Macromolecules
ARTICLE

Macromolecules **2009**, *42*, 7155–7163 **7155**
DOI: 10.1021/ma900848j

High-Pressure Micellar Solutions of Symmetric and Asymmetric Styrene−Diene Diblocks in Compressible Near-Critical Solvents: Micellization Pressures and Cloud Pressures Respond but Micellar Cloud Pressures Insensitive to Copolymer Molecular Weight, Concentration, and Block Ratio Changes

Winoto Winoto, Sugata P. Tan, Youqing Shen, and Maciej Radosz*

Soft Materials Laboratory, Department of Chemical & Petroleum Engineering, University of Wyoming, Laramie, Wyoming 82071-3295

Kunlun Hong and Jimmy W. Mays

Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6494

Received April 17, 2009; Revised Manuscript Received August 3, 2009

ABSTRACT: High-pressure solutions of polystyrene-*block*-polybutadiene and polystyrene-*block*-polyisoprene in compressible propane or propylene exhibit a robust micellar region that grows in pressure−temperature coordinates with increasing copolymer concentration, molecular weight, and styrene/diene block ratio. This happens because, while the micellization pressure strongly increases with increasing copolymer concentration, molecular weight, and styrene/diene block ratio, the micellar cloud pressure (the pressure at which the micelles aggregate and precipitate from solution) is largely insensitive to these variables. In other words, neither the block size nor the block ratio nor the copolymer concentration seems to affect much the copolymer separation from solution in the micellar region.

Introduction

In contrast to micellar solutions of block copolymers in *incompressible* liquid solvents, which have been extensively studied,[1] micellar solutions of block copolymers in *compressible* solvents,[2−6] such as pressure-sensitive near critical fluids, are poorly understood. In our recent work, we focused on model styrene−diene block copolymers in a compressible alkane solvent, such as propane, to characterize their bulk and micellar phase behavior. For example, symmetric polystyrene-*block*-polyisoprene was demonstrated to exhibit robust micellization and micelle decomposition in supercritical and subcritical propane induced by changing either pressure or temperature or both.[7] At a constant copolymer concentration, both micellization temperature and pressures were found to fall around a decreasing micellar phase boundary curve in pressure−temperature coordinates, which lies above the copolymer cloud-point curve and below the polystyrene cloud-point curve. The onset of micellization and the onset of bulk transition (cloud point) were not only measured but also realistically estimated[8] for styrene−isoprene and styrene−butadiene block copolymers in propane from statistical associating fluid theory (SAFT1) using universal SAFT1 parameters characteristic of the segment volumes and segment energies, without readjustment. It turned out that the experimental cloud pressures of the micellar solutions (the micellar cloud pressures, MCP) were lower than the cloud pressures (CP) calculated from SAFT1 for a hypothetical random solution.[8,9] Such a cloud-pressure reduction, MCP vs CP, indicates the extent to which micelle formation enhances the apparent diblock solubility in near-critical and hence compressible propane.

The effect of micelle formation on diblock copolymer solubility is illustrated in Figure 1 with a typical phase diagram replotted from our previous work[9] that shows an example of a cloud-pressure reduction between a calculated CP curve (solid) and an experimental MCP curve (dash-dotted). The MCP curve and the actual CP curve (dashed with half-filled circles above 100 °C) cross at a pressure−temperature point beyond which no micelles can be formed, referred to as the micellization end point (MEP, shown with a diamond), which corresponds to a “critical micelle temperature”.[9] A micellization pressure (MP) curve shown with filled circles, which also terminates at MEP, indicates pressures below which micelles can form and above which micelles decompose.

Those previous studies provided intriguing clues that the bulk and micellar cloud pressures, micellization pressures, and micellization end points may depend on the copolymer type, size, and structure, but those data were not enough to understand and explain it.

Therefore, the goal of this work is to determine micellar and bulk (cloud) transitions in compressible solutions of uniform and well-characterized polystyrene-*block*-polybutadiene and polystyrene-*block*-polyisoprene, symmetric and asymmetric, that systematically and significantly differ in total molecular weight and block ratio by keeping the styrene block constant but varying the diene block size and vice versa, using the same solvents as those used in the previous studies, that is, propane and propylene. The purpose is to probe the sensitivity of the cloud pressure, micellar cloud pressure, micellization pressure, and micellization end point to the copolymer type and structure. This is needed to understand, in general, how to design efficient copolymer structures and pressure−temperature paths for making micellar

---

*Corresponding author: E-mail radosz@uwyo.edu.

nanoparticles that can encapsulate trace components, such as cancer drugs.

Experimental Section

Materials. The homopolymers and diblock copolymers used in this work were either purchased or synthesized via living anionic polymerization using well-established vacuum line techniques, as documented in recent reviews.[10,11] Briefly, the diblocks were prepared by sequential monomer addition, with sampling of the first block (polystyrene). Microstructure of the polybutadiene and polyisoprene was controlled through the choice of solvent and use of polar additions (tertiary amines and ethers).[12,13] Molecular weights and polydispersity indices were characterized using size exclusion chromatography (SEC) with online light scattering detection. Microstructure of the polydienes and composition of the block copolymers were determined using proton nuclear magnetic resonance (^{1}H NMR).

The polybutadiene and polyisoprene samples are at least 90% of the 1,4-addition type for both homopolymer and diblock copolymer. The molecular weights and polydispersity indices of all samples are provided in Table 1, including their short names used throughout this paper.

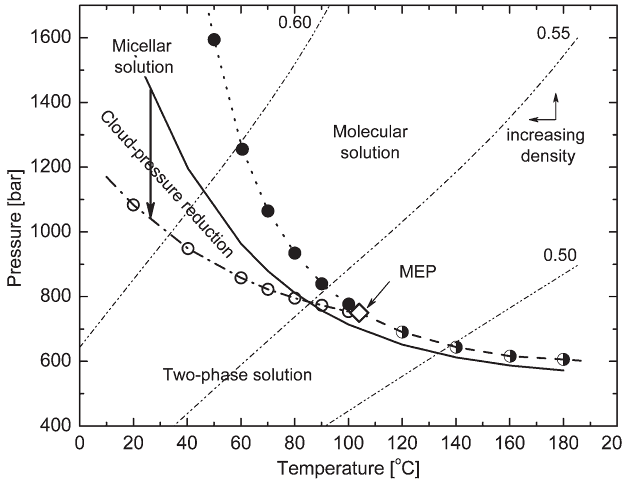

Figure 1. Cloud pressure (half-filled), micellar cloud pressure (open), and micellization pressure (filled) as a function of temperature for 0.5 wt % solution of polystyrene-*block*-polybutadiene (S−B(15−13)) in propane. Cloud-point curve (dashed), micellar cloud-point curve (dash-dotted), and micellization boundary (dotted) intersect around a micellization end point (MEP; diamond), indicating the highest temperature of the micellar region for a constant-concentration solution.[9] The diagonal dash-double-dotted curves stand for constant propane density in g/mL. The curves shown in this figure are not calculated, except for the solid curve, which was calculated from SAFT1.

The propane is 99.0% grade from Matheson Trigas, Inc.; the propylene is 99.5% grade from Airgas, Inc. The solvents are used without further purification.

Experimental Method. The onset of bulk phase transition of a clear homogeneous polymer solution is usually observed as the onset of its turbidity and hence referred to as the cloud point, that is, the pressure and temperature at which the homogeneous solution turns cloudy, referred to as the cloud pressure (CP; represented by half-filled points) and the cloud temperature (CT). When the bulk phase transition occurs from a micellar solution, it is referred to as the micellar cloud pressure (MCP; represented by open points) and the micellar cloud temperature (MCT). Normally, bulk phase disengagement and complete separation can be achieved upon penetrating the two-phase region below the cloud pressure, which requires either a rapid but significant pressure quench or a small but slow quench. In this work, however, such a bulk phase separation is undesirable because it requires long time to redissolve the polymer.

The onset of micelle formation in a block copolymer solution is measured from the change of the scattered-light intensity upon reducing the pressure at constant temperature, which results in the micellization pressure (MP; represented by filled points), or reducing the temperature at constant pressure, which results in the micellization temperature (MT). Typical transmitted- and scattered-light intensity traces upon decreasing pressure of a homogeneous random solution, which leads to micelle formation (at MP) and bulk phase separation (at MCP) are illustrated in Figure 2. The scattered-light intensity increases sharply upon micelle formation while the transmitted-light intensity stays constant. Upon further decompression into the micellar region both the scattered-light intensity and the transmitted-light intensity do not change much until they drop sharply as the solution reaches its bulk phase transition at MCP. The micelle-containing solution is referred to as the micellar solution, in contrast to the homogeneous solution observed upon micelle decomposition or the two-phase solution observed upon a bulk phase separation.

In this work, CP, MCP, and MP are measured in a small high-pressure variable-volume cell equipped with transmitted- and scattered-light intensity probes, with a borescope for visual observation of the phase transitions, and with pressure and temperature probes accurate to within ±2 bar and ±0.1 °C, respectively. The experimental temperature range in this work is 20−180 °C, and the pressure range is up to 1600 bar.

In a typical experiment, a known amount of polymer and solvent is loaded into the cell to achieve a desired polymer concentration, which is then brought to and maintained at a desired pressure and temperature, high enough for the polymer to form a homogeneous molecular solution, for about 1 h prior to taking TLI and SLI data using transmitted-light and scattered-light detectors (TL and SL D). A simplified schematic of

Table 1. Polymers Used in This Work

polymer	short name	M_n[a]	PDI[b]	reference[c]
polystyrene	S(37)	36.8	1.02	this work
polybutadiene	B(9)[d]	8.8	1.04	ref 8
	B(38)	38.2	1.05	this work
polystyrene-*block*-polybutadiene	S−B(5−5)[d]	5.4−5.35	1.03	ref 8 for 0.5 wt %; this work for 0.1 wt %
	S−B(9−9)[d]	9.4−9.0	1.03	ref 8 for 0.5 wt %; this work for 3.3 wt %
	S−B(15−13)[d]	15.0−13.0	1.05	this work
	S−B(37−36)	36.8−35.9	1.01	this work
	S−B(16−9)	15.5−9.4	1.02	this work
	S−B(28−14)[d]	28.4−13.6	1.03	ref 8
	S−B(37−13)	36.8−12.9	1.03	this work
	S−B(38−113)	37.8−113.4	1.01	this work
polystyrene-*block*-polyisoprene	S−I(11−10)[d]	11.5−10.5	1.04	ref 8
	S−I(37−37)	36.8−37.4	1.02	this work
	S−I(37−14)	36.8−14.3	1.02	this work
	S−I(9−23)	9.0−23.0	1.01	ref 8 for CP; this work for MCP and MP

[a] M_n = number-average molecular weight (kg/mol). [b] Polydispersity index = M_w/M_n; M_w = weight-average molecular weight. [c] Original source of tabulated data. [d] Purchased from Polymer Source, Inc.

the experimental setup is shown in Figure 3. A detailed description of the apparatus and experimental procedure can be found in Winoto et al.[7] In this work, attempts to reproduce CP, MCP, and MP for different cell loads suggest that the measured data are reproducible to within 30 bar. The micelle diameters estimated from the light-scattering data are reproducible to within 20%, as reported in ref 7, and accurate to within 23%.

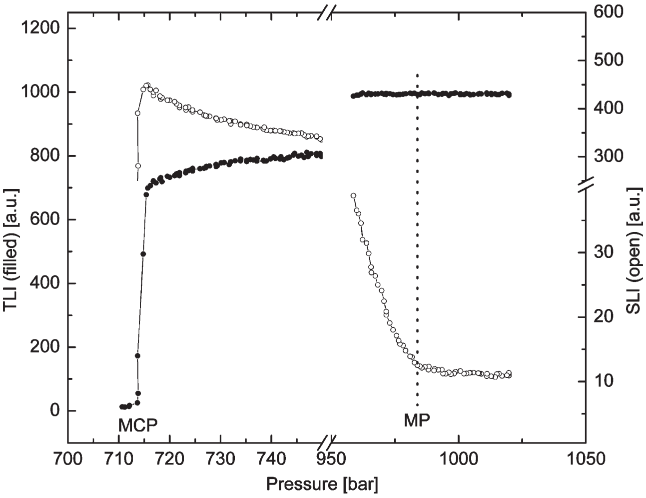

Figure 2. Typical transmitted-light intensity (TLI, filled circles) and scattered-light intensity (SLI, open circles) traces upon decreasing pressure of a homogeneous random solution, which show the micellization pressure (MP) and the micellar cloud pressure (MCP).

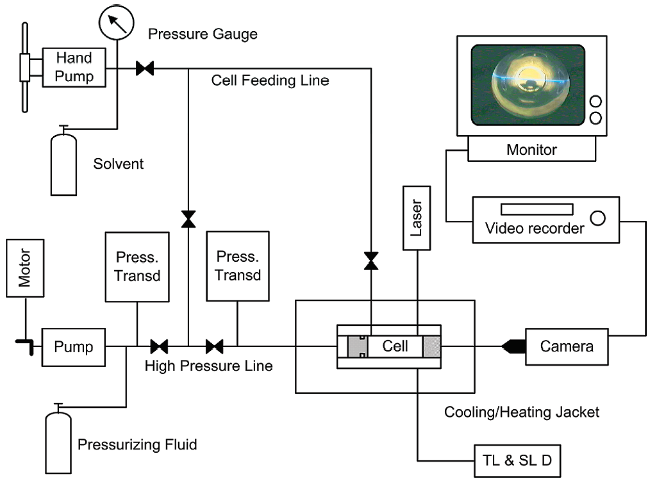

Figure 3. A simplified schematic of the apparatus.

Computational Model. A version of statistical associating fluid theory referred to as SAFT1[14] was demonstrated to represent the cloud points of homopolymers and diblock copolymers in propane.[8] SAFT1 parameters used in this work are the same as those previously derived from experimental CP data for polystyrene,[15] polydienes, and their diblock copolymers in propane, without further adjustment.[8] These SAFT1 parameters were demonstrated to represent the cloud pressure of diblock copolymers in the absence of micelles.[8] SAFT1-calculated data are presented as curves in all figures, unless stated otherwise.

Results and Discussion

All new experimental results obtained in this work are presented in Tables S1−S8 in the Supporting Information. They are analyzed in the following sections for copolymer concentration and molecular weight effects, diene type and solvent type effects, and styrene/diene block ratio effects.

Copolymer Concentration Effect. An example shown in Figure 4a (replotted in this work for a 0.5 wt % solution of S−B(9−9) in propane on the basis of experimental data from ref 8) illustrates cloud pressure (CP) as a function of temperature for a small symmetric diblock and its corresponding homopolymers. This example brings out a subtle but significant change of slope of the diblock CP curve at low temperatures, which may suggest the onset of micellization at the micellization end point (MEP; the highest temperature of the micellar region, around 39 °C in this case). One way to verify this hypothesis would be to extend the experimental temperature range to very low temperatures, which is doable but not practical. An alternative approach is to increase the copolymer concentration, which should increase the CP and enlarge the micellar region by shifting MEP to higher temperatures. The result of this approach shown in Figure 4b confirms our hypothesis: a 3.3 wt % copolymer solution is found to exhibit a large micellar region and a distinct MEP around 100 °C (a low temperature limit of the CP curve). Despite the significant differences in CP and MP, both micellar cloud pressure (MCP) curves nearly coincide, the first clue that MCP may not depend much on the copolymer concentration, at least for dilute solutions (below the critical copolymer concentration).

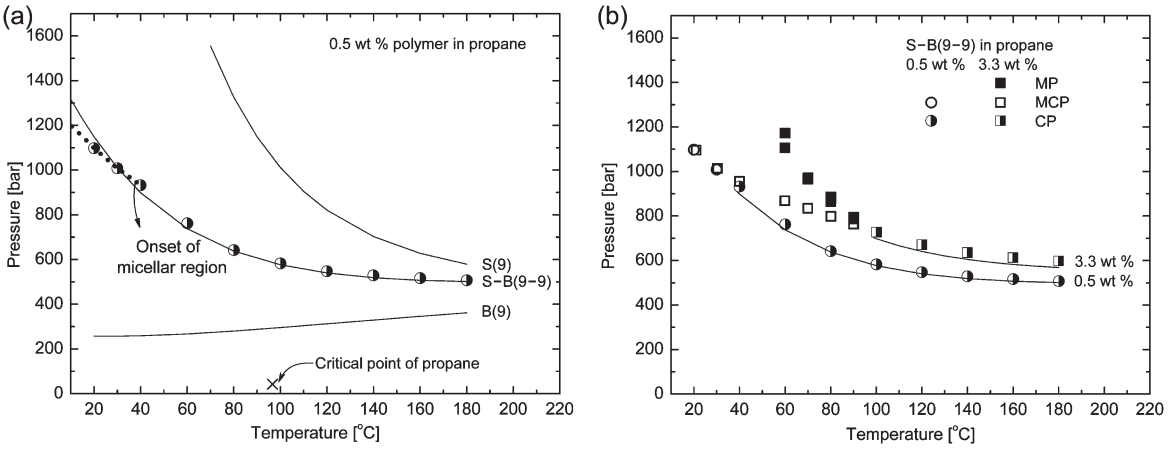

Figure 4. CP and MCP of S−B(9−9) in propane for (a) 0.5 wt % copolymer (this figure also shows the corresponding homopolymers in propane) and (b) both 0.5 and 3.3 wt % copolymer in propane including MP for 3.3 wt % solution; MCP for 0.5 wt % (open circles) and 3.3 wt % (open squares) overlap below 40 °C.

This reassuring finding is further explored for a larger diblock, S−B(37−36) in propane, at two copolymer concentrations, 0.1 and 0.5 wt %. Figure 5 confirms that its MCP is quite insensitive to such a concentration shift (the circles and triangles nearly coincide), which is in contrast to its hypothetical CP in the absence of a micellar phase, shown as dashed curves calculated from SAFT1, and to the CP data calculated and measured for S−B(5−5) also shown in Figure 5 for comparison. The CP for S−B(5−5) exhibits a measurable increase in going from 0.1 to 0.5 wt %, but Figure 5 does not tell us much about the impact of concentration on MCP because S−B(5−5) does not exhibit micellization in the temperature and concentration range investigated in this work. Conversely, even at the lower concentration of 0.1 wt % S−B(37−36) does not exhibit MEP up to 180 °C, so there are no experimental CP data available for this copolymer.

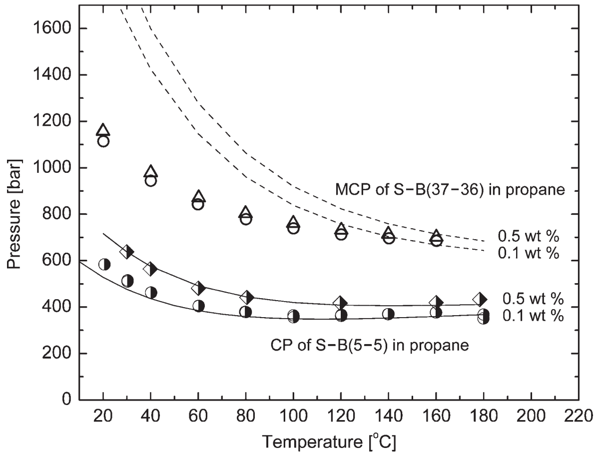

Figure 5. CP data, but not MCP data, depend on S−B(37−36) in propane concentration, as do those for S−B(5−5); MCP is insensitive to the polymer concentration shift.

Table 2. Hydrodynamic Diameter of Polystyrene-*block*-polybutadiene Micelles Insensitive to Copolymer Concentration

		micelle diameter for S−B(37−36) (std dev) (nm)	
temp(°C)	pressure (bar)	0.5 wt %	2.7 wt %
20	1400	n/a	73 (1)
60	1400	n/a	66 (3)
100	1400	n/a	57 (7)
100	1300	62 (2)	59 (12)
100	1200	n/a	67 (9)
100	900	73 (1)	71 (2)

Similar to the micellar cloud pressure (MCP), the hydrodynamic micelle diameter is found to be insensitive to the copolymer concentration. For example, the micelle diameters measured for the 0.5 and 2.7 wt % solutions of S−B(37−36) in propane are around 60−70 nm as shown in Table 2. The stronger scattered-light intensity measured for the higher concentration reflects a greater number of micelles, but an average micelle size does not change much. The micelle diameters presented in Table 2 are not systematic or complete enough to draw any general conclusions, but they seem to increase with decreasing pressure and temperature. Let us stress however that, while reproducible, the measured micelle diameter changes are essentially within experimental error.

Copolymer Molecular Weight Effect. The phase diagrams of two propane solutions of nearly symmetric copolymers that differ in molecular weight, S−B(15−13) and S−B-(37−36), both at 0.5 wt % copolymer, are shown side by side in Figure 6 to illustrate the extent to which the copolymer molecular weight itself can impact the micellization (MP) and bulk phase transitions (CP and MCP).

Similar to increasing copolymer concentration discussed in the previous section, increasing copolymer molecular weight increases the micellar region and shifts the MEP to

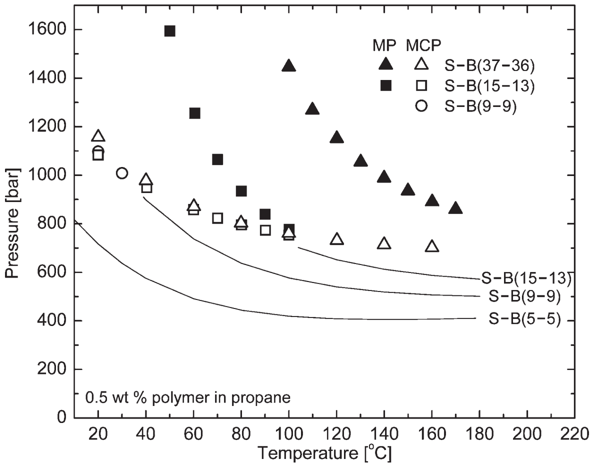

Figure 7. Effects of molecular weight on phase behavior; MCP (open triangles, open squares, and open circles) overlap; the calculated CP curves terminate at MEP.

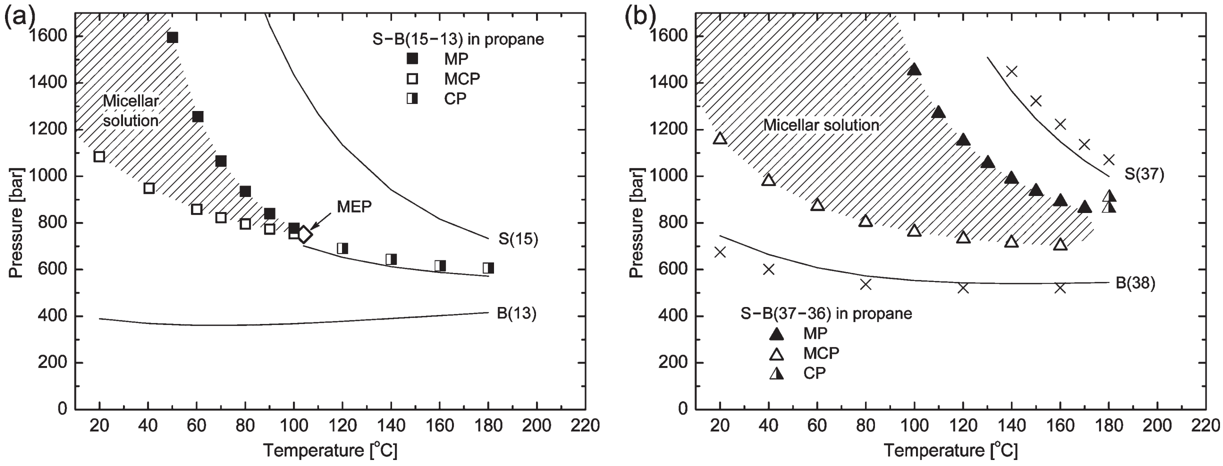

Figure 6. Phase behavior in propane for 0.5 wt % (a) S−B(15−13) and (b) S−B(37−36) along with their corresponding homopolymer cloud points; ×: experimental cloud pressure for homopolymers.

higher temperatures. The MEP of S−B(15−13) is about 104 °C, as shown in Figure 6a, while that of S−B(37−36) is above 180 °C, beyond our experimental window, as shown in Figure 6b. Efforts to measure its MCP at 180 °C led to two points (half-filled triangles) that are a bit off, most likely due to a slight but reproducible thermal decomposition of the diblock, but they are both shown in Figure 6b for completeness.

An attempt at summarizing the molecular weight effects on the CP (SAFT1 curves represent experimental points, which are not shown for clarity), MP (filled points), and MCP (open points) for symmetric S−B (5−5), (9−9), (15−13), and (37−36) is presented in Figure 7. This summary confirms that all the MCP curves nearly coincide, which means that the onset of the bulk phase separation of the micellar solution (measured as the micellar cloud pressure, MCP) is insensitive to the copolymer molecular weight. However, the micellization end point (MEP; the low-temperature limit of the CP curves) temperatures drastically increases with increasing molecular weight, as do the non-micellar cloud pressures (CP) and the micellization pressures (MP), which happens to coincide with increasing homopolymer cloud pressures upon increasing molecular weight.

Diene Type Effect. Figure 7 suggests that the micellar region of symmetric S−B diblocks in propane, measured by their MEP, starts to appear within our experimental window at a total molecular weight of about 18 kg/mol, that is for S−B (9−9). In other words, a minimum molecular weight for S−B symmetric diblocks to form micelles at or above the ambient temperature is about 18 kg/mol. One way to lower this minimum, and to expand the micellar region at the same molecular weight, is to use a corona that has a higher affinity to propane, for example, an isoprene corona instead of the butadiene corona. This is because isoprene methyl branches increase the polymer interaction energy with the propane.[16] In order to confirm and illustrate this hypothesis, we use a pair of S−I diblock copolymers in propane roughly corresponding in size to the pair of S−B diblocks shown in Figure 7. Phase diagrams for these S−I diblocks are shown in Figure 8. For S−I(11−10), the MEP is about 138 °C, which is much higher than that of both S−B(9−9), 39 °C, and S−B(15−13), 104 °C, which bracket its molecular weight.

For the record, the hydrodynamic micelle diameters for the S−I diblocks shown in Figure 8 are found to be comparable to those for the S−B diblocks, within experimental error, for example around 50−70 nm for S−I(37−37) and around 60−70 nm for S−B(37−36), which means that the diene type does not seem to affect the micelle size much.

Solvent Effect. As mentioned earlier, reducing the S−B-(37−36) concentration to 0.1 wt % (as shown in Figure 5) was not enough to reduce the MEP temperature into the experimentally accessible window, where the copolymer is

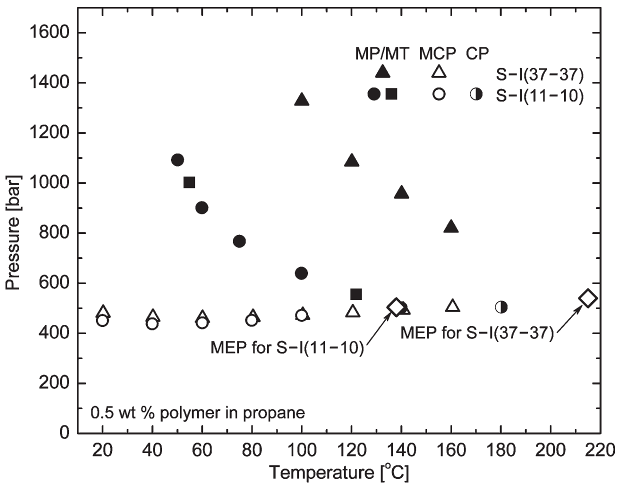

Figure 8. Phase behavior of S−I diblock copolymers in propane.

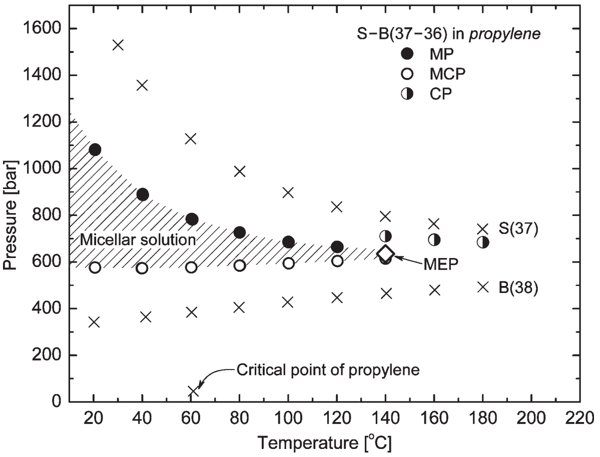

Figure 9. Phase behavior of 0.5 wt % S−B(37−36) in *propylene* along with its corresponding homopolymers in *propylene*; ×: experimental cloud pressure for homopolymers.

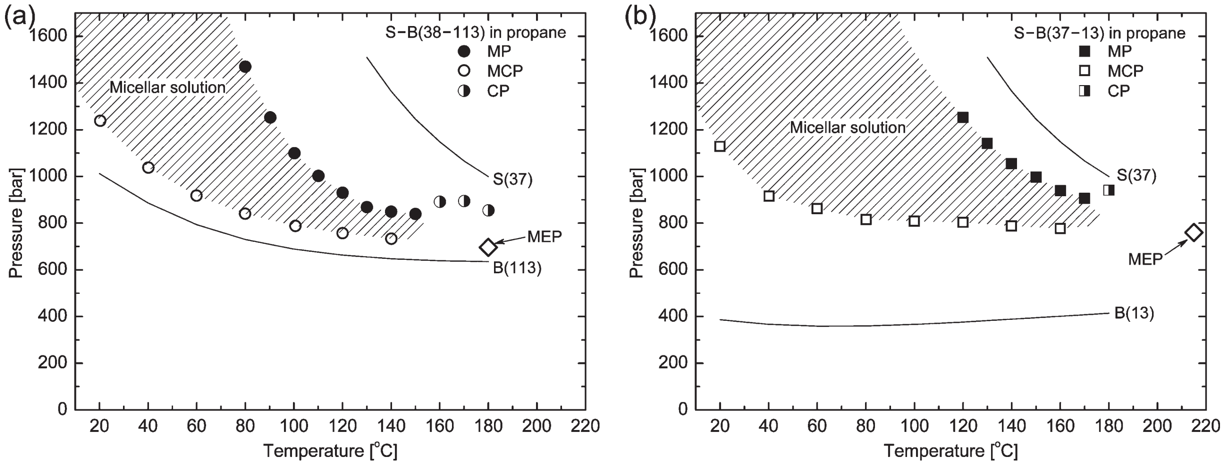

Figure 10. Phase behavior of 0.5 wt % S−B copolymers in propane: (a) S/B block ratio of 1:3 and (b) S/B block ratio of 3:1 (note that the smaller diblock exhibits a greater micellar region, in contrast to Figure 6).

thermally stable. An alternative approach is to replace propane by a better solvent for both blocks, for example by *propylene*, as a better solvent should reduce MP and MCP and hence shift the MEP to lower temperatures. Propylene is a better solvent than propane due to its $\pi-\pi$ interactions with both blocks. An example of a phase diagram for a 0.5 wt % S−B(37−36) solution in propylene illustrated in Figure 9 confirms our hypothesis; a robust MEP in propylene is found around 140 °C. Similar to high-temperature data in Figure 6b, a slight thermal decomposition causes a discontinuity of the CP and MCP curves shown in Figure 9. It is clear from this figure that the slope of MP follows that of the solvent-phobic block (polystyrene) and the slope of MCP follows that of the solvent-philic block (polybutadiene), similar to S−B(15−13) and S−B(37−36) shown in Figure 6, indicating that styrene dominates micellization while polydiene dominates the onset of micelle aggregation and precipitation at the micellar cloud pressure (MCP).

Block Ratio Effect: Fixed Styrene Block, Variable Butadiene Block. The block ratio is defined as the ratio of the solvent-phobic block molecular weight to the solvent-philic block molecular weight, styrene/diene (S/B or S/I) in our case. In order to illustrate its effect on the diblock micellization and phase separation, three model S−B diblock copolymers are investigated. They all have nearly identical styrene blocks (37K−38K) but different butadiene blocks (13K−113K), which results in different S/B block ratios, about 1:3, 1:1, and 3:1. The MP and MCP curves for the copolymers with the lowest and the highest S/B ratios are illustrated in Figures 10a and 10b, respectively. In both cases, the diblock MCP slope corresponds to the polybutadiene CP slope, and the diblock MP slope corresponds to the polystyrene CP slope. The location of MP relative to the polystyrene CP (the gap between them) and, separately, the location of MCP relative to butadiene CP, and thus the size of each micellar phase region (the gap between MP and MCP), strongly depend on the S/B block ratio. As result, the micellar region grows and moves closer to the polystyrene CP curve as the block ratio increases (as the butadiene block size decreases), and vice versa.

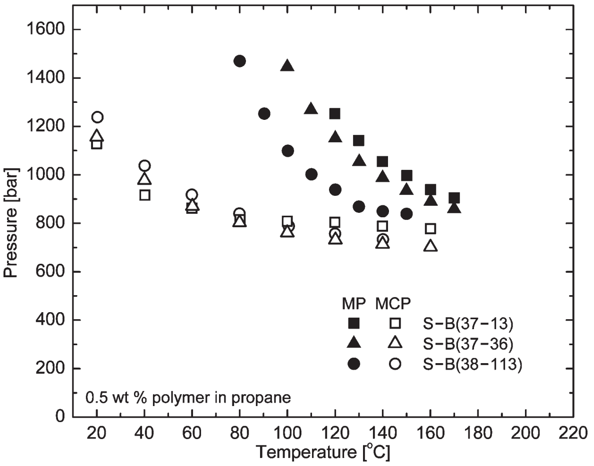

Figure 11. Micellar region (between MP and MCP) for three different S/B block ratios.

In contrast to the total molecular weight effect for the symmetric diblocks, where the micellar region grows with increasing molecular weight, for example as shown in Figure 6, the micellar region for asymmetric diblocks can shrink upon increasing molecular weight. For example, a smaller diblock S−B(37−13) exhibits a greater micellar region than a larger diblock S−B(38−113), as shown in Figure 10. This turns out to be a consistent trend, as illustrated in Figure 11 for all three diblocks with similar styrene blocks, including the symmetric S−B(37−36). Namely, for a fixed styrene block, the micellar region grows with decreasing molecular weight due to the decreasing size of the butadiene block size and hence increasing block ratio. The example shown in Figure 11 suggests that the block ratio effect on the micellization (MP curve), and hence (given similar MCP curves) on the size of the micellar region, is significant but weaker than that of the total molecular weight.

Directionally similar, but somewhat smaller, block ratio and molecular weight effects are also observed for styrene−isoprene (S−I) block copolymers, as illustrated in Figure 12 for two pairs of S−I diblocks, two smaller diblocks shown in Figure 12a, symmetric (circles/squares) and asymmetric (low S/I ratio, triangles) and two larger diblocks shown in Figure 12b, symmetric (triangles) and asymmetric (high S/I ratio, squares). Within each pair, styrene blocks are similar in size, around 10 kg/mol in Figure 12a and around 37 kg/mol in Figure 12b. The smaller asymmetric diblock shown in Figure 12a has a micellar region below our experimental temperatures, but increasing the S/I ratio, by going to the symmetric diblock, shifts the micellar region to higher temperatures, well into our experimental temperature range.

A more direct comparison of the isoprene and butadiene diblocks, to further illustrate the diene effect for asymmetric diblocks, is summarized in Figure 13. Polyisoprene exhibits lower CP than polybutadiene.[8] Therefore,

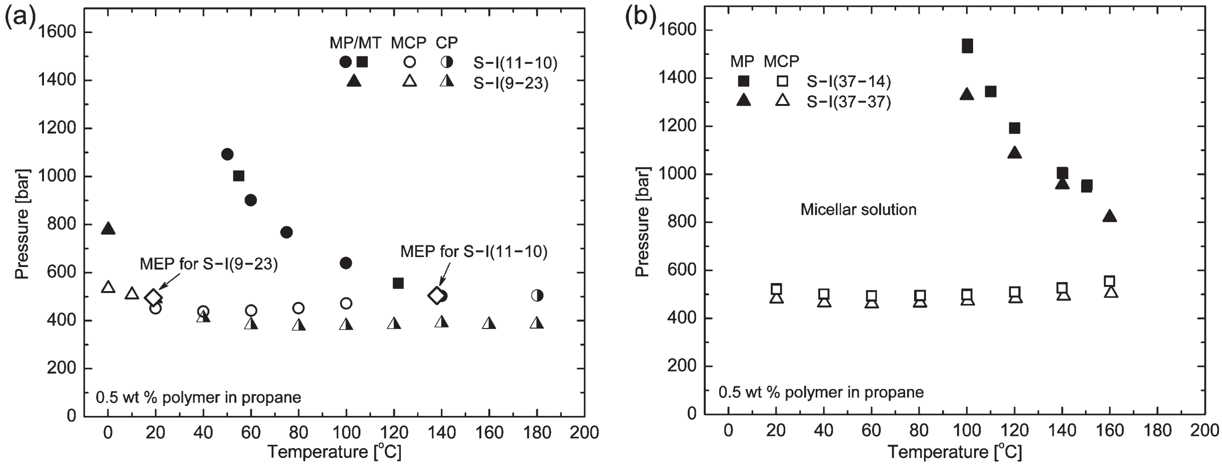

Figure 12. Micellar region (between MP and MCP) for different S/I block ratios: (a) smaller diblocks and (b) larger diblocks.

polystyrene-*block*-polyisoprene exhibits substantially lower micellar cloud pressure (MCP) than polystyrene-*block*-polybutadiene. For example, the MCP for S−I(37−14) and S−I(37−37) varies from 500 to 600 bar, while that for S−B(37−13) and S−B(37−36) varies from 700 to 1200 bar, as illustrated in Figure 13. Evidently, the diene type significantly affects the copolymer MCP. This is because the micellar cloud pressure is reminiscent of the more soluble, corona-forming diene block; its molecular weight has a negligible effect, at least in this range.

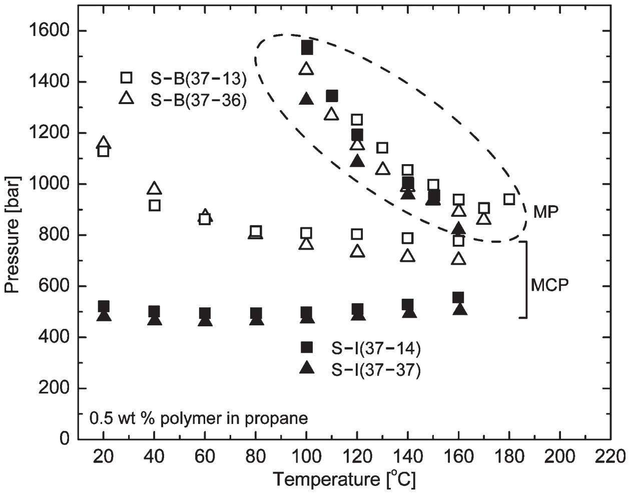

Figure 13. Diblock copolymers with identical styrene blocks exhibit similar micellization pressures (MP).

Equally interesting, Figure 13 shows that the micellization of all diblocks with the same styrene block of 37 kg/mol, regardless of diene type and size, occurs around the same micellization pressure (MP) curve. This is consistent with our earlier observation for the symmetric diblocks that MP is reminiscent of the styrene homopolymer cloud pressure (CP). Since the MP curves are close, regardless of the diene type, while the S−I MCP curves lie at lower pressures, the S−I micellar region (between the MP and MCP curves) is larger than that of the corresponding S−B, but both MCP curves are insensitive to the copolymer molecular weight.

The block ratio effect on the CP shown in Figure 12a cannot be systematically explained with experimental data alone, but it can be illustrated with approximate SAFT1 calculations for a series of model polystyrene-*block*-polydiene copolymers with a fixed styrene block but increasing diene block. The calculated CP results, hypothetically in the

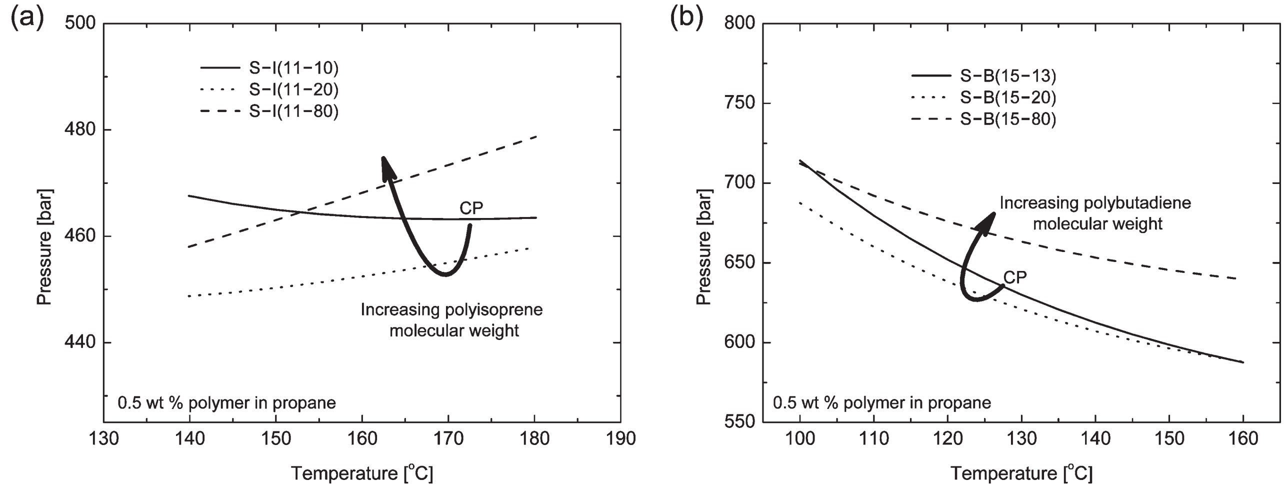

Figure 14. Nonmonotonic effects of increasing diene block (decreasing block ratio) on the cloud pressure (CP; SAFT1-calculated) of (a) polystyrene-*block*-polyisoprene and (b) polystyrene-*block*-polybutadiene.

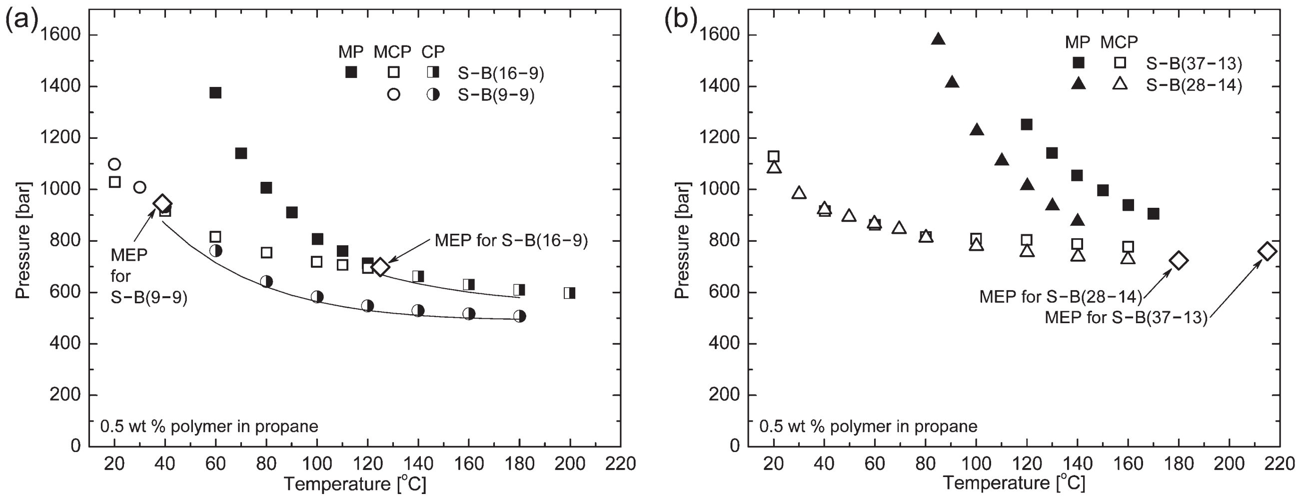

Figure 15. Micellar region (between MP and MCP) for different S/B block ratios: (a) smaller diblocks; (b) larger diblocks; MEP estimated from MP, MCP, and CP data via (a) interpolation or (b) extrapolation.

absence of micellization,[8] are shown in Figure 14a for polystyrene-*block*-polyisoprene and in Figure 14b for polystyrene-*block*-polybutadiene. In reality, these calculated CP results are always above the MEP temperature, except for S−B-(15−13), whose MEP is about 104 °C. Such SAFT calculations may not be very accurate in absolute terms, for example to pinpoint the crossover temperatures and pressures, but the trends shown in Figure 14 can help explain the nonmonotonic CP block ratio dependence, including the CP slope changes.

Specifically, Figure 14a illustrates that increasing the isoprene block from 10 to 20 (solid to dotted curve) at a constant styrene block not only shifts CP to lower pressures but also changes its slope from UCST-type (decreasing; upper critical solution temperature) to LCST-type (increasing; lower critical solution temperature). However, increasing further the isoprene block from 20 to 80 (dotted to dashed curve) increases the CP as the total molecular weight dominates the block ratio effect. A similar nonmonotonic block ratio effect is illustrated for polystyrene-*block*-polybutadiene in Figure 14b.

Table 3. Hydrodynamic Micelle Diameter (in nm) for Diblocks Differing in Butadiene Block

		micelle diameter for 0.5 wt % polymer (std dev) (nm)	
temp (°C)	pressure (bar)	S−B(37−13)	S−B(38−113)
20	1400	55 (3)	109 (14)
60	1400	54 (1)	131 (8)
60	1000	60 (3)	122 (4)
100	1000	65 (3)	104 (n/a)

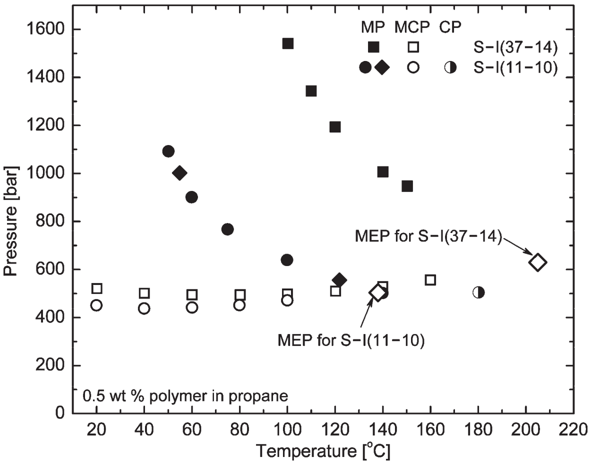

Figure 16. Micellar region (between MP and MCP) for different S/I block ratios.

The slope changes shown in Figure 14, from negative (decreasing) for styrene-rich diblocks, such as S−I(11−10), to less negative or positive (increasing) for diene-rich diblocks, such as S−I(11−80), are not surprising. They are consistent with the findings documented in ref 8, namely, that the diblock CP approaches the polystyrene CP, and its negative slope, for the styrene-rich diblocks, and it approaches the polydiene CP, and its positive slope, for the diene-rich diblocks. This is because the diblock CP is roughly a weighted average of the corresponding block-forming homopolymers.

For the record, Table 3 illustrates the extent of an expected increase in micelle diameter upon increasing the butadiene block at a constant styrene block.

Block Ratio Effect: Fixed Diene Block, Variable Styrene Block. Block ratios can also be changed by varying the molecular weight of the polystyrene block, examples of which are shown in Figure 15 for four S−B copolymers with different S/B ratios (a pair of smaller styrene blocks on the left and a pair of larger styrene blocks on the right). Similar examples for two S−I copolymers differing in molecular weight and block ratio are shown in Figure 16.

The results shown in Figures 15 and 16 lead to conclusions that are consistent with those for the variable diene block discussed in the previous section. First, increasing the S/B or S/I block ratio leads to a larger micellar region, primarily by shifting the MP curve to higher pressures. Second, the MCP curve is weakly affected by the block ratio.

For the record, increasing the styrene block at a constant butadiene block, for example in going from S−B(28−14) to S−B(37−13), increases the hydrodynamic micelle diameter approximately from 49 to 65 nm at 100 °C and 1000 bar.

Qualitative Analysis of MP Slope. All diblock copolymer solutions examined in this work exhibit a negative MP slope, where MP decreases with increasing temperature. This is because MP is reminiscent of the core-forming homopolymer, polystyrene in our case, which exhibits an upper critical solution temperature (UCST) behavior resulting in a negative CP slope. However, there can be diblock solutions that exhibit a positive MP slope,[2,3] for example block copolymers whose core-forming (solvent-phobic) block exhibits a lower critical solution temperature (LCST) phase behavior resulting in a positive CP slope.

Both types of phase diagrams are qualitatively illustrated in Figure 17, one with a negative MP slope (on the left) and one with a positive MP slope (on the right). For both types of systems, increasing the cloud pressure (CP) shifts MEP to higher temperatures, thus increasing the size of the micellar region. Normally, CP increases with increasing molecular weight and with increasing (solvent-phobic/solvent-philic) block ratio. In dilute solutions, below the critical copolymer

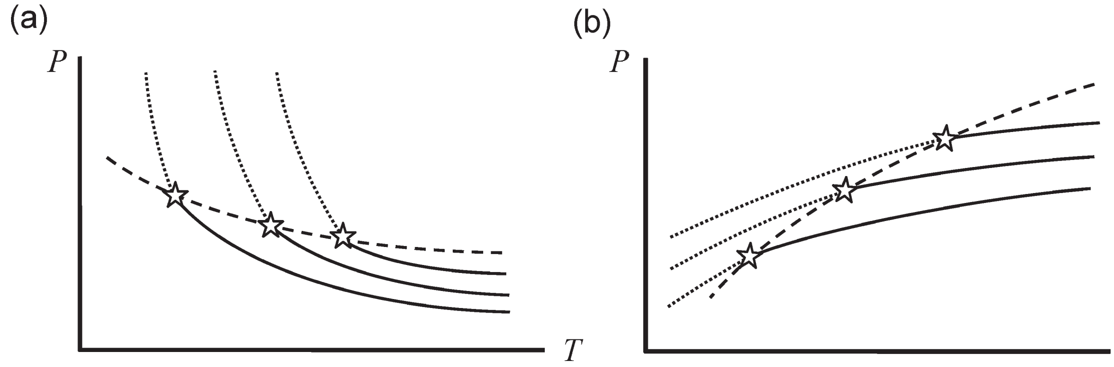

Figure 17. Qualitative phase diagram of diblock copolymers in selective solvent with MP (dotted curves) having (a) negative slope and (b) positive slope: dashed curves, MCP; solid curves, CP; stars, MEP.

concentration, CP also increases with increasing concentration.

Conclusion

Compressible solutions of styrene–diene copolymers, such as polystyrene-*block*-polybutadiene and polystyrene-*block*-polyisoprene in propane or propylene, are found to exhibit a robust micellar region that grows in pressure–temperature coordinates with increasing copolymer concentration, molecular weight, and styrene/diene block ratio. This happens because, while the micellization pressure strongly increases with increasing copolymer concentration, molecular weight, and styrene/diene block ratio, the micellar cloud pressure (the pressure at which the micelles aggregate and precipitate from solution) is largely insensitive to these variables. In other words, somewhat counterintuitively, none of the polymer and solution properties investigated, e.g., the block size, the block ratio, and the copolymer concentration, seems to affect the copolymer separation from solution in the micellar region.

Acknowledgment. This work is funded by a National Science Foundation Grant CTS-0625338 at the University of Wyoming. Part of this research was done at Oak Ridge National Laboratory's Center for Nanophase Materials Sciences, which was sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy, through User Project CNMS2006-114.

Supporting Information Available: Tables of data. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Loh, W. In *Encyclopedia of Surface and Colloid Science*; Hubbard, A., Ed.; Marcel Dekker: New York, 2002; p 802.
(2) Zhou, S.; Chu, B. *Macromolecules* **1998**, *31*, 7746–7755.
(3) Buhler, E.; Dobrynin, A. V.; DeSimone, J. M.; Rubinstein, M. *Macromolecules* **1998**, *31*, 7347–7355.
(4) Triolo, R.; Triolo, A.; Triolo, F.; Steytler, D. C.; Lewis, C. A.; Heenan, R. K.; Wignall, G. D.; DeSimone, J. M. *Phys. Rev. E* **2000**, *61*, 4640–4643.
(5) Triolo, A.; Triolo, F.; Celso, F. L.; Betts, D. E.; McClain, J. B.; DeSimone, J. M.; Wignall, G. D.; Triolo, R. *Phys. Rev. E* **2000**, *62*, 5839–5842.
(6) Colina, C. M.; Hall, C. K.; Gubbins, K. E. *Fluid Phase Equilib.* **2002**, *194–197*, 553–565.
(7) Winoto, W.; Adidharma, H.; Shen, Y.; Radosz, M. *Macromolecules* **2006**, *39*, 8140–8144.
(8) Tan, S. P.; Winoto, W.; Radosz, M. *J. Phys. Chem. C* **2007**, *111*, 15752–15758.
(9) Winoto, W.; Tan, S. P.; Shen, Y.; Radosz, M.; Hong, K.; Mays, J. W. *Macromolecules* **2009**, *42*, 3823–3826.
(10) Hadjichristidis, N.; Pitsikalis, M.; Pispas, S.; Iatrou, H. *Chem. Rev.* **2001**, *101*, 3747–3792.
(11) Uhrig, D.; Mays, J. W. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 6179–6222.
(12) Hattam, P.; Gauntlett, S.; Mays, J. W.; Hadjichristidis, N.; Young, R. N.; Fetters, L. J. *Macromolecules* **1991**, *24*, 6199–6209.
(13) Mays, J. W.; Hadjichristidis, N.; Fetters, L. J. *Macromolecules* **1984**, *17*, 2723–2728.
(14) Adidharma, H.; Radosz, M. *Ind. Eng. Chem. Res.* **1998**, *37*, 4453–4462.
(15) Tan, S. P.; Meng, D.; Plancher, H.; Adidharma, H.; Radosz, M. *Fluid Phase Equilib.* **2004**, *226*, 189–194.
(16) Pan, C.; Radosz, M. *Ind. Eng. Chem. Res.* **1998**, *37*, 3169–3179.