Chapter 2

USING THE “SWITCHABLE” QUALITY OF A LIQUID CRYSTAL SOLVENT TO MEDIATE SEGREGATION BETWEEN COIL AND LIQUID CRYSTALLINE HOMOPOLYMERS

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2.1 Introduction

The thermodynamics governing phase behavior in polymer solutions is strikingly different from that of regular, small-molecule solutions. The entropy of mixing that favors miscibility between small-molecule species is substantially reduced by the covalent connectivity of monomers in a polymer chain. The usually unfavorable enthalpy of mixing two species is, therefore, more difficult to overcome when one of them is a polymer. The competition between entropy and enthalpy is summarized by the Flory-Huggins equation[1] which expresses the free energy of mixing, ΔF_{mix}, as a function of the polymer's volume fraction, ϕ, and degree of polymerization, N, as well as an interaction parameter, χ, that quantifies the enthalpy of mixing:

$$\frac{\Delta F_{mix}}{kT} = \frac{\phi}{N}\ln\phi + (1-\phi)\ln(1-\phi) + \chi\phi(1-\phi), \tag{2.1}$$

where k is Boltzmann's constant and T is the temperature. The Flory interaction parameter is usually positive and has been found empirically to depend on temperature according to

$$\chi(T) = A + \frac{B}{T}, \tag{2.2}$$

where A and B are constants.[1]

Small-molecule nematic liquid crystals (LCs) are particularly interesting as solvents for polymers because they can undergo a first-order transition between ordered (nematic) and disordered (isotropic) fluid phases, and the χ parameter changes discontinuously at the nematic-isotropic transition temperature (T_{NI}). Below T_{NI} the entropic penalty of dissolving a random-coil polymer in ordered solvent is lumped into the χ parameter, which grows with the solvent's degree of orientational order, but above T_{NI} this penalty is lost and the LC behaves like a conventional solvent.[2] If, however, the polymer also has liquid crystalline character, χ may switch from being positive to negative when the solvent becomes isotropic. In either case, the miscibility of a polymer with an LC solvent may change drastically in the small temperature window around T_{NI}.

Rich thermodynamics result from dissolving a coil polymer and a side-group liquid crystal polymer (SGLCP) together in an LC solvent. The ternary phase behavior of such a polymer-polymer-solvent system is determined by the entropy of mixing balanced with polymer-solvent interactions (characterized by χ_{AS} and χ_{BS}) as well as polymer-polymer interactions (characterized by χ_{AB}).[3-7] In a nematic solvent, all three χ parameters change discontinuously at T_{NI} and the solution's phase behavior is altered accordingly.

In this chapter, the binary phase behavior of a random-coil polymer (polystyrene, PS) in an LC solvent (4-pentyl-4′-cyanobiphenyl, 5CB) is compared to solutions of an SGLCP in

5CB in order to correlate polymer properties with changes in polymer miscibility that take place at T_{NI}. These results elucidate the physics behind the rich phase behavior of ternary solutions of PS, SGLCP, and 5CB that has consequences for solutions of coil-SGLCP block copolymers discussed in later chapters.

2.2 Experimental

2.2.1 Materials

A side-group liquid crystal homopolymer, 490HSiCB4, was synthesized and characterized according to the methods described in Appendix A (Figure 2.1). A 63 kg/mol 1,2-polybutadiene (PB) prepolymer was synthesized via living anionic polymerization by Steven Smith of Proctor and Gamble, Inc. (see Appendix A for characterization). After attaching the mesogenic side-groups, the polymer's molecular weight (M_n) is 489 kg/mol and 97 mol % of the monomers have SiCB4 mesogens attached. Of the remaining 4 mol %, 1 mol % of the monomers are residual 1,2-butadiene and 3 mol % are unreactive 1,4-butadiene. The polydispersity (PDI = M_w / M_n) is 1.48 (Table 2.1). Monodisperse polystyrene (PS) homopolymer with M_n = 44 kg/mol was purchased and used as received from Aldrich. The nematic LC solvent 4-pentyl-4′-cyanobiphenyl (5CB) was used as received from TCI America.

2.2.2 Methods

Ternary mixtures of 490HSiCB4 homopolymer and PS homopolymer in 5CB were made by combining the three components in controlled quantities for a total mass of approximately 50 mg then dissolving them together in ~100 μL of tetrahydrofuran (THF). Samples were mixed for at least an hour to ensure complete dissolution of all three components. A small drop of the THF solution was placed in the shallow well of an indented microscope slide and the THF was evaporated away at elevated temperature (~100 ^{o}C). Slides were examined using a Zeiss Universal optical microscope equipped with a Mettler FP82 hot stage and removable polarizers. Each sample was first heated from room temperature at a rate of 2 ^{o}C/min to observe the nematic to isotropic phase transition; the temperature at which the colorful, birefringent texture viewed between crossed polarizers (Figure 2.2a) disappeared was recorded as the isotropization point (T_{NI}). Next, the polarizers were removed and the sample was heated further until droplets characteristic of two-phase, isotropic/isotropic coexistence (Figure 2.2b) were no longer observed (Figure 2.2c). Then, the sample was cooled at a rate of 10 ^{o}C/min and the temperature at which droplets reappeared was recorded as a nominal upper critical solution temperature (UCST). This measurement was repeated five times, examining a different area on the slide each time, and the results averaged. To set a bound on the subcooling required for observable drops to form on cooling, several samples were raised to 5 °C above the nominal UCST. Consistently, a single phase formed over time. Therefore, the true UCST lies within 5 °C of the nominal one. Since the changes in UCST with solution composition were very large, this uncertainty did not affect the conclusions of this study.

2.3 Results

Binary solutions of 490HSiCB4 with 5CB were observed to be single phase both above and below T_{NI} (Figure 2.3a). Binary solutions of PS with 5CB exhibit a small biphasic window in the isotropic phase of 7.4 ^{o}C or less (Figure 2.3b) and are single-phase above an upper critical solution temperature (UCST). This result is consistent with previously established phase diagrams of PS with 5CB,[8, 9] which found the two to be miscible above 40 ^{o}C, provided the concentration of PS is less than 50 wt %.

Ternary mixtures of PS, 490HSiCB4, and 5CB were observed to phase separate below T_{NI} into coexisting nematic and isotropic phases at all compositions tested (up to 20 wt %). The measured isotropization points in ternary mixtures (i.e., transition from N + I to I + I biphase or N + I to I) were found to be within 3.5 ^{o}C of the bulk T_{NI} of 5CB (35 ^{o}C), indicating that the nematic phase contains little or no isotropic diluent and partitioning of the polymers into an SGLCP-rich, nematic phase and a PS-rich, isotropic phase must therefore be nearly complete. Above T_{NI} wide miscibility gaps were observed up to the UCST.

The UCST of ternary mixtures of PS, 490HSiCB4, and isotropic 5CB was found to be highly sensitive to the concentrations of the two polymers and an effective solubility limit was quickly reached with increasing concentrations (Figure 2.4). For example, holding the concentration of 490HSiCB4 fixed at 4.5 wt %, the addition of 0.5 wt % PS opens up a 14 ^{o}C miscibility gap (UCST = 49 ^{o}C) which expands to 97 ^{o}C (UCST = 132 ^{o}C) when the concentration of PS is 6 wt %. When the overall concentration of polymer, PS and 490HSiCB4 combined, exceeds approximately 10 wt %, the UCST cannot be reached before the sample thermally degrades, representing an effective solubility limit. This steep increase in UCST with increasing polymer concentration is surprising because each of the two polymers dissolves in all proportions tested in isotropic 5CB alone.

2.4 Discussion

Binary and ternary mixtures of 490HSiCB4 and PS dissolved in 5CB show that nematic 5CB is strongly selective solvent for the SGLCP. As previously reported by Hori et al.,[9] PS is insoluble in nematic 5CB; mixtures phase separate into an isotropic, PS-rich phase and a nematic phase nearly devoid of PS altogether. On the other hand, 490HSiCB4 is soluble in nematic 5CB at all concentrations tested (up to 20 wt %). The liquid crystalline order of the nematic solvent imposes a large entropic penalty to solvation of a random coil polymer (e.g. PS),[9-11] but the chemically similar side-groups and liquid crystalline nature of the SGLCP facilitate miscibility with the nematic solvent.[2]

The observation of large miscibility gaps in ternary mixtures of PS, 490HSiCB4, and 5CB was surprising because single-phase solutions are easily achieved in binary mixtures of 5CB with either polymer alone. One reason for the polymers' poor solubility in ternary solutions is that unfavorable interactions between the polymers themselves (a large contribution of χ_{AB}) increase the free energy of mixing.[7] However, this effect is weak in dilute solutions where polymer-polymer interactions are effectively screened by solvent. Small-angle neutron scattering experiments presented in Chapter 5 demonstrate that 5 wt % solutions of similar SGLCPs (310HSiCB4 and 780HSiCB4) are in the semidilute regime, but when the concentration of 490HSiCB4 is substantially lower the polymer chains should be dilute and non-interacting. The overlap concentration of PS is calculated[12] to be approximately 7 wt % at 35 °C in cyclohexane[13] which represents a lower bound on the dilute regime since 5CB is not as good a solvent for PS as cyclohexane. A portion of the measured phase diagram is, therefore, well within a regime where the free energy contribution of inter-polymer interaction (χ_{AB}) should be small.

Besides polymer-polymer interactions, polymer-solvent interactions also contribute to the system's thermodynamics, as described by the Patterson[6]-Prausnitz[3] treatment of the Scott[4]-Tompa[5] theory for ternary polymer-polymer solutions. Patterson and Prausnitz found that any differential preference of the solvent for one polymer over the other ($\chi_{AS} \neq \chi_{BS}$), even if that preference is small, can induce phase separation. Furthermore, the effect is exacerbated when the molecular weight difference between the polymers is large. The asymmetric solvent effect is, therefore, predicted to play a substantial role in the thermodynamics governing phase separation of solutions of PS and 490HSiCB4 in 5CB: the chemical structure of the two polymers is sufficiently different to cause an appreciable difference in polymer-solvent interactions between the two, and the molecular weight ratio of PS to HSiCB4 is approximately 1:10. Isotropic 5CB is, therefore, not a neutral solvent ($\chi_{AS} = \chi_{BS}$), but is better classified as "slightly selective" ($|\chi_{AS} - \chi_{BS}| << \chi_{AS} \approx \chi_{BS}$).

Compared to conventional solvents, 5CB is unique in its ability to undergo a discontinuous, thermally-induced change in its miscibility with polymers. Solvent quality is typically a monotonic function of temperature,[1] but the first-order nematic-isotropic phase transition results in an abrupt change so that increasing temperature less than 1 °C can cause an initially insoluble polymer to become miscible with 5CB. This phenomenon is termed "switchable solvent quality."

2.5 Conclusions

The "switchable" solvent quality of an LC solvent results in rich ternary solution thermodynamics. Unfavorable polymer-polymer interactions work together with strong solvent selectivity to drive macroscopic phase separation in the nematic phase. In the isotropic phase, favorable interactions between the solvent and both polymers are balanced against polymer-polymer incompatibility and the asymmetric solvent effect, resulting in phase behavior that is strikingly sensitive to changes in the solution's composition. Modulation between the two regimes is achieved with temperature changes of less than 1 °C.

The unique phase behavior of homopolymer solutions in an LC solvent suggests that the driving force for self-assembly of a coil-SGLCP block copolymer could also be modulated by the solvent's transition between the nematic and isotropic phases. Below T_{NI} the solvent's orientational order would drive the block copolymer to self-assemble into a structure that segregates the coil-block from the LC host. Above T_{NI} this driving force would be lost, but self-assembly could still occur as a result of the same thermodynamic interactions that drive phase separation in the isotropic homopolymer solutions. This topic is explored in detail in Chapter 3.

2.6 Tables

Table 2.1 Molecular weight, conversion, and polydispersity of the side-group liquid crystal homopolymer. Details of characterization are presented in Appendix A.

Name	M_n [kg/mol]	Mole Fraction 1,2 PB	Mole Fraction 1,4 PB	Mole Fraction LC	PDI[a]
490HSiCB4	489	0.01	0.03	0.96	1.48

[a] PDI = Polydispersity Index (M_w/M_n)

2.7 Figures

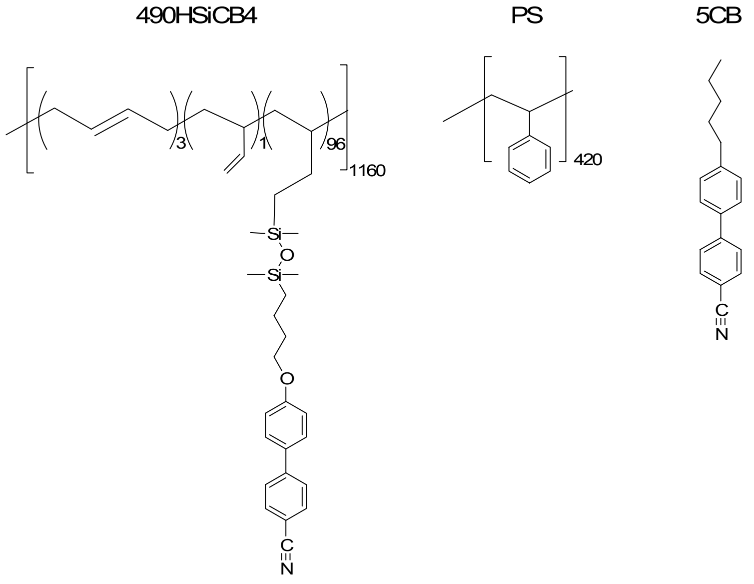
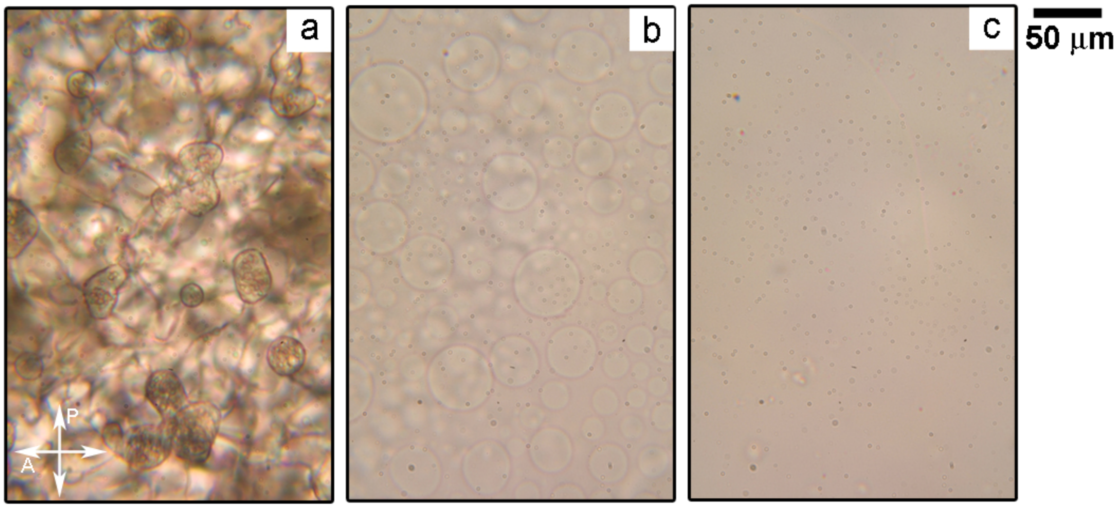


Figure 2.1 Chemical structures of side-group liquid crystal polymer (490HSiCB4), polystyrene (PS), and nematic liquid crystal solvent (5CB). The SGLCP's name is derived from its molecular weight (489 kg/mol), the letter "H" to indicate a homopolymer, and "SiCB4" to indicate end-on attachment of the mesogens. In addition to monomers having an attached mesogen, the polymer also contains ~ 1 mol % each of residual 1,2- and 1,4-butadiene monomers. Its properties are summarized in Table 2.1 and the details of its synthesis and characterization are presented in Appendix A.



$T < T_{NI}$ $T_{NI} < T < UCST$ $UCST < T$

Figure 2.2 Optical micrographs typical of ternary blends of PS, 490HSiCB4, and 5CB at temperatures (a) below T_{NI}, (b) between T_{NI} and the UCST, and (c) above UCST. The sample is imaged between crossed polarizers in the nematic phase ($T < T_{NI}$). These particular micrographs are of 2.25 wt % PS and 4.57 wt % 490HSiCB4 in 5CB at (a) 34 °C, (b) 70 °C, and (c) 90 °C.

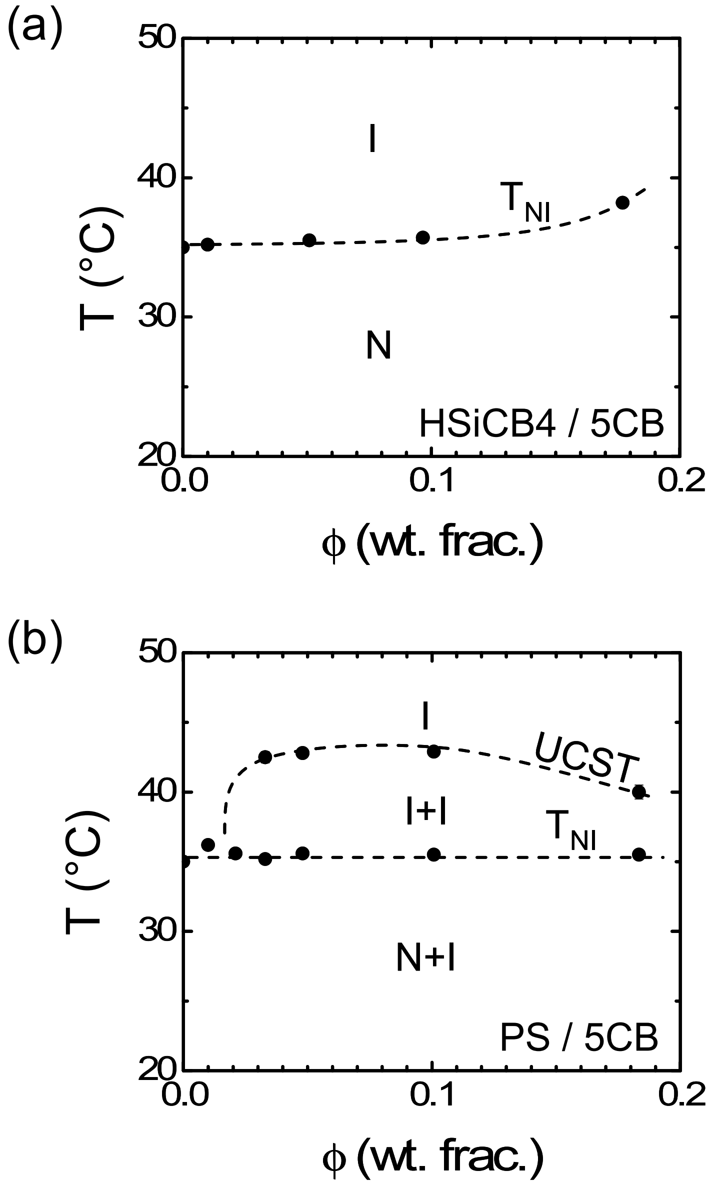


Figure 2.3 Partial binary phase diagrams of (a) 490HSiCB4 homopolymer in 5CB and (b) polystyrene homopolymer with 5CB. Dashed lines are drawn to guide the eye toward plausible phase boundaries. The letters “N” and “I” indicate a single nematic or isotropic phase, respectively. “I+I” indicates two coexisting isotropic phases and “N+I” indicates coexisting nematic and isotropic phases.

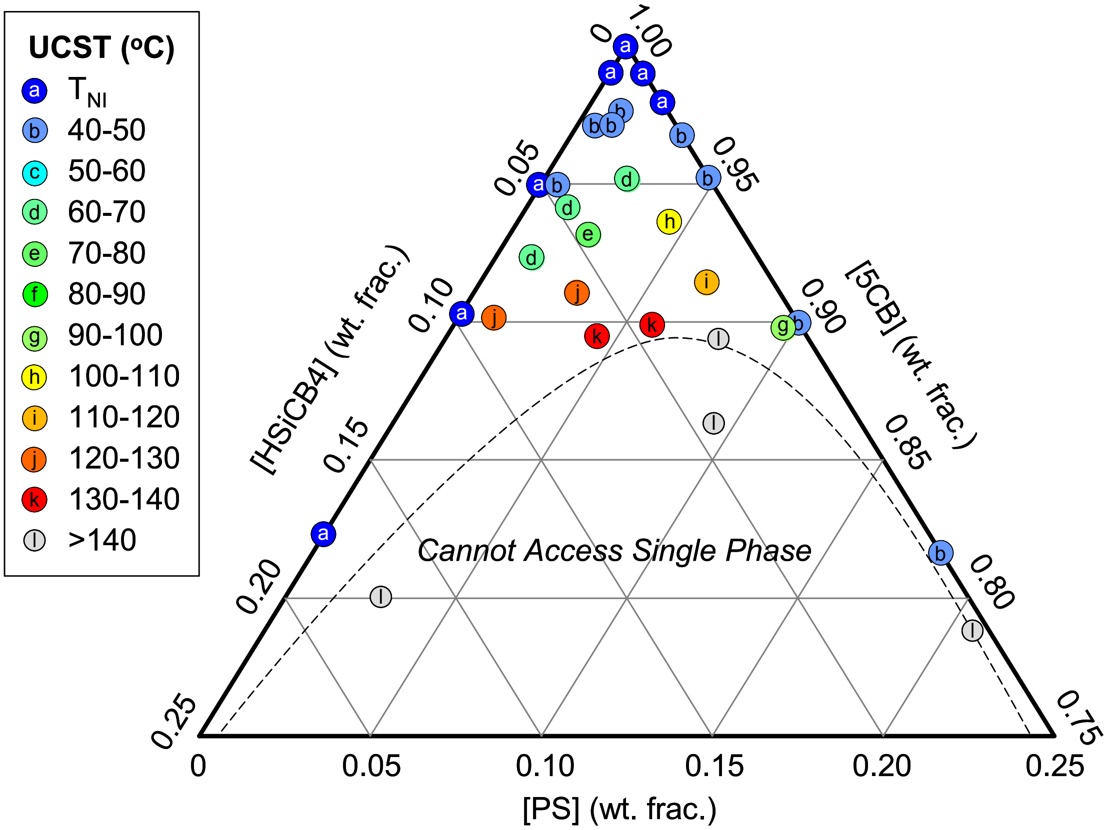


Figure 2.4 Partial ternary phase diagram of PS (44 kg/mol), 490HSiCB4, and isotropic 5CB determined from optical microscopy. The shading and letter of each point expresses the upper critical solution temperature (UCST) at which a single-phase solution is obtained. A UCST equal to T_{NI} means the solution became single-phase immediately upon transitioning to the isotropic phase. A UCST > 140 °C means a single phase was inaccessible because the mixture began to decompose. The dashed line is drawn to guide the eye to the region where a single-phase solution cannot be reached.

2.8 References

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