase, data are represented by open symbols. In the isotropic phase, half-filled symbols indicate a viscoelastic solution and filled symbols are used in the terminal regime where solutions behave as viscous fluids.



Figure 3.25 Frequency (ω) dependence of the magnitude of the complex viscosity ($|\eta^*|$) of solutions of PS-SGLCP diblock copolymer 700(70)ABSiCB4 at concentrations of (a) 2 wt %, (b) 10 wt %, and (c) 20 wt %. The complex viscosity is reduced by the bulk viscosity of 5CB (η_{5CB}) at the same temperature. In the nematic phase, data are represented by open symbols. In the isotropic phase, half-filled symbols indicate a viscoelastic solution and filled symbols are used in the terminal regime where solutions behave as viscous fluids.



Figure 3.26 Frequency (ω) dependence of the magnitude of the complex viscosity ($|\eta^*|$) of solutions of PMMA-SGLCP diblock copolymer 950(70)BdMMASiCB4 at concentrations of (a) 2 wt %, (b) 5 wt %, (c) 10 wt %, and (d) 20 wt %. The complex viscosity is reduced by the bulk viscosity of 5CB (η_{5CB}) at the same temperature. In the nematic phase, data are represented by open symbols. In the isotropic phase, half-filled symbols indicate a viscoelastic solution and filled symbols are used in the terminal regime where solutions behave as viscous fluids.



Figure 3.27 The form factor of spheres with radius, *R*, of 400 and 500 Å. In the low *q* limit, both form factors are equal (P(q) = 1), but the maximum scattered intensity is measured at the minimum accessible q ($q_{min} = 0.00666$ Å⁻¹). Thus, changing the size of the particles can result in changes to the measured I_{max} .



Figure 3.28 The storage modulus (*G'*) of 5 wt % PS-SGLCP diblock solutions at $\omega = 10$ rad/s and temperatures of 25 °C ($T \ll T_{NI}$), 32-34 °C ($T \ll T_{NI}$), 40 °C ($T > T_{NI}$), and 60 °C ($T \gg T_{NI}$). Blue bars indicate the solution is a gel, green bars indicate a viscoelastic fluid, and red bars indicate a viscous fluid. The letters "M" and "F" indicate that the diblock exists as micelles or free chains, respectively.

3.8 References

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