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Nanostructure of Solid Precipitates Obtained by Expansion of Polystyrene-*block*-Polybutadiene Solutions in Near Critical Propane: Block Ratio and Micellar Solution Effects

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Abstract

In contrast to incompressible liquid solutions, compressible near-critical solutions of block copolymers allow for controlling rapid structure transformations with pressure alone. For example, when dissolved in near-critical propane, polystyrene-*block*-polybutadiene can form a random molecular solution at high pressures, a micellar solution at moderate pressures, and a solvent-free precipitate at low pressures. In contrast to the unstructured virgin copolymer, such a propane-treated precipitate rapidly self assembles toward structures characteristic of equilibrated block copolymers, such as lamellae, spheres or cylinders, which depend on the block ratio rather than on the decompression rate or temperature, at least within the rate and temperature ranges investigated in this work. At lower temperatures, however, say below 40 °C, glass transition of the styrene-butadiene diblocks can inhibit independent structure formation while crystallization of their hydrogenated-butadiene analogs can preserve the micellar-solution structure.

Keywords

TEM; block copolymer; supercritical solution; self-assembly; crystallization

Introduction

Block copolymers are known to self assemble and form nanophase-separated materials. One of the most common model systems used to understand nanostructures formed by block copolymers is polystyrene-*block*-diene, for which nearly pure and uniform samples can be obtained from living anionic polymerization.^{1, 2} There are numerous references and reviews^{3, 4} concerning characterization of such materials, processed either in melt or in liquid solution, all of which are incompressible. For example, Huang et al.⁵ demonstrated

that the microstructure of polystyrene-*block*-polybutadiene thin films is changed dramatically when changing the casting conditions. Others studied structure of thin films formed of polystyrene-*block*-polybutadiene-*block*-polystyrene⁶ and polystyrene-*block*-polybutadiene blends,⁷ just to mention a few of many examples of previous work on such incompressible systems.

A more recent alternative to processing block copolymers and equilibrating their structures is to use compressible near-critical, sub- or supercritical, solvents. In contrast to the conventional liquid solvents, such near-critical solvents sensitively respond to changes in pressure. Therefore, one can control their capacity and selectivity, and hence copolymer micellization and precipitation, with pressure alone, without having to rely on temperature as the only micellization variable (for a given solvent). Such a near-critical fluid approach offers unique advantages, for example, a much faster equilibration due to higher mass transfer rates, a much better structure control, and moderate temperatures that prevent thermal degradation of the copolymer, not to mention an easy solvent removal. For example, Winoto et al.⁸ demonstrated reversible micelle formation for model polystyrene-*block*-polybutadiene in near-critical propane. They also found that increasing the concentration or molecular weight of the polymer increases the cloud pressure and micellization pressure.⁹ However, there are no data to understand the structure of the solid material precipitated from compressible near-critical solutions, and how it may be affected by the copolymer composition and decompression path.

Therefore, the goal of this paper is to characterize qualitatively the structure of model diblock copolymers, polystyrene-*block*-polybutadiene (S-B), precipitated from near-critical propane using TEM. Specifically, we aim at understanding how the copolymer block ratio, say S/B from 1/3 to 3, and the decompression path can affect the nanostructure of the precipitated material. For example, we want to explore isothermal paths at different temperatures, low and high decompression rates, from 0.25 bar/s to 1,000 bar/s, paths that cross micellar versus molecular solution alone, and decompression paths that may involve crystallization transition for a hydrogenated-butadiene analog, such as S-hB.

Experimental Section

Materials

The homopolymers and diblock copolymers used in this work were synthesized at Oak Ridge National Laboratory via living anionic polymerization using well-established vacuum line techniques, as documented in recent reviews.^{1, 2} Briefly, the diblocks were prepared by sequential monomer addition, with sampling of the first block (polystyrene). Microstructure of the polybutadiene was controlled through the choice of solvent and use of polar additives, tertiary amines and ethers.^{10, 11} 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 was determined using nuclear magnetic resonance (NMR). Hydrogenation of the polybutadiene blocks was performed at 85°C and 600–800 psi using rhodium complex catalysts.¹² The polymers were again characterized by multi-detector SEC after hydrogenation to assure lack of degradation, including built-in light scattering and viscosity detectors. The extent of hydrogenation was measured by NMR.

The polybutadiene samples are at least 90% of the 1,4-addition type for both homopolymer and diblock copolymer. Therefore, their hydrogenated polybutadiene analogs are crystallizable; their degree of hydrogenation is at least 99%. The molecular weights and polydispersity indices of all samples are provided in Table 1, including their short names.

The propane used in this work without further purification is 99% grade from Matheson Tri-gas, Inc.. Osmium tetroxide, Ruthenium tetroxide, and Spurr resin were purchased from Electron Microscopy Sciences.

Experiments

The onset of bulk phase transition in polymer solutions, the “cloud point,” is characterized by the pressure at which a homogenous solution turns cloudy upon decreasing pressure at constant temperature, and hence referred to as the cloud pressure (CP). At a given temperature, the onset of micelle formation and decomposition in a homogenous and random molecular block copolymer solution is characterized by the micellization pressure (MP). The nanosized-micelle-containing phase is referred to as the micellar solution, in contrast to the molecular solution observed following micelle decomposition. If a bulk phase transition, such as polymer precipitation, originates from micellar solution instead of from molecular solution it is referred to as the micellar-cloud pressure (MCP).¹³ In this work, the label CP will be limited to fluid phase transitions, with no crystalline solid present. If crystallization and melting are observed they will be referred to by their full names, implying the crystallization temperature (normally measured at the onset of solid formation) and melting temperature (normally measured at the end of solid disappearance) at a constant pressure.

The cloud, micellization, and crystallization-melting transitions are measured in a small high-pressure variable-volume cell coupled with transmitted- and scattered-light intensity probes and with a borescope for visual observation of the phase transitions. This apparatus is equipped with pressure and temperature measurement to within ± 2 bar and ± 0.1 °C. A temperature change rate of 0.4 °C/min is used for measuring the crystallization-melting temperatures.

In a typical experiment, a known amount of polymer (0.5 wt %) and solvent is loaded into the cell, which is then brought to and maintained at a desired pressure and temperature, at which polymer can be dissolved. A detailed description of the apparatus and experimental procedure has been reported previously.^{8, 14} In this work, attempts to reproduce data at the same concentration and condition, but for a different cell load, leads to cloud and micellization pressures to within 30 bars. Following a complete phase transition and solid precipitation experiment, the solvent is vented and the S-B precipitate is collected for TEM characterization.

When we refer to rapid or slow decompression, rapid is taken to mean approximately 1000 bar/s and slow is taken to mean approximately 0.25 bar/s. Also, it is worth noting that during this decompression step, the pressure drops to the solvent vapor pressure, rather than the atmospheric pressure. This means that the polymer co-exists with the solvent at its vapor pressure for a few minutes (up to 20 minutes in some cases) as the cell is cooled and detached from the unit. Then the solvent is vented completely from the cell, and the precipitate collected.

A MRC-MXTL Ultramicrotome is used to obtain ultrathin sections (50–70 nm) for transmission electron microscopy (TEM). First, the S-B precipitate samples are stained using the vapor of a 4% aqueous osmium tetroxide (OsO_4) solution for 4 hours. In the case of S-hB, samples are stained using the vapor of a 5% aqueous ruthenium tetroxide (RuO_4) solution for 3 hours. Next, the stained samples are placed in Spurr resin, and the resin is cured at 60 °C overnight. Then, sections are cut at room temperature using a diamond knife. Finally, the sections are placed on 400 mesh uncoated copper grids for TEM. Since the polybutadiene domain is preferentially stained by OsO_4 , it appears dark whereas the

polystyrene domain appears light. TEM was conducted on Hitachi H-7000 electron microscope operated at 75kV accelerating voltage.

Results and Discussions

In order to explore how the block ratio can affect the structure of the precipitated polymer, we use three diblock samples that have nearly the same styrene block but differ in the size of the butadiene block and hence the block ratio, S/B, from about 3 to about 1/3, namely S-B (37-13), S-B (37-36), and S-B (38-113). For all three samples, the precipitate is formed by rapid decompression of a micellar solution in propane at 40 °C. The decompression paths and resulting TEM images are shown in Figure 1. The first image on the left suggests a dominant light (styrene) phase with distributed dark domains (butadiene), perhaps irregular styrene cylinders with a butadiene cores. By contrast, the second image in Figure 1 for a roughly symmetric diblock suggests a dark background with distributed light domains, perhaps butadiene cylinders with styrene cores. The third image in Figure 1 also has dark background formed by the dominant butadiene block, but this time with light spherical domains formed by the styrene block, which are styrene cores with butadiene coronas that form the continuous phase. In other words, consistent with the literature data for polymer melts,¹⁵ the core and corona can flip depending on the block ratio (the smaller block is likely to form the core).

This is in contrast to a dilute micellar solution in propane where, due to a higher affinity of butadiene to propane relative to styrene, one always expects the styrene core, regardless of the micelle shape. This means that the precipitated structure forms independently of the micellar solution structure. It can have a styrene core similar to the solution structure, as for S-B (38-113), or it can have an inverted structure, with a butadiene core, as for S-B (37-13). These results suggest that, despite the rapid decompression, the solid precipitate structure depends on the block ratio, rather than on the solution structure. This means that the structure of the precipitated polymer can rearrange upon crossing the MCP. If this is the case, does it make a difference whether one decompresses a micellar solution versus a random molecular solution, MCP versus CP?

In order to address this question, one has to find a temperature above the micellar end point (MEP, which corresponds to the critical micelle temperature) where MCP becomes CP, and hence where we can decompress a random solution directly into a two-phase region without crossing a micellar solution region. Since the three samples shown in Figure 1 likely decompose (at 180 °C or so) before they reach MEP, we have to use other materials with a lower MEP, for example a smaller diblock with a high S/B ratio or a diblock similar in size but with a low S/B ratio.

The process outlined above is explained with an example of a quantitative phase diagram shown in Figure 2 for a small diblock with a high S/B ratio, namely S-B (16-9). This diblock exhibits MEP (open diamond) within our experimental temperature range, at around 125 °C, with a micellar-solution region at lower temperatures (between the circles and squares) and a molecular-solution region at higher temperatures (above the squares and above the filled circles). Therefore, we can accomplish two distinct decompression experiments, for example, one at 40 °C that crosses the micellar-solution region, along path A, and one at 140 °C that does not cross the micellar-solution region, along path B. The background fill qualitatively suggests the state of the system, random molecular solution where the decompression starts, likely spherical micelles in the micellar solution (between the squares and open circles), and an unknown structure of the precipitated solid at low pressures. We want to know if the rapid decompression allows enough time for structural rearrangement, and hence if there is a difference between the two paths A and B.

Rapid decompression of the S-B (16-9) solution in propane leads to two images presented in Figure 3, one on the left obtained along path A at 40 °C, crossing a micellar solution region, and one on the right obtained along path B at 140 °C, from a molecular solution. Apart from minor image quality differences, both structures seem to be nearly identical: layered, evenly distributed dark and light phases. The fact that the precipitate structures are the same regardless of the solution structure (micellar versus molecular) suggests that the history of the polymer before crossing the CP has little impact on the precipitate structure, at least at the decompression rates (1,000 bar/s) and post-decompression solvent exposure (at ambient vapor pressure) used in this work.

Since S-B (16-9) forms lamellae structures (shown in Figure 3) only, we want to test this hypothesis using a much larger copolymer of opposite asymmetry (a small styrene block and a large butadiene block), which is likely to form spherical structures. Examples of TEM images for such a copolymer, namely S-B (38-113), are shown in Figure 4, both obtained for solid samples precipitated by rapid decompression of dilute propane solutions. The image on the left is for the sample precipitated from a micellar solution at 40 °C. The image on the right is for the sample precipitated from a molecular solution, above MEP, at 170 °C. Both images shown in Figure 4 suggest nearly identical spherical structures with styrene cores (light dots) and butadiene coronas (dark background). This confirms that the structure of the precipitated solid is independent of the starting solution state, micellar or molecular, and independent on the temperature, at least in this range, and at least if the decompression path does not involve crystal or glass transition.

A simple way to probe for the effect of crystallinity is to use a crystallizable analog of one of the amorphous S-B diblocks for which we already have TEM structures. Such an analog can be obtained by selective hydrogenation of the straight-chain butadiene block alone, for example hydrogenation of the amorphous S-B (37-36) used in the experiments shown in Figure 1 toward a crystallizable S-hB (37-37). Figure 5 shows TEM images obtained for the S-hB (37-37) samples collected via two different paths. For the image on the left, the path was to crystallize the copolymer by cooling the solution from 85 to 40 °C at 900 bar, then to decompress the solution (Path 1). This image displays a somewhat layered structure, with no recognizable pattern. In this figure, the light and dark do not correspond to the different blocks of the copolymer as before; they simply reflect the thickness of the sample at that point, the darker the thicker. The image on the right corresponds to an isothermal decompression at 85 °C followed by cooling at ambient pressure (Path 2). This image suggests a collection of small spheres perhaps reminiscent of micelles in the micellar solution. It is not clear why the unhydrogenated analog produced different, worm-like structures (shown in the middle of Figure 1) along the same path. However, by comparing the structures in Figure 5, we observe that they are drastically different. Path 2 produces a solid precipitate that may have retained the micellar nano-structure, while path 1 allows for a rearrangement characteristic of crystalline structure.

One way to explain this difference between the two paths is on the basis of the chain mobility in supercritical solution. At high pressures, high solvent densities allow for fast rearrangement of the copolymer chains. Therefore, if we crystallize the copolymer at such high pressures, the chains of the copolymer have more mobility, and can thus rearrange in an energetically favorable crystalline form. However, if we first lower the pressure, and hence drastically reduce the solvent density to the point of precipitating the copolymer, before crystallizing it, the chain mobility is much lower. This prevents the rearrangement to the crystalline structure, and thereby can preserve the micellar structure from the solution. The difference between the hydrogenated and unhydrogenated analogs may be due to corona crystallization that preserves the spherical micellar structure. This conjecture calls for

additional experiments aimed at more direct evidence, which is an objective of an upcoming project.

To further determine how collection process may affect the solid structure, we need to investigate the rate effects and the temperature effects. It turns out that the decompression rate itself does not change the structure of the precipitated much. This is demonstrated in Figure 6 for S-B (38–113), which also includes an image of the virgin polymer (on the left). The images of solid precipitates collected by slow (middle) and rapid (right) decompression are similar, black butadiene phase with light styrene cores, despite the drastically different decompression rates, by a factor of 4,000. Both structures are quite different from that of the virgin polymer, which suggests that the treatment in near-critical fluid solution can change the structure, but the decompression rate, at least within our range, does not seem to make much of a difference.

Therefore, for the same copolymer S-B (38–113), we select a constant high decompression rate and probe for temperature sensitivity along decompression paths that are isothermal but systematically differ in temperature. Such paths at temperatures from 20 to 140 °C are shown in the lower left corner of Figure 7. Figure 7 shows the corresponding structure images of solid precipitates. All structures in the temperature range of 40–140 °C turn out to be spherical with a styrene core, which suggests that, in this range, the decompression temperature does not affect the structure of the solid precipitate. By contrast, the structure obtained at 20 °C is quite different and reminiscent of amorphous solid, which may be due to a glass transition of the styrene blocks in going from 40 to 20 °C.

While this work is aimed at fundamental understanding of expansion-driven nanophase transitions and structures using simple but uniform and well-defined model block copolymers in a compressible solvent, these findings inspire future research on other, more practical systems, such as amphiphilic block copolymers used for drug delivery,¹⁶ processed in near-critical solvents, for example, research aimed at understanding how the block-ratio and crystallizability may impact the precipitate structure upon expansion. It goes without saying that much more work on model systems is needed to quantify such effects.

Conclusion

When dissolved in near-critical propane, polystyrene-*block*-polybutadiene can form a random molecular solution at high pressures, a micellar solution at moderate pressures, and a solvent-free precipitate at low pressures. In contrast to the unstructured virgin copolymer, such a propane-treated precipitate rapidly self assembles toward structures characteristic of equilibrated block copolymers, such as lamellae, spheres or cylinders, which depend on the block ratio rather than on the decompression rate or temperature, at least within the rate and temperature ranges investigated in this work. At lower temperatures, say below 40 °C, glass transition of the styrene-butadiene diblocks can inhibit independent structure formation while crystallization of their hydrogenated-butadiene analogs can preserve the micellar-solution structure.

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References

1. Hadjichristidis N, Pitsikalis M, Pispas S, Iatrou H. Polymers with Complex Architecture by Living Anionic Polymerization. *Chemical Reviews*. 2001; 101(12):3747–3792. [PubMed: 11740920]
2. Uhrig D, Mays JW. Experimental techniques in high-vacuum anionic polymerization. *Journal of Polymer Science Part A: Polymer Chemistry*. 2005; 43(24):6179–6222.
3. Hamley, IW. *The Physics of Block Copolymers*. Oxford University Press; New York: 1998.
4. Legge, NR.; Holden, G.; Schroeder, HE. *Thermoplastic Elastomers*. Hanser Publishers; Munich: 1987.
5. Huang H, Hu Z, Chen Y, Zhang F, Gong Y, He T, Wu C. Effects of Casting Solvents on the Formation of Inverted Phase in Block Copolymer Thin Films. *Macromolecules*. 2004; 37:6523–6530.
6. Kim G, Libera M. Morphological Development in Solvent-Cast Polystyrene-Polybutadiene-Polystyrene (SBS) Triblock Copolymer Thin Films. *Macromolecules*. 1998; 31:2569–2577.
7. Guo R, Huang H, Chen Y, Gong Y, Du B, He T. Effect of the Nature of Annealing Solvent on the Morphology of Diblock Copolymer Blend Thin Films. *Macromolecules*. 2008; 41:890–900.
8. Winoto W, Adidharma H, Shen Y, Radosz M. Micellization Temperature and Pressure for Polystyrene-block-polyisoprene in Subcritical and Supercritical Propane. *Macromolecules*. 2006; 39(23):8140–8144.
9. Winoto W, Tan SP, Shen Y, Radosz M, Hong K, Mays JW. 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. *Macromolecules*. 2009; 42(18):7155–7163.
10. Hattam P, Gauntlett S, Mays JW, Hadjichristidis N, Young RN, Fetters LJ. Conformational characteristics of some model polydienes and polyolefins. *Macromolecules*. 1991; 24:6199–6209.
11. Mays JW, Hadjichristidis N, Fetters LJ. Characteristic ratios of model polydienes and polyolefins. *Macromolecules*. 1984; 17:2723–2728.
12. Hadjichristidis N, Xenidou M, Iatrou H, Pitsikalis M, Poulos Y, Avgeropoulos A, Sioula S, Paraskeva S, Velis G, Lohse DJ, Schulz DN, Fetters LJ, Wright PJ, Mendelson RA, García-Franco CA, Sun T, Ruff CJ. Well-Defined, Model Long Chain Branched Polyethylene. 1. Synthesis and Characterization. *Macromolecules*. 2000; 33:2424–2436.
13. Winoto W, Tan SP, Shen Y, Radosz M, Hong K, Mays JW. High-Pressure Micellar Solutions of Polystyrene-block-polybutadiene and Polystyrene-block-polyisoprene in Propane Exhibit Cloud-Pressure Reduction and Distinct Micellization End Points. *Macromolecules*. 2009; 42(11):3823–3826.
14. Chan AKC, Hemmingsen PV, Radosz M. Fluid-Liquid and Fluid-Solid Transitions of Tetracontane in Propane. *Journal of Chemical & Engineering Data*. 2000; 45(2):362–368.
15. Khandpur AK, Foerster S, Bates FS, Hamley IW, Ryan AJ, Bras W, Almdal K, Mortensen K. Polyisoprene-Polystyrene Diblock Copolymer Phase Diagram near the Order-Disorder Transition. *Macromolecules*. 1995; 28(26):8796–8806.
16. Tyrrell Z, Shen Y, Radosz M. Fabrication of micellar nanoparticles for drug delivery through the self-assembly of block copolymers. *Progress in Polymer Science*. 2010; 35:1128–1143.
17. Winoto W, Radosz M, Hong K, Mays JW. Amorphous polystyrene-block-polybutadiene and crystallizable polystyrene-block-(hydrogenated polybutadiene) solutions in compressible near critical propane and propylene – Hydrogenation effects. *Journal of Non-Crystalline Solids*. 2009; 355:1393–1399.

Figure 1. TEM images of S-B (37-13), S-B (37-36), and S-B (38-113) upon rapid decompression from left to right, respectively. The scale is the same in all three images and is shown only on the left. The phase diagrams of each polymer (0.5 wt%) in propane are shown for reference, and are replotted on the basis of data taken from Winoto *et. al.*⁹ The vertical line in each represents the collection path used.

Figure 2. Precipitation from micellar solution (A) and from molecular solution (B) of 0.5 wt% polystyrene(16k)-*b*-polybutadiene(9k) in propane. Open squares, open circles, and closed circles represent the micellization pressure, micelle-cloud pressure, and cloud pressure, respectively. The open diamond represents the micellization end point. Replotted on basis of data taken from Winoto *et. al.*⁹

Figure 3. TEM image of S-B (16-9) rapidly precipitated from micellar (40 °C) and molecular (140 °C) solution, respectively. The scale is the same for both images and is shown only on the left.

Figure 4.

TEM image of S-B (38–113) rapidly precipitated from micellar (40 °C) and molecular (170 °C) solution, respectively. The scale is the same for both images and is shown only on the left. Phase diagram provided of each polymer (0.5 wt%) in propane for reference, and is replotted on the basis of data taken from Winoto *et. al.*⁹

Figure 5.

TEM comparison of solid precipitate of S-hB (37-37) from crystallization/decompression (path 1) versus from decompression/cooling (path 2) from left to right, respectively. The scale is the same in both images and is shown only on the left. Phase diagram provided for reference, and is replotted on the basis of data taken from Winoto *et. al.*¹⁷

Figure 6.

TEM images of S-B (38–113) virgin polymer and solid precipitates from slow decompression, and rapid decompression, from left to right, respectively. The scale is the same for all three images and is shown only on the left.

Figure 7.

TEM comparison of solid precipitate of S-B (38–113) from rapid decompression at 20 °C, 40 °C, 60 °C, 100 °C, and 140 °C from left to right, top to bottom, respectively. Phase diagram provided for reference, and is replotted on the basis of data taken from Winoto *et al.*⁹ The vertical lines represent the collection path used.

Table 1

Polymers Used in This Work

polymer	abbreviation	Mn ^a (x 1000 g/mol)	polydispersity index ^b
Polystyrene- <i>block</i> - polybutadiene	S-B (16-9)	15.5-9.4	1.02
	S-B (37-13)	36.8-12.9	1.03
	S-B (37-36)	36.8-35.9	1.01
	S-B (38-113)	37.8-113.4	1.01
Polystyrene- <i>block</i> - poly(hydrogenated polybutadiene)	S-hB (37-37)	36.8-37.1	1.01

^a Mn = number-averaged molecular weight

^b Polydispersity index = M_w/M_n ; M_w = weight-averaged molecular weight