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Scaling of Domain Spacing in Concentrated Solutions of Block Copolymers in Selective Solvents

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ABSTRACT: The dependence of block copolymer interdomain spacing d on polymer volume fraction ϕ_P in solution, $d \sim \phi_P^{-\beta}$, is examined through a series of styrene−isoprene diblock copolymers in four solvents, three of them strongly selective (nonsolvents for polystyrene). The exponent β is found to depend on solvent selectivity (both temperature and chemical identity of solvent; β increases with selectivity), on mesophase (β is largest when the insoluble blocks form lamellae, then cylinders, then spheres), and on diblock composition within a given mesophase (β is largest when the soluble blocks are most highly diluted). Values of β as large as unity are observed, indicating that selective solvents can swell d quite substantially over the value for the bulk diblock. In one example, a 2.5-fold increase in d is obtained when a cylinder-forming polystyrene-rich diblock is diluted into its mirror-image polystyrene-poor cylindrical mesophase.

Introduction

An attractive feature of block copolymers is the ability to tune the size of the microphase-separated domains simply by changing molecular weight. Potential applications where control over the microdomain spacing is essential include the formulation of soft solids with controllable modulus and yield stress, both of which depend on the domain spacing,[1,2] in the application of block copolymers as lithographic masks[3] or templates,[4] and in the production of visible-wavelength photonic crystals.[5] In strongly segregated melts, it is now well-established that the characteristic microdomain spacing d increases approximately as the $^2/_3$ power of molecular weight,[6] providing a straightforward guideline for adjusting d via synthesis.

It is also possible to adjust d by diluting a block copolymer with solvent. Adding a nonselective ("neutral") solvent reduces d, by screening the unfavorable interactions between unlike segments at the microdomain interface. This reduction is often approximated by a power law in the volume fraction of polymer, ϕ_P:

$$d \sim \phi_P^{-\beta} \qquad (1)$$

where $\beta < 0$ would correspond to a reduction in d upon dilution. Experimentally, $\beta = -0.50$ was found for lamellar-phase (L) toluene solutions of a polystyrene−polyisoprene (S/I) diblock,[7] while $\beta = -0.32$ was reported for S/I diblock solutions in dioctylphthalate (DOP) exhibiting the styrene-poor gyroid (G_S) phase;[8] both toluene and DOP are good solvents for both blocks and nearly neutral between S and I. Self-consistent-field (SCF) calculations[9,10] for L-phase concentrated solutions in neutral solvents predict a range of values for β, depending on segregation strength: $\beta = -0.5$ right at the order−disorder transition, with the dependence weakening to $\beta \approx -0.2$ in strong segregation. Finally, a scaling treatment[11] for semidilute solutions predicts $\beta = -0.12$ for weakly segregated L-phase solutions in neutral solvents. While these β values differ somewhat, the undisputed consensus is that neutral solvent addition produces a reduction in domain spacing.

For selective solvents—especially strongly selective solvents, which are precipitants for one of the blocks—the situation is more complex and less well-understood. SCF calculations presented by Hanley et al.[12] show that β depends strongly on solvent selectivity and can actually become positive as the solvent becomes progressively poorer for the precipitated block, since the domain spacing increases to minimize energetically unfavorable contacts between the solvent and the precipitated block. Values as high as $\beta = 0.20$ for L-phase solutions were predicted as the Flory−Huggins interaction parameter χ between solvent and precipitated block increased to unity.[12] Values of $\beta > 0$ have been observed experimentally as well. For a polystyrene−polybutadiene (S/B) diblock in the B-selective solvent tetradecane, whose solutions exhibited a morphology of styrene-rich spheres (S_S) packed onto a cubic lattice, Shibayama et al.[13] found $\beta = 0.14$. For an S/I diblock diluted with the S-selective solvent diethyl phthalate into mesophases exhibiting I-rich cylinders (C_I) or I-rich spheres (S_I), Hanley et al.[12] found positive values of β as large as 0.33. A homopolymer having the same chemical structure as one of the two blocks may also be viewed as a selective "solvent". Extensive data of Winey et al.[14] for L-phase blends of an S/I diblock with homopolystyrene of varying molecular weights yield $\beta = 0.72$ when the homopolymer has 1.4 times the molecular weight of the S block in the diblock; β decreases systematically with homopolymer molecular weight, to essentially zero when the homopolymer has only 1/10 the molecular weight of the S block in the diblock. These general features have also been captured in self-consistent-field calculations by Vavasour and Whitmore,[10] who showed that $\beta = {}^2/_3$ when the "solvent" is homopolymer of the same molecular weight as the

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analogous block in the diblock (for modest homopolymer contents, as in the experiments of Winey et al.).

Selective solvents are an attractive tool for increasing d, in some ways more attractive than simply increasing molecular weight, because the solvent dilutes out chain entanglements which hinder the development of long-range order of the microdomains.[15] Moreover, fine adjustment of d is relatively easy to achieve through addition of solvent or homopolymer as compared with synthesizing a new diblock. However, a firmer understanding of the factors that determine β is required for this approach to be successful. Here, we elucidate these factors by determining d vs ϕ_P relations experimentally for several diblock–solvent combinations spanning a range of mesophases and demonstrate that larger positive values of β can be achieved than previously reported.

Experimental Section

Synthesis and characterization of the S/I diblocks, preparation of the solutions, and characterization of the solution structure by small-angle X-ray scattering (SAXS) have all been described in detail elsewhere, as part of a study of the phase behavior of such systems.[16] Only a few essential features will be repeated here. All diblocks were synthesized by sequential anionic polymerization; all have polydispersities < 1.05, no detectable homopolymer contaminants (<0.2 wt %), and matched polyisoprene microstructures (93% 1,4-addition). Diblocks are coded as "S/I *i*/*j*", where "*i*" and "*j*" represent the molecular weights of the polystyrene and polyisoprene blocks in kg/mol. Precise compositions (weight fraction of polystyrene, W_S) were determined by ^{1}H NMR. All materials contained either a commercial stabilizer package or 0.2 wt % butylated hydroxytoluene (relative to polymer) to forestall thermooxidative degradation.

Four solvents were employed in this work: 1,3,5-triisopropylbenzene, TIPB (bp 232 °C, $\rho = 0.845$ g/cm^3 at 25 °C), tetradecane, TD (bp 252 °C, $\rho = 0.763$ g/cm^3), tri(*n*-butyl-amine), TBA (bp 216 °C, $\rho = 0.778$ g/cm^3), and squalane, SQ (bp 176 °C at 0.05 Torr, $\rho = 0.810$ g/cm^3). The low vapor pressures of these solvents led to negligible evaporation during testing. All solutions were optically clear and showed SAXS patterns characteristic of a single mesophase. The measured weight fraction of polymer in each solution was converted to a volume fraction of polymer ϕ_P using the densities of polystyrene[17] (1.05 g/cm^3) and polyisoprene[18] (0.90 g/cm^3) at 25 °C, assuming no volume change of mixing. The slight temperature dependence of ϕ_P was neglected.

One-dimensional SAXS data were collected with a compact Kratky camera kept under helium (vacuum for melts) and a position-sensitive detector. A microprocessor-controlled hot-stage was used for temperature control.[19] After heating to above the order–disorder transition temperature (T_{ODT}), the specimen was cooled to below 50 °C and then reheated from 50 °C in steps; thermal equilibration and SAXS data acquisition typically required 16 min per step. Data were reduced using previously reported procedures[20] to desmeared absolute intensity vs the scattering vector $q = 4\pi \sin \theta/\lambda$, where λ is the Cu Kα radiation wavelength and 2θ is the scattering angle. Bragg spacings d were determined from the position q^* of the lowest-order peak as $d = 2\pi/q^*$; thus, d corresponds to d_1 for lamellar structures, d_{10} for hexagonally packed cylinders, and d_{110} for a body-centered-cubic (bcc) packing of spheres (the only packing symmetry observed for spheres in our solutions).

The temperature dependence of d for the different solutions and diblock melts, presented briefly below, is discussed in greater detail elsewhere.[21] To frame the discussion, temperatures of 60 and 100 °C were chosen for detailed analysis. For all of the solutions, d was simply obtained from the SAXS pattern at the temperature of interest, and each solution was verified to have the equilibrium spacing by measurement of q^* vs T, as illustrated in the Results and Discussion section. For the diblock melts, however, data were not acquired at temperatures below 140 °C, due to the proximity of the polystyrene glass transition. Instead, q^* vs T curves were generated at higher temperatures and linearly extrapolated to 100 °C to provide the requisite value of d. The modest and nearly linear temperature dependence of typical diblock melts,[22] including S/I,[21,23] ensures that this procedure does not introduce substantial error.

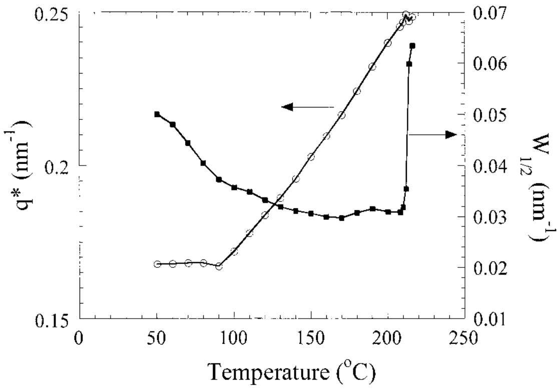

Figure 1. Primary SAXS peak position q^* (○, left axis) and peak full width at half-maximum intensity $W_{1/2}$ (■, right axis) obtained for an SQ solution of S/I 19/7 ($\phi_P = 0.352$) on heating. "Frozen" nature of specimen below 90 °C is evident from invariance of q^*.

Results and Discussion

Since we are interested here in how the *equilibrium* microdomain spacing changes with dilution, it is important to verify that the SAXS patterns truly reflect equilibrated structures. Both chain entanglements and the proximity of the polystyrene glass transition temperature to the temperatures of interest make incomplete equilibration a possibility. A typical set of q^* vs T data (S/I 19/7 in SQ, $\phi_P = 0.352$, styrene-rich cylinders (C_S)) is presented in Figure 1, along with the full width at half-maximum intensity of the SAXS primary peak ($W_{1/2}$). The order–disorder transition at 212 °C (T_{ODT}) is evident from the abrupt increase in $W_{1/2}$. Below T_{ODT}, q^* changes smoothly and roughly linearly with temperature, while $W_{1/2}$ remains relatively constant. Below 90 °C, however, q^* has an abrupt change of slope. Moreover, the $W_{1/2}$ values are significantly larger below 90 °C than above (0.04–0.05 nm^{-1} vs 0.03 nm^{-1}), indicating a more disordered lattice at the lower temperatures (prior to the heating ramp). Thus, this solution would be deemed equilibrated at 100 °C, but not at 60 °C. Replicate measurements on a few solutions confirmed the reproducibility of the q^* values in the smoothly varying region extending up to T_{ODT}.

Before examining the experimental dependence of lattice spacing on concentration, it is instructive to consider limiting cases, assuming negligible partitioning of solvent into the domains formed by the insoluble block. If the insoluble domains were to remain unchanged in size as the diblock is diluted, the domain spacing d would vary affinely with the volume fraction of polymer ϕ_P:

$$d \sim \phi_P^{-1/n} \tag{2}$$

where n is the dimensionality of the lattice ($n = 1$ for lamellae, 2 for cylinders of the insoluble block, 3 for spheres of the insoluble block). With affine swelling, the microdomain interfacial area per chain, A_c, would be

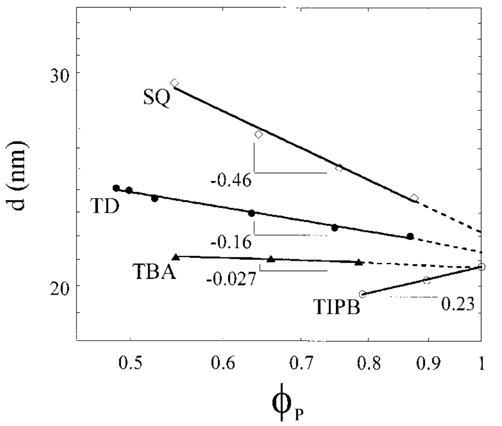

Figure 2. Effect of dilution (ϕ_P) on Bragg spacing (*d*) at 100 °C for solutions of S/I 19/7 in four different solvents: (○) TIPB (C_I phase); (▲) TBA (L phase, I-selective); (●) TD (L phase, I-selective); (◇) SQ (L phase, I-selective). For the C_I phase, *d* corresponds to the separation between (10) planes in the hexagonal macrolattice, while for the L phase, *d* corresponds to the fundamental lamellar repeat distance. Solid lines correspond to best power-law fits to each data set, with exponents indicated. Dashed lines indicate extrapolation to bulk polymer ($\phi_P = 1$).

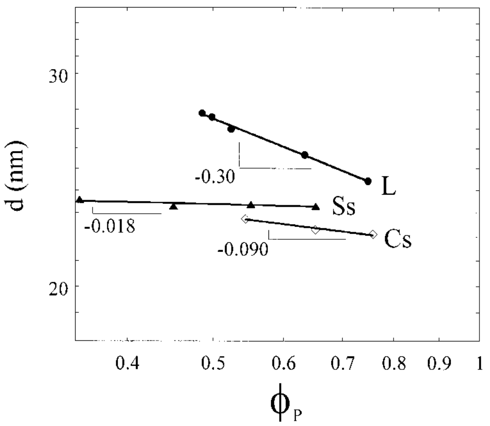

Figure 3. Effect of dilution (ϕ_P) on Bragg spacing (*d*) at 60 °C for TD solutions of three S/I diblocks, each exhibiting a different mesophase: (●) S/I 19/7 (L phase); (◇) S/I 10/16 (C_S phase); (▲) S/I 8/26 (S_S phase). Solid lines correspond to best power-law fits to each data set, with exponents indicated.

constant. In general, however, the addition of solvent will change A_c, due to two factors: (1) replacement of A−B interactions by D−A and D−B interactions, where "D" denotes "diluent" (solvent), and "A" and "B" denote the monomers of the two blocks, and (2) swelling of the solvated block. These effects are not simple to capture quantitatively, as SCF calculations[9,10,24] show, but if A_c also follows a power law,

$$A_c \sim \phi_P^{-a} \tag{3}$$

then the domain spacing would follow:

$$d \sim A_c^{-1} \phi_P^{-1/n} \sim \phi_P^{a-1/n} \tag{4}$$

where comparison of eqs 1 and 4 yields $\beta = 1/n - a$. SCF calculations presented by Hanley et al.[12] for *d* in the L phase conform satisfactorily to eq 4, suggesting that A_c is adequately described by a power law over a substantial range of both ϕ_P and segmental interaction strengths.

We consider three factors on which the exponent *a* should depend. The first factor is solvent selectivity (chemical identity of D, A, and B as well as temperature), with *a* increasing as solvent selectivity decreases, as discussed in the Introduction. The second factor is the mesophase exhibited by the solution, because smaller changes in A_c are required to swell the chains on the convex side of a microdomain interface. Consequently, we expect *a* to decrease in the order L > C_S > S_S for solutions in I-selective solvents. The third factor is the composition of the bulk diblock from which the solution is formed, as this will influence the extent to which conformational changes in the insoluble block are required to accommodate swelling of the solvated block. We expect that *a* should be smaller for smaller fractions of the soluble block, which upon dilution form structures often referred to as "crew-cut" micelles.[25,26] We organize the discussion which follows along these lines, assessing the effect of each of these factors on β (or *a*) individually.

Figure 2 illustrates the first of these three factors—solvent selectivity—with solutions of S/I 19/7 in four solvents at 100 °C: the nonselective TIPB and the increasingly I-selective TBA, TD, and SQ. We established this ranking of solvent selectivity previously,[16] based on the dilutions at which lyotropic phase transitions occur between different mesophases, as well as the measured glass transition temperature of the polystyrene-rich microdomains in SQ, TD, and TBA solutions. The bulk diblock ($\phi_P = 1$) exhibits the C_I mesophase, as do the solutions in TIPB; by contrast, at the dilutions represented in Figure 2, the TBA, TD, and SQ solutions are all in the L mesophase. In the neutral good solvent TIPB, $\beta = -0.23$, which may be compared with experimental values of −0.50 for the L phase[7] and −0.32 for the G_S phase[8] and SCF predictions of −0.50 to −0.2 (magnitude decreasing with increasing segregation strength) for L-phase solutions.[9,10] As solvent selectivity is increased, β increases substantially, to 0.03 in TBA, 0.16 in TD, and 0.46 in SQ. This enormous range for the scaling exponent, even between three very selective solvents, was anticipated by the SCF calculations presented by Hanley et al.[12] and by Vavasour and Whitmore,[10] where increasing "solvent" selectivity is achieved by increasing homopolymer molecular weight. Finally, note that in Figure 2, while the line describing the TBA solutions (with $\beta \approx 0$) extrapolates well to the *d* value for the bulk diblock (at $\phi_P = 1$), the lines for the TD and SQ solutions do not. Extrapolating L-phase solution data to $\phi_P = 1$ does not reach the minimum free energy state, as the bulk diblock shows the C_I phase, so the discrepancy in measured vs extrapolated *d* values is not unexpected.

Figure 3 illustrates the second of these factors—the effect of mesophase on β—using TD solutions at 60 °C. Three different diblocks are employed (with differing W_S), so as to obtain three different mesophases (L, C_S, and S_S) over comparable ranges of ϕ_P. Note that β decreases systematically through this series: from 0.30 for L, to 0.09 for C_S, to 0.02 for S_S. This is qualitatively consistent with eq 4, but quantitatively, the exponents found in the different mesophases are less different than predicted on the basis of the changes in *n* ($1 \rightarrow 2 \rightarrow 3$). This demonstrates that, in fact, *a* varies substantially according to which mesophase the solutions adopt.

Compendia of β values for all the solutions investigated are given in Table 1 (at 100 °C) and Table 2 (at 60 °C). To facilitate comparison, solutions are grouped by mesophase (column 1), then grouped by solvent

Table 1. Domain Scaling Exponents β at 100 °C for S/I Diblock Solutions

meso-phase	solvent	bulk W_S	diblock S/I	ϕ_P range	β	std dev[b]
C_S	TD	0.334[a]	8/17[e]	0.74−1	0.04	0.07
	TD	0.378[a]	10/16	0.65−0.87	−0.04	0.02
	TD	0.393[a]	10/15	0.65−0.91	0.02	0.02
	TD	0.716	19/7	0.33−0.43	0.08	0.01
	TD	0.803	24/6	0.24−0.45	0.32	0.02
L	SQ	0.716[a]	19/7	0.54−0.88	0.46	0.04
	SQ	0.803	24/6	0.44−0.75	1.03	0.17
	TD	0.516[a]	11/10[f]	0.76−1	0.03	0.06
	TD	0.677[a]	17/9	0.53−0.88	0.13	0.02
	TD	0.716[a]	19/7	0.48−0.87	0.16	0.01
	TD	0.803	24/6	0.45−0.64	0.37	0.07
	TBA	0.716[a]	19/7	0.54−0.78	0.03	0.01
C_I	TD	0.803[a]	24/6[c]	0.72−1	0.30	0.05
	TBA	0.716[a]	19/7[d]	0.87−1	0.00	0.02
	TIPB	0.716[a]	19/7[d]	0.79−1	−0.23	0.01

[a] Bulk diblock requires no more than modest dilution to exhibit the mesophase of interest; $V^* < 1$, as defined by eq 5. [b] One standard deviation of the power-law fit, eq 1. [c] Melt d ($\phi_p = 1$) extrapolated to 100 °C from 140 to 156 °C. [d] Melt d ($\phi_p = 1$) extrapolated to 100 °C from 140 to 200 °C. [e] Melt d ($\phi_p = 1$) extrapolated to 100 °C from 140 to 158 °C. [f] Melt d ($\phi_p = 1$) extrapolated to 100 °C from 168 to 177 °C.

Table 2. Domain Scaling Exponents β at 60 °C for S/I Diblock Solutions

meso-phase	solvent	bulk W_S	diblock S/I	ϕ_P range	β	std dev[b]
S_S	TD	0.241[a]	8/26	0.35−0.65	0.02	0.01
	TD	0.334	8/17	0.34−0.54	0.04	0.01
	TD	0.378	10/16	0.25−0.45	0.05	0.02
	TD	0.393	10/15	0.25−0.44	0.03	0.01
	TD	0.516	11/10	0.16−0.34	0.08	0.05
C_S	TD	0.378[a]	10/16	0.54−0.76	0.09	0.02
	TD	0.716	19/7	0.33−0.47	0.23	0.02
	TD	0.803	24/6	0.24−0.45	0.39	0.03
L	TD	0.677[a]	17/9	0.53−0.75	0.26	0.05
	TD	0.716[a]	19/7	0.48−0.75	0.30	0.01
	TBA	0.716[a]	19/7	0.54−0.78	0.10	0.01

[a] Bulk diblock requires no more than modest dilution to exhibit the mesophase of interest; $V^* < 1$, as defined by eq 5. [b] One standard deviation of the power-law fit, eq 1.

selectivity (column 2), then ranked by weight fraction of S in the bulk diblock, W_S (column 3). Temperature has a measurable effect on the value of β, due to an increase in selectivity as temperature decreases even in these highly selective solvents; this complements the results in Figure 2, where it was demonstrated that even among strongly selective solvents (SQ, TD, TBA), variations in solvent selectivity can lead to substantial variation in β. Where direct comparisons can be made between Tables 1 and 2 (TD and TBA solutions in the C_S and L phases), β increases by 0.12 (±0.05 range) on cooling from 100 to 60 °C. A similar increase in β (by 0.09, from −0.02 at 100 °C to 0.07 at 60 °C) was reported by Hanley et al.[11] for L-phase solutions of an S/I diblock in DEP. This quantitative similarity was unexpected, since DEP solutions show a more substantial effect of temperature on the phase boundaries (e.g., which mesophase is stable at a given ϕ_P and T), implying a stronger temperature dependence of the selectivity.

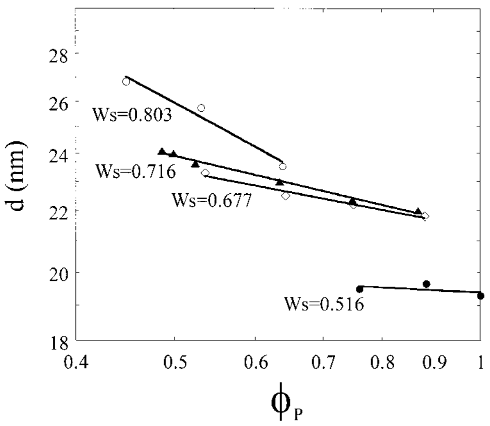

Figure 4. Effect of dilution (ϕ_P) on Bragg spacing (d) at 100 °C for TD solutions of four S/I diblocks of varying composition, all in the L mesophase: (○) S/I 24/6 (W_S = 0.803, β = 0.37); (▲) S/I 19/7 (W_S = 0.716, β = 0.16); (◇) S/I 17/9 (W_S = 0.677, β = 0.13); (●) S/I 11/10 (W_S = 0.516, β = 0.03). Solid lines correspond to best power-law fits to each data set.

Figure 4 reveals the third of the factors identified above—the effect of diblock composition on β. Data are shown at 100 °C for TD solutions prepared from four different diblocks; all solutions are in the L phase. The value of β increases steadily as W_S is increased, from 0.03 (for S/I 11/10, $W_S = 0.516$, for which L is also the equilibrium phase in bulk) to 0.37 (for S/I 24/6, $W_S = 0.803$). As anticipated, this effect arises because the solutions prepared from diblocks with high W_S have rather diluted soluble blocks and hence begin to approach the simple "affine dilution" case described by eq 2, or eq 4 with $a = 0$. For the most I-poor diblock studied, S/I 24/6, in the L phase at 100 °C, $\beta = 0.37$ in TD and 1.03 in SQ (where $a = 0$ for the L phase would yield $\beta = 1$); in the C_S phase, $\beta = 0.32$ in TD (where $a = 0$ for the C_S phase would yield $\beta = {}^1/_2$). Note that the "affine dilution" case is not a fundamental limit; it should be possible for a to be negative, if the solvent is so poor for the insoluble block that additional chain stretching is less energetically costly than are contacts between solvent and insoluble block. It is noteworthy, however, that the value of $\beta = 1.03$ for L-phase solutions in SQ actually exceeds that for L-phase blends of an S/I diblock with S homopolymer[14] ($\beta = 0.72$, when homopolymer has 1.4 times the molecular weight of the S block, consistent with SCF predictions[10]). Clearly, homopolymer does not represent the limit in "solvent" selectivity; indeed, while homopolymer is approximately a Θ-solvent for its "like" block, SQ or other selective solvents can behave as good solvents for the soluble block while remaining strong precipitants for the other block.

Figure 4 makes the comparison for only one mesophase and in one solvent. To evaluate the generality of this behavior, it is useful to classify systems by comparison with two limiting cases: (A) where the bulk diblock forms the mesophase of interest and (B) where the diblock must be highly diluted before the desired mesophase becomes stable. To quantify cases between these two extremes, we choose the volumetric ratio V of solvent to I block present in the solution, evaluated where the diblock is diluted just to the point where the mesophase of interest becomes stable, ϕ^*_P:

$$V^* \equiv \frac{1 - \phi^*_P}{\phi^*_P f_I} \tag{5}$$

where ϕ^*_P is slightly above the upper end of the ϕ_P range[16] for each entry in Tables 1 and 2 and f_I is the volume fraction of isoprene in the bulk diblock, calculated from W_S and the homopolymer densities. Case A thus corresponds to $V^* = 0$, while case B corresponds to $V^* \gg 1$. As a benchmark, we choose $V^* = 1$ as the dividing line; those systems which have $V^* < 1$ are denoted by footnote "*a*" in column 3 of Tables 1 and 2. Conceptually, these systems may be thought of as ones where the microdomain interface curvature in the solution is generally similar to that for the bulk diblock; by contrast, limiting case B includes systems where the solution and bulk diblock have interface curvatures of opposite sign (e.g., a diblock forming I cylinders in bulk, diluted until it forms S cylinders).

An assessment of how diblock composition influences β can thus be made by first selecting a particular mesophase and solvent and then comparing the values of β for solutions formed from diblocks having V^* values either greater or less than unity, our choice for the dividing line. For a given mesophase (column 1) in a given solvent (column 2), Tables 1 and 2 show that, for the systems with $V^* < 1$, β is relatively constant and much smaller than for the entries with $V^* > 1$. For example, in Table 1, for the C_S-phase TD solutions, $\beta \approx 0.00$ (± 0.04 range) for the three systems with $V^* < 1$ vs $\beta \approx 0.20$ (± 0.12 range) for the two entries with $V^* > 1$. Similarly, for the L-phase TD solutions whose data are presented in Figure 4, $\beta \approx 0.10$ (± 0.07 range) for the three systems with $V^* < 1$ vs $\beta = 0.37$ for the entry with $V^* > 1$. Comparable effects can be seen for the L-phase SQ solutions in Table 1 and the C_S-phase TD solutions in Table 2.

By contrast, for the S_S-phase TD solutions in Table 2, the small difference in β between the systems with $V^* < 1$ and with $V^* > 1$ is not statistically significant. This suggests that the magnitude by which diblock composition affects β depends, in turn, on the solution mesophase considered. Indeed, while the data presented here clearly confirm the importance of all three factors (solvent selectivity, mesophase type, and diblock composition) in setting d and while the qualitative influence of each factor on β is consistent across the systems studied, it is equally clear that the value of β is *not* determined by a simple sum of three independent constants with values corresponding to each of these three important factors.

Nonetheless, our results demonstrate the substantial range over which β, and consequently d, can be varied through judicious choice of diblock and solvent. The largest values of β will be obtained with the most strongly selective solvent and with a diblock wherein the soluble block has as small a weight fraction as possible. As a specific example, bulk S/I 24/6 (C_I phase) shows $d = 19.0$ nm at 120 °C (value extrapolated slightly from 18.5 nm at 140 °C). When this same diblock is diluted with SQ into the mirror-image C_S phase (40 wt % polymer), $d = 47.4$ nm at 120 °C—a 2.5-fold increase. The value of d could, of course, be increased further by employing a diblock of higher molecular weight. Though the largest increases in d are achieved when the diblock contains the smallest weight fraction of soluble block, the eventual limit here is that sufficient soluble block must be present to avoid macrophase separation between diblock and solvent. To exemplify where this limit is exceeded, we prepared mixtures of TD with an S/I diblock having $W_S = 0.898$ (S/I 60/7) but were unable to obtain macroscopically homogeneous solutions.

These results may be compared with those of Hajduk et al.[27] on aqueous solutions of poly(ethylene oxide)−poly(ethylethylene) diblocks, PEO−PEE, where water has an extremely high selectivity for the PEO block, at least near room temperature. For a diblock with $f_{EO} = 0.39$, a 2.2-fold increase in d at 50 °C was obtained on dilution to 40 wt % polymer, similar to the factor of 2.5 which we find for S/I 24/6 solutions in SQ. This PEO−PEE diblock is close to the "solubility limit", as Hajduk et al. found that polymers with $f_{EO} \leq 0.34$ were essentially immiscible in water (as we find for S/I diblocks with $W_I < 0.11$ in TD). While specific hydration of PEO likely drives extensive conformational changes in these PEO−PEE diblocks,[27] our results here show that comparable increases in d can be achieved even in systems with simple dispersive interactions.

Finally, the strong temperature dependence of d in these systems (an example of which is shown in Figure 1) may find application as well, in sensitive tuning of the domain spacing or the creation of structures with a gradient of d. For example, in this same 40 wt % solution of S/I 24/6 in SQ, d decreases from 47.4 nm at 120 °C to 30.5 nm at 210 °C, a change of more than 35%. By contrast, the interdomain spacing in typical diblock melts,[22] including S/I,[21,23] changes by 10% or less over a similar temperature range. This strong temperature dependence is implicit in our finding that β decreases with increasing temperature (by an average of 0.12, on heating from 60 to 100 °C). Hence, the temperature dependence (dq^*/dT) increases progressively as ϕ_P decreases.

Conclusions

While the addition of a neutral solvent to a block copolymer reduces the interdomain spacing d, the addition of selective solvents can increase d or yield d essentially independent of concentration. Even with highly selective solvents—those which are precipitants for the homopolymer of one block—a substantial variation in the scaling exponent β can be achieved through temperature variation. The value of β also depends strongly on the mesophase exhibited by the solution, decreasing as the dimensionality of the lattice increases (β smallest when the insoluble block forms spheres). Despite the strong selectivity of the solvents employed here, solvent addition still produces an *increase* in interfacial area per chain ($a > 0$)—a feature shared qualitatively with neutral solvents—in nearly all cases. Finally, β depends on the composition of the diblock from which the solution is formed, being largest when the soluble block is most highly diluted within the mesophase of interest. Therefore, the greatest expansions of the lattice are obtained with diblocks that have the minimum fraction of soluble block needed to preserve solution homogeneity.

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