

Ordering Transition of Block Copolymer Films

Abraham Arceo and Peter F. Green*

Department of Chemical Engineering and Texas Material Institute, The University of Texas at Austin, Austin, Texas 78712

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It is well-known that a bulk, symmetric, A-*b*-B diblock copolymer forms a lamellar morphology, with period L , below an order–disorder transition (T_{ODT}) temperature, for $\chi N < 10.5$; χ is the Flory–Huggins interaction parameter and N is the degree of polymerization of the copolymer. The ordering temperatures of poly(styrene-*b*-methyl methacrylate) (PS-*b*-PMMA) thin film diblock copolymers of thickness $h \leq 2L$, supported by SiO₂/Si substrates, in vacuum environments, are shown to increase beyond the bulk, and estimates of the temperature shifts indicate that small changes of χN are associated with unusually large shifts of the transition temperature. Further, we find that in compressed CO₂ environments, these films are ordered at temperatures where the films are disordered in vacuum (or air) environments. This latter observation is of particular significance because small molecule diluents, including compressed CO₂, are known to decrease the ODT of the bulk (enhanced miscibility).

Introduction

A-*b*-B diblock copolymers have diverse applications that range from adhesives to optoelectronics. Below an order–disorder transition (ODT) temperature, they phase separate into A-rich and B-rich phases.^{1–9} Phase separation is accompanied by a minimization of the interfacial area of contact between dissimilar phases resulting in a reduction of the enthalpy, which is balanced by a reduction of the conformational entropy of the chains, largely connected with stretching, and of the translational entropy. The connectivity between the A and B blocks prohibits large-scale macrophase separation, so phase separation length scales occur on the order of nanometers, determined by the size of the chains. Below the ODT temperature, spatial arrangement of the phases exhibits varying symmetries, body centered cubic, hexagonal, lamellar, and bicontinuous gyroid structures.

The phase diagram is determined by the fraction of A monomers, f , that compose the chain and by χN , where χ is the Flory–Huggins interaction parameter and N is the total degree of polymerization of the chain ($\chi \propto 1/T$, where T is the temperature).^{1,2} For symmetric diblock copolymers ($f \sim 0.5$) the sample undergoes an isotropic to lamellar transition when $(\chi N)_{\text{bulk-ODT}} > 10.5$. In the so-called strong segregation limit, where $\chi N \gg 10.5$, the interlamellar spacing $L \propto \chi^{1/6} N^{2/3}$. This is the regime where the A-rich and B-rich phases are relatively pure and the width of the interfacial region between them $d \ll L$.

In thin films, interactions between the A, or B, segments and the external interfaces (free surface or substrate) determine the local segmental concentration profile near the interfaces. In typical situations one component is preferentially attracted to an external interface.^{4–11} Due largely to the connectivity between the blocks and to the preferential affinity of an interface for one of the blocks, the effective interface potential of a block copolymer thin film is an oscillating function of film thickness,

h . The locations of the minima in the free energy denote the stable film thicknesses. This means that the free surface of a sufficiently thin film of thickness h , supported by a substrate, will remain flat, stable, if h corresponds to the location of any minima in the free energy function. If the same component is attracted to the free surface and to the substrate, the free energy minima are located at film thicknesses $h = nL$, where n is an integer. For the asymmetric wetting case (different component at the free surface and at the substrate) the minima are located at film thicknesses $h = (n + 1/2)L$. For films whose thicknesses do not meet the appropriate stability criteria, associated with a minimum, a discontinuous layer of thickness L develops at the free surface. The topography is typically composed of “islands” or “holes,” depending on how far the film thickness deviates, δh , from the appropriate stability criterion. The “islands” and “holes” account for the excess thickness, δh , and are indicative of self-organization, or order, within the film.

The interlamellar spacing of an A-*b*-B diblock copolymer may be influenced by blending with another homopolymer, or by blending with another A-*b*-B copolymer of a different molecular weight. In the case of copolymer/homopolymer mixtures, the homopolymer chains will segregate within the appropriate copolymer domains to minimize the enthalpy, provided they are sufficiently short. Consequently, the domain spacing increases. If the homopolymer chains are too long then the entropy prohibits incorporation within the domains and they form a separate phase.^{11–15} The addition of an A-*b*-B diblock copolymer may also affect the domain spacing because the junctions of these chains segregate to the junctions of the host chains to minimize the unfavorable A–B interactions. Because the segmental density of the chains must remain spatially uniform, the domain spacing must adjust to accommodate any differences in chain length between the constituents to meet this criterion. In such cases the interlamellar spacing is dictated by the average molecular weight of the mixture.

In recent years there has been interest in understanding the effect compressible solvents, such as CO₂, have on the phase behavior of homopolymer blends and block copolymers.^{16–20} The solvent quality of CO₂ may be tuned by manipulating the density (pressure and temperature) of the fluid. Generally, with small molecule diluents, supercritical solvents or slightly selective organic solvents, the system exhibits a tendency toward phase mixing, reducing the ODT. The tendency of the copolymer toward phase mixing in CO₂, like other small molecule diluents, is due to the screening of unfavorable enthalpic interactions between the A and B blocks and a lowering of the interfacial tension between the A and B-blocks.^{21–26}

In the present study we examine the influence of a SiO_x/Si substrate on the ordering of thin film symmetric PS-*b*-PMMA copolymers with thicknesses less than twice the lamellar period ($h < 2L$) in (1) vacuum environments at 170 °C and (2) compressed CO₂ environments at 170 °C. We show that whereas bulk copolymer mixtures are phase mixed in a vacuum (or air), the Si/SiO_x substrate induces significant order in thin films, shifting the ODT within a range $0.24 < [(\chi N)_{\text{bulk-ODT}} - (\chi N)_{\text{film-ODT}}]/(\chi N)_{\text{bulk-ODT}} < 0.26$, which would correspond to an increase of the ordering temperature of up to 250 deg. In compressed CO₂ the shift of the ordering transition temperature is larger, not smaller!

Experimental Section

Mixtures of two symmetric poly(styrene-*b*-methyl methacrylate) (PS-*b*-PMMA) copolymers of molecular weights $M_n = 20\,500$ ($N = 201$, molecular weight distribution $M_w/M_n = 1.06$) and $65\,500$ ($N = 650$, $M_w/M_n = 1.14$) were blended in different proportions to prepare samples of varying number average degrees of polymerization, from $N = 201$ to 650 . The fractions of the PS component of the copolymers were $f_{\text{PS}} = 0.51$ and $f_{\text{PS}} = 0.54$, for the long and short chains, respectively. These copolymers were standards purchased from Polysciences Inc.

The value of the PS–PMMA Flory–Huggins interaction parameter, χ , at 170 °C is 0.0368¹⁶ and because N in this study ranged from 201 to 650, the values of χN for the samples ranged from 7.4 to 25.8 at this temperature. The mixtures were dissolved in toluene and spin cast onto polished silicon wafers. A native oxide layer of approximately 1.5 nm resided on the Si substrate, as measured by ellipsometry. Different thicknesses, h , of each mixture were spin cast onto the substrates, Si/SiO_x. The thicknesses ranged from 10 to 40 nm; i.e., all samples are of thickness $h < 2L$, where $6\text{ nm} < L < 30\text{ nm}$ (actual values of L are shown later in Figure 3 for different values of N). A series of films were scored at the center and then annealed under vacuum at 170 °C for approximately 16 h, which provided more than sufficient time for the topographies to develop. Generally, techniques such as transmission electron microscopy or scattering measurements are reliably used to demonstrate order or disorder in these systems. However, because the existence of the topography is indicative of order (phase segregation), analysis involving scanning force microscopy (SFM) is a viable alternative.

The samples were subsequently quenched to room temperature after processing and then scanned using scanning force microscopy (SFM) in the contact mode. A second series of samples of the same thickness range was processed under a CO₂ atmosphere (Matheson 99.9999% purity) at 170 °C and a pressure of 145 bar, enclosed within a fixed volume, high-pressure cell. After a processing period of 24 h, the cell was

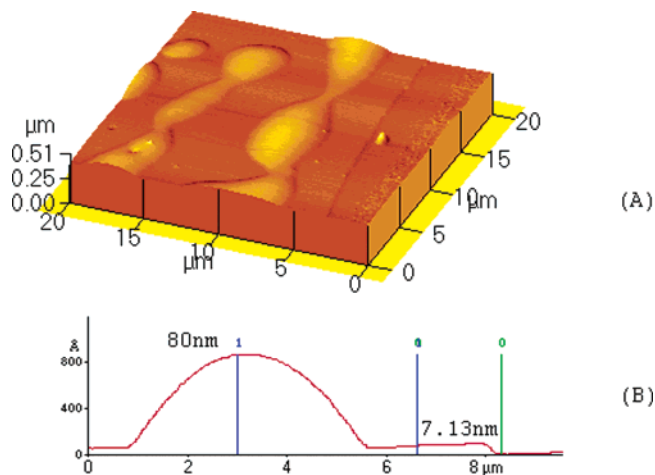


Figure 1. SFM image of a 20 nm film of $N = 208$ annealed at 170 °C (a). Droplets reside on the brush layer of thickness $L/2 = 7.14\text{ nm}$, as indicated by the accompanying line scan in part (b). The sizes of the droplets bear no relation to L .

cooled to $\sim 25\text{ °C}$, depressurized to ambient pressure at a rate of 1 bar/s, and then scanned using contact mode scanning force microscopy.

Results and Discussion

Diblock Copolymer in a Vacuum at 170 °C. A series of samples were annealed under vacuum conditions at a temperature of 170 °C, which corresponds to the bulk order–disorder transition of a sample with $N = 292$. In a vacuum (or air), PS is preferentially attracted to the free surface because of its lower surface tension at this temperature, whereas PMMA is preferentially attracted to the SiO_x/Si substrate. A common feature of all the films is that a “brush” layer of copolymer is formed at the SiO_x/Si substrate after annealing.^{3–11} The brush layer represents the self-organization of a single layer of copolymer chains; hence its thickness is $L/2$ (Figure 1), where L is the interlamellar spacing. Droplets reside on this brush layer and the dimensions of the droplets bear no relation to L . The chains within the droplet lack the order (large number of PS–PMMA contacts) of the chains in the brush.

Previous studies of thin films of the $N = 200$ ($M_w = 20\,500$) copolymer sample were conducted by Limary and Green.^{9,26–27} This sample is disordered in the bulk, and in thin films a brush layer of thickness $h = L/2 = 7\text{ nm}$ resides on the Si/SiO substrate. Beyond this brush layer the sample is disordered as droplets, whose dimensions bear no relation to L and are much larger than L , reside on its surface. To understand this, it suffices to mention that thin liquid films on a substrate exist in a morphologically stable, unstable or metastable state. The stability is determined by an effective interface potential (free energy of interaction per unit area), which depends on film thickness.^{8,9} For this copolymer thin film, the interface potential is characterized by a damped oscillatory profile with a large minimum at $h = L/2$, which corresponds to a stable film thickness (asymmetric wetting).⁹ This layer is one-half of the interlamellar spacing because the PS component is preferentially attracted to the free surface and PMMA to the substrate.^{3–10} It is the thickness of the brush layer. The local shape of the effective interface potential at the relevant film thickness provides information about the stability of a film, and when the curvature of the profile is negative, transient spinodal patterns develop; otherwise holes develop throughout the surface of the film. These topographies eventually form droplets on the brush layer.

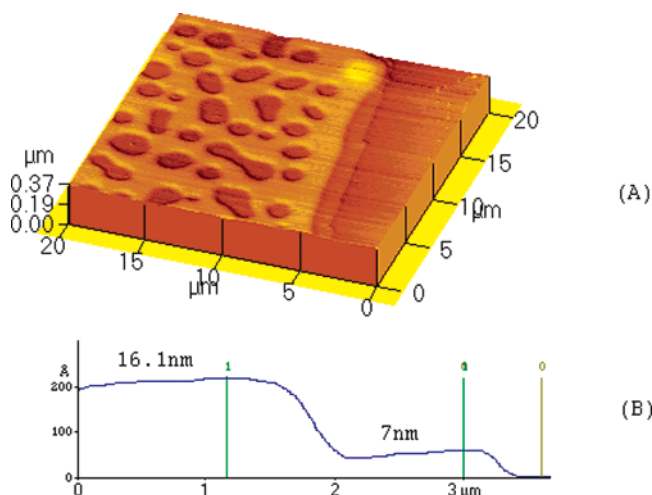


Figure 2. SFM image of the topography of a sample of $N = 216$ ($\chi N = 7.94$) ($N = 208$) with thickness $h = 20$ nm annealed at 170 °C (a). The line scan (b) indicates that the second layer is ordered and of thickness twice that of the brush layer.

In fact, on the basis of the shape of the potential, no stable, ordered, layer is expected above this first (brush) layer; droplets are expected and are observed on this brush layer. Sufficiently thick films are kinetically stable.

The topography of the film illustrated in Figure 1 is readily rationalized in terms of a single minimum in the damped oscillatory profile, as was done by Limary et al. for the copolymer of $N = 201$ ($M = 20\,500$ g/mol). Specifically, the brush layer would correspond to a lamellar thickness of $L/2$; the droplets on the layer are expected on the basis of the shape of the effective interface potential at the relevant film thickness. In fact, films of N equal to and less than 210 exhibited similar behavior, formation of a single brush layer on which droplets resided.

Samples composed of chains with degrees of polymerization of $N > 216$ were ordered throughout; terraces (islands or holes) of height L resided on the brush layer of thickness $L/2$ in each case (Figure 2a). Figure 2b shows a typical line scan of holes in a sample of initial thickness $h = 20$ nm ($N = 216$). There the brush layer is of thickness $h_0 = 7$ nm and the second layer of height $L = 16.1$ nm. These results indicate that this sample is ordered throughout the thickness range of up to $2L$ (droplets reside on the surfaces of films with thicknesses $h > 2L$ and sufficiently thick films of h greater than $\sim 4L$ remain kinetically stable).

An estimate of the upper bound of the shift of the ODT associated with the ordering of the second layer due to the influence of the substrate may be obtained from our data. Because the $N = 210$ sample is disordered above the brush layer, an approximate range of the transition for a film of thickness $3L/2$ would be

$$7.73 < (\chi N)_{\text{film-ODT}} < 7.94 \quad (1)$$

whereas $(\chi N)_{\text{bulk-ODT}} \approx 10.5$. This would correspond to a shift of the ordering transition in relation to the bulk by $0.24 < [(\chi N)_{\text{bulk-ODT}} - (\chi N)_{\text{film-ODT}}]/(\chi N)_{\text{bulk-ODT}} < 0.26$. For the sample with $N = 216$, the bulk ODT would occur at a temperature of $T_{\text{ODT}}(\text{bulk}) = -84$ °C. The film is ordered over the thickness range of $h < 2L$ at 170 °C, indicating that the ODT may be increased as much as 254 °C (recall that $\chi \propto 1/T$). These foregoing results demonstrate that small differences in χN lead to large shifts of the ODT in temperature.

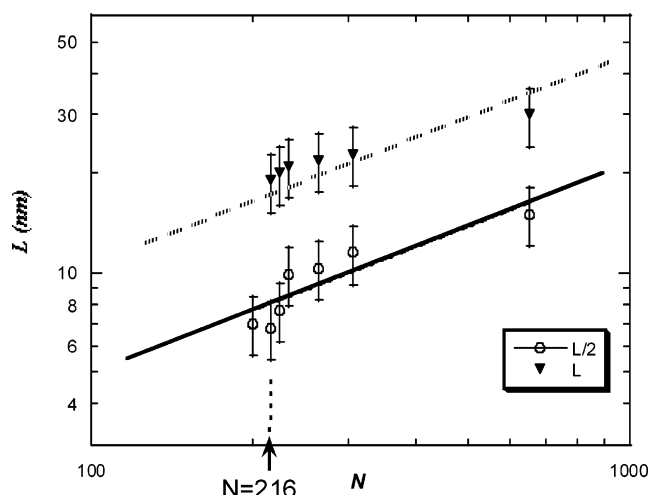


Figure 3. Chain length dependencies of interlamellar spacing obtained from the height of the topographical features (L) and from the height of the brush layer ($L/2$) are shown here. The line drawn through the data has a slope of $2/3$.

It is important to examine the average chain length dependence of the interlamellar spacings, L , in this system because it can be indicative of the extent of the degree of segregation. Numerous line scans were taken of the brush layer and of the terraces of samples of $h < 2L$. All measurements were averaged and the data plotted in Figure 3. The measurements of the brush layer thicknesses are represented by circles and those of the terraces represented by triangles. The line drawn through the data, though limited in range, has a slope of $2/3$. The $2/3$ power law is consistent with strong segregation behavior. Regardless of the slope, the main point is that samples of $N > 216$ were ordered throughout, for all these films of thickness $h < 2L$.

The increase of the order–disorder transition temperature, T_{ODT} , of the PS-*b*-PMMA (vacuum) thin films supported by SiO_x/Si substrates relative to the bulk is readily understood. PMMA exhibits a strong affinity for the oxide layer,^{3,5–11} which has the effect of excluding PS from the substrate. PS has a lower surface energy and is preferentially attracted to the free surface, though the free surface interaction is weak in comparison. The preferential interactions between PS and the free surface (air/vacuum) and between PMMA and the substrate lead to a more repulsive interaction between PS and PMMA in the vicinity of the substrate, which would correspond to a larger effective interaction parameter between PS and PMMA, $\chi_{\text{eff}}(\text{PS-PMMA}) > \chi_{\text{bulk}}(\text{PS-PMMA})$, and an associated higher T_{ODT} for the thin film.¹

The influence of the proximity of the substrate on the interactions may be better understood by considering the following. A sample of $N = 245$ ($\chi N \approx 9.07$) at the same temperature is ordered for thicknesses of up to $h = 5L/2$ (droplets form on a layer of thickness $5L/2$ for thicker films). It would therefore be anticipated that the extent to which order would be induced throughout a thick sample in the vicinity of the substrate would depend on the proximity of the χN of the sample to the bulk condition, $(\chi N)_{\text{bulk-ODT}} \approx 10.5$.

Diblock Copolymer in CO_2 at 170 °C. The effect of CO_2 on the ordering transition of the copolymers is now discussed. As mentioned above, bulk studies of PS-*b*-PMMA indicate that CO_2 should have the effect of enhancing the miscibility, i.e., lowering the ODT. We found that all thin film samples of $h < 2L$ processed in CO_2 at 170 °C and 145 bar exhibited ordering throughout, indicating the opposite behavior. We begin by showing an SFM scan of the sample of $N = 201$ in Figure 4.

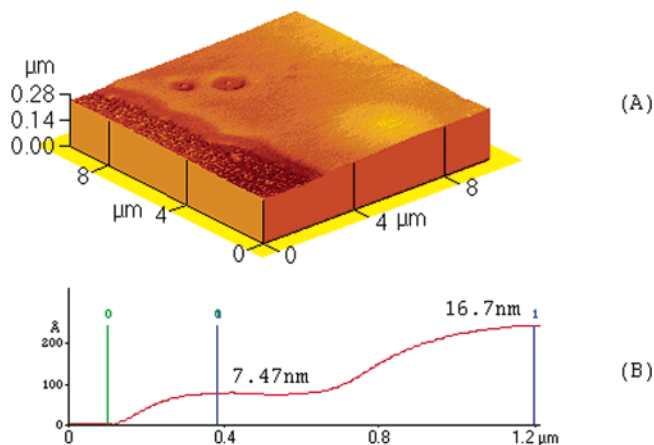


Figure 4. SFM scan of the sample of $N = 201$ and $h = 20$ nm annealed at $170\text{ }^{\circ}\text{C}$ under 145 bar of CO_2 . The line scan indicates that unlike the sample in Figure 1, annealed in a vacuum at the same temperature, both layers are ordered.

The accompanying line scan indicates that a second layer of thickness L , above the brush layer, is ordered. The surprising observation in Figure 4 is that the 20 nm film in CO_2 at $170\text{ }^{\circ}\text{C}$ is ordered throughout whereas for the same sample annealed in a vacuum at the same temperature the chains above the brush layer are disordered. The shift of the transition in relation to pure bulk PS-*b*-PMMA is at least $[(\chi N)_{\text{bulk-ODT}} - (\chi N)_{\text{film-ODT}}]/(\chi N)_{\text{bulk-ODT}} > 0.29$.

It is straightforward to rationalize the increase of the ODT temperature for the thin film Si/SiO_x/PS-*b*-PMMA/ CO_2 system over that of the bulk PS-*b*-PMMA/ CO_2 system. In the bulk, recall that whereas CO_2 preferentially interacts with the PMMA phase, CO_2 molecules are distributed throughout the PS and the PMMA phases due to entropic considerations because the molecules increase their translational entropy by residing in both PS and PMMA phases. Consequently, the relative interactions between the unlike PS and PMMA segments are mediated and the effective χ -parameter between PS and PMMA is lower, leading to a decrease of the ODT temperature.^{23,25} On the other hand, for thin films supported by a substrate that exhibits a strong preferential interaction for one component of the copolymer, the effective PS and PMMA interactions become more repulsive in the vicinity of the substrate; i.e., χ_{eff} is larger. Consequently, the ODT of the thin film Si/SiO_x/PS-*b*-PMMA/ CO_2 system is larger than that of the bulk transition temperature, T_{ODT} .

If the identical argument used above to explain the shift of the ODT temperature for the bulk PS-*b*-PMMA/ CO_2 system is applied to the thin film Si/SiO_x/PS-*b*-PMMA/ CO_2 system, then it would suggest that the ODT temperature of the Si/SiO_x/PS-*b*-PMMA/ CO_2 system should be lower than the ODT temperature of the Si/SiO_x/PS-*b*-PMMA/vacuum system. This, of course, is not the case. We might begin to understand why the ordering transition temperature of the Si/SiO_x/PS-*b*-PMMA/ CO_2 system is higher (i.e., more incompatible) by first considering the following independent observations. Regardless of the film thickness, the relative interactions between PS and CO_2 and between PMMA and CO_2 are different. In fact, the nature of the interactions between CO_2 and each of the polymers is thickness dependent; specifically, the disparity between the CO_2 -PS and CO_2 -PMMA interactions in thin films is much larger than in the bulk. The evidence of such an increasing disparity is based on CO_2 devitrification measurements of each homopolymer, supported by Si/SiO_x substrates.^{28,29} To begin with, in thin films, the T_g of a PMMA film on the Si/SiO_x

substrate increases with decreasing film thickness, whereas PS films on the same substrate exhibit the opposite trend. At a temperature of $75\text{ }^{\circ}\text{C}$, for example, a CO_2 pressure of 45 atm is required to plasticize a PS film of 100 nm whereas a pressure of approximately 42 atm is required to plasticize a PMMA film of the same thickness on the same substrate. However, for a PMMA film of 25 nm , a pressure of 15 atm is required whereas for a PS film of the same thickness on the same substrate a pressure of 34 atm , twice as large, is required to plasticize the PS film. In short, an increasing disparity of the interactions between CO_2 and PS and between CO_2 and PMMA occurs with decreasing film thickness.

Unlike the bulk, confinement to a thin film introduces entropic penalties on the configurations of the chains. This disparity of the CO_2 -PS and CO_2 -PMMA interactions over a wide temperature range leads to a difference between the compressibilities of the swollen phases. The increasing disparity between the CO_2 interactions with each phase, with decreasing h , coupled with the entropic penalties associated with the fact that one component remains strongly adsorbed to the substrate (morphological stability) leads to phase separation and the associated increase of the ODT temperature. However, if the film is morphologically unstable due to the nature of the long-range intermolecular interactions (interface potential), then the behavior would be different; dewetting and droplet formation would be expected.

Finally, it should be further emphasized that small changes in the effective interactions between copolymer components are associated with large changes in ordering temperatures because the χ -parameter has a large entropic, temperature independent, term, A , and a second term B/T ($\chi \approx A + B/T$); in polymers the magnitudes of A and B are such that large changes in T are associated with small changes in χ . Future studies should focus on quantifying the interactions between small molecules and polymer systems in thin film geometries where entropic and enthalpic effects differ considerably from bulk systems and can lead to unexpected behavior.

Conclusions

Bulk, symmetric, A-*b*-B diblock copolymers undergo an isotropic-to-lamellar transition below the ODT transition temperature (enhanced miscibility) characterized by the condition $\chi_{\text{bulk}}N > 10.5$. We have shown that thin films of PS-*b*-PMMA copolymers undergo this transition for $\chi_{\text{bulk}}N < 10.5$, a substrate induced transition. This is because interactions of PMMA with the substrate leads to a larger effective $\chi_{\text{substrate}} > \chi_{\text{bulk}}$ in the vicinity of the substrate compared to the bulk.

The important finding is that experiments conducted in the environment of a compressible fluid, which is generally expected to reduce the bulk ODT shows the opposite effect in thin films. Our results reveal that the effective ODT of this system is not only larger than the bulk but also larger than the ODT of the system in a vacuum environments. This result is particularly noteworthy because CO_2 is known to plasticize both PS and PMMA homopolymers and hence decrease their viscosities considerably. However, in this case diblock copolymers of the same polymers self-organize. The implication is that whereas it would be easy to process thin film homopolymers because of the reduced viscosity, the effective viscosity of the self-organized diblock copolymers would be much larger that one would initially anticipate. The specifics of the copolymer, substrate and solvent system should be examined to understand conditions for self-organization.

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