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ESI: Critical Role of Lattice Vacancies in Pressure-Induced Phase Transitions of Baroplastic Diblock Copolymers

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1 Compressible Self-Consistent Field Theory for Diblock Copolymer Systems

Let us consider a compressible system of diblock copolymers A-*block*-B (d) under constant temperature T and isotropic pressure P. Let n_{d} be the number of diblock copolymers, and let N_{A} and N_{B} be the number of segments of each block, respectively. The total number of segments is $N_{\mathrm{d}} = N_{\mathrm{A}} + N_{\mathrm{B}}$, and the block ratio of the A-component is $f = N_{\mathrm{A}}/N_{\mathrm{d}}$. Based on the lattice vacancy concept[1–3], we consider the free volume of the system, described as voids (v) below. This model treats voids as another component of n_{v} conceptual solvent molecules composed of a single segment ($N_{\mathrm{v}} = 1$), enabling the straightforward conversion of the classical incompressible lattice model to a compressible one. In this model, changes in the number of voids express changes in the system volume V. The average segment number density is written as $\rho_0 = (n_{\mathrm{d}}N_{\mathrm{d}} + n_{\mathrm{v}})/V$. For simplicity, we assume that all segments occupy equal volume, $v_0 = 1/\rho_0$, and polymer segments have equal Kuhn length, $a = a_{\mathrm{A}} = a_{\mathrm{B}}$, as in the usual SCF theories[4].

The compressible SCF theory with voids can be formulated in the straightforward way of the incompressible SCF theory[5]. The detailed procedure for deriving SCF equations and a free energy functional of an incompressible system is explained in references[4,6–8]. Consequently, we here outline the formulation of the compressible SCF theory.

The Hamiltonian $\mathcal{H}$ of the system is divided into the ideal chain part $\mathcal{H}_0$ and the non-bonded interaction part $\mathcal{W}$. The ideal chain part is given by $\mathcal{H}_0 = (3/2N_{\mathrm{d}}a^2)\int_0^1 ds\,(d\boldsymbol{r}_\alpha(s)/ds)^2$, where s is the counter variable from 0 to 1 scaled by the chain length, and $\boldsymbol{r}_\alpha(s)$ specifies the space curve of the α-th chain of the block copolymer. We give the dimensionless density operators at position $\boldsymbol{r}$, $\hat{\phi}_{\mathrm{A}}(\boldsymbol{r}) = (N_{\mathrm{d}}/\rho_0)\sum_{\alpha=1}^{n_{\mathrm{d}}}\int_0^f ds\,\delta(\boldsymbol{r} - \boldsymbol{r}_\alpha(s))$, $\hat{\phi}_{\mathrm{B}}(\boldsymbol{r}) = (N_{\mathrm{d}}/\rho_0)\sum_{\alpha=1}^{n_{\mathrm{d}}}\int_f^1 ds\,\delta(\boldsymbol{r} - \boldsymbol{r}_\alpha(s))$, and $\hat{\phi}_{\mathrm{v}}(\boldsymbol{r}) = (1/\rho_0)\sum_{\gamma=1}^{n_{\mathrm{v}}}\delta(\boldsymbol{r} - \boldsymbol{r}_\gamma)$ where $\boldsymbol{r}_\gamma$ expresses a local position of the γ-th void. Then, the partition function $\mathcal{Z}$ can be written as

$$\mathcal{Z} = \int \prod_{\alpha=1}^{n_{\mathrm{d}}} \tilde{\mathcal{D}}\boldsymbol{r}_\alpha \prod_{\gamma=1}^{n_{\mathrm{v}}} d\boldsymbol{r}_\gamma\ \delta(1 - \hat{\phi}_{\mathrm{A}} - \hat{\phi}_{\mathrm{B}} - \hat{\phi}_{\mathrm{v}}) \exp(-\beta\mathcal{W}) \tag{1}$$

where $\beta \equiv 1/k_{\mathrm{B}}T$, and the first functional integral over all configurations is weighted with the ideal chain part, $\tilde{\mathcal{D}}\boldsymbol{r}_\alpha \equiv \mathcal{D}\boldsymbol{r}_\alpha \exp(-\beta\mathcal{H}_0)$. The delta functional enforces the incompressibility constraint of $\hat{\phi}_{\mathrm{A}}(\boldsymbol{r}) + \hat{\phi}_{\mathrm{B}}(\boldsymbol{r}) + \hat{\phi}_{\mathrm{v}}(\boldsymbol{r}) = 1$. The non-bonded interaction part of the Hamiltonian, $\mathcal{W}$, can be written with the Flory interaction parameters, χ_{ij}, as $\beta\mathcal{W} = (\rho_0/2)\int d\boldsymbol{r}\sum_{i,j}\chi_{ij}\hat{\phi}_i\hat{\phi}_j$ where $i, j = \mathrm{A}, \mathrm{B}, \mathrm{v}$. The Flory interaction parameters are defined as $\chi_{ij} = \chi_{ji} \equiv \beta(\epsilon^*_{ii} + \epsilon^*_{jj} - 2\epsilon^*_{ij})$ where $\epsilon^*_{ij}(\geq 0)$ is the characteristic self-interaction energy between the i-th and the j-th components having a unit of [J]. In the lattice vacancy model, the interactions between the i-th components and voids are assigned zero energy, $\epsilon^*_{\mathrm{Av}} = \epsilon^*_{\mathrm{Bv}} = \epsilon^*_{\mathrm{vv}} = 0$ [J][1–3].

After the replacement of operators by field valuables and the saddle-point approximation, the partition function can be rewritten as

$$\mathcal{Z} = \int \prod_i (\mathcal{D}\phi_i\mathcal{D}\omega_i)\mathcal{D}\xi \prod_k \left(\frac{\mathcal{Q}_k^{n_k}}{n_k!}\right) \exp\left\{-\frac{\rho_0}{N_\mathrm{d}}\int d\boldsymbol{r}\left[\frac{1}{2}\sum_{i,j}\chi_{ij}N_\mathrm{d}\phi_i\phi_j - \sum_i \omega_i\phi_i - \xi\left(1 - \sum_i \phi_i\right)\right]\right\} \tag{2}$$

where $k = \mathrm{d}, \mathrm{v}$, and $\mathcal{Q}_\mathrm{d}$ and $\mathcal{Q}_\mathrm{v}$ are the partition functions for a single molecule of the diblock copolymer and the void, respectively. The field valuables, ϕ_i, ω_i, and ξ, denote the density field of the i-th component, the self-consistent field of the i-th component, and the Lagrange multiplier field. The partition function gives free energy of

$$\frac{N_\mathrm{d}F}{\rho_0 k_\mathrm{B}TV} = -\sum_k\left[\frac{N_\mathrm{d}}{N_k}\bar{\phi}_k \ln\left(\frac{N_k\mathcal{Q}_k}{N_\mathrm{d}V\bar{\phi}_k}\right)\right] + \frac{1}{V}\int d\boldsymbol{r}\left[\frac{1}{2}\sum_{i,j}\chi_{ij}N_\mathrm{d}\phi_i\phi_j - \sum_i\omega_i\phi_i - \xi\left(1 - \sum_i\phi_i\right)\right] \tag{3}$$

where $\bar{\phi}_k$ is the average volume fraction of the k-th component. The SCF equations are also derived from the partition function as follows:

$$\omega_i(\boldsymbol{r}) = \sum_j \chi_{ij}N_\mathrm{d}\phi_j(\boldsymbol{r}) + \xi(\boldsymbol{r}) \tag{4}$$

$$\phi_\mathrm{A}(\boldsymbol{r}) + \phi_\mathrm{B}(\boldsymbol{r}) + \phi_\mathrm{v}(\boldsymbol{r}) = 1 \tag{5}$$

$$\phi_\mathrm{A}(\boldsymbol{r}) = \frac{\bar{\phi}_\mathrm{d}V}{\mathcal{Q}_\mathrm{d}}\int_0^f ds\ q(\boldsymbol{r}, s)q^\dagger(\boldsymbol{r}, s) \tag{6}$$

$$\phi_\mathrm{B}(\boldsymbol{r}) = \frac{\bar{\phi}_\mathrm{d}V}{\mathcal{Q}_\mathrm{d}}\int_f^1 ds\ q(\boldsymbol{r}, s)q^\dagger(\boldsymbol{r}, s) \tag{7}$$

$$\phi_\mathrm{v}(\boldsymbol{r}) = \frac{\bar{\phi}_\mathrm{v}V}{\mathcal{Q}_\mathrm{v}}\exp\left[-\frac{1}{N_\mathrm{d}}\omega_\mathrm{v}(\boldsymbol{r})\right] \tag{8}$$

The end-segment distribution function of the diblock copolymers, $q(\boldsymbol{r}, s)$, is the solution to the modified diffusion equation of $\partial q/\partial s = (1/6)N_\mathrm{d}a^2\nabla^2 q - \omega_\mathrm{d}q$ where $\omega_\mathrm{d}(\boldsymbol{r}, s) = \omega_\mathrm{A}(\boldsymbol{r})$ for $s \in [0, f]$ and $\omega_\mathrm{d}(\boldsymbol{r}, s) = \omega_\mathrm{B}(\boldsymbol{r})$ for $s \in [f, 1]$. The initial condition is $q(\boldsymbol{r}, 0) = 1$. A second end-segment distribution function for the opposite chain end $q^\dagger(\boldsymbol{r}, s)$ satisfies the above-modified diffusion equation with a minus sign on the right-hand side and the initial condition $q^\dagger(\boldsymbol{r}, 1) = 1$. The single-molecule partition functions can be written as $\mathcal{Q}_\mathrm{d} = \int d\boldsymbol{r}\ q(\boldsymbol{r}, 1)$ and $\mathcal{Q}_\mathrm{v} = \int d\boldsymbol{r}\ \exp[-\omega_\mathrm{v}(\boldsymbol{r})/N_\mathrm{d}]$. In this study, the modified diffusion equation was solved by the pseudo-spectral method[6,9]. One-dimensional calculation cell dimensions were optimized by the valuable cell shape method[6,10]. We continued the iterative calculation until the differences of the self-consistent fields were less than 10^{-6}. Note that applications of this compressible SCF theory to copolymer systems of more complicated structures, such as linear multiblock copolymers and starpolymers, are straightforward[6,7,11–13].

The number of voids can be determined using the Sanchez-Lacombe equation of state (SL-EOS), derived based on the lattice vacancy model[1–3]. The segment volume and the segment number are written as $v^*_i = k_\mathrm{B}T^*_i/P^*_i$ and $N_i = M_i/\rho^*_i v^*_i$, where $P^*_i(= \epsilon^*_{ii}/v^*_i), T^*_i(= \epsilon^*_{ii}/k_\mathrm{B})$, and ρ^*_i are the i-th pure-component EOS parameters, and M_i is the molecular weight of the i-th component. The EOS parameters for mixtures, P^*, T^*, and ρ^* can be obtained by combining pure-component parameters. The combining rules of diblock copolymers (binary case) are given by[2,3]

$$v_0 = \frac{f}{f + (v^*_\mathrm{A}/v^*_\mathrm{B})(1-f)}v^*_\mathrm{A} + \frac{1-f}{(1-f) + (v^*_\mathrm{B}/v^*_\mathrm{A})f}v^*_\mathrm{B} \tag{9}$$

$$P^* = f^2 P^*_{\mathrm{A}} + (1-f)^2 P^*_{\mathrm{B}} + 2f(1-f)P^*_{\mathrm{AB}} \tag{10}$$

$$T^* = P^* v_0 / k_{\mathrm{B}} \tag{11}$$

$$\rho^* = \frac{1}{w_{\mathrm{A}}/\rho^*_{\mathrm{A}} + w_{\mathrm{B}}/\rho^*_{\mathrm{B}}} \tag{12}$$

where w_{A} and w_{B} are the weight fractions of A and B. The cross term of characteristic pressure, P^*_{ij}, is written with a dimensionless adjustable parameter ξ_{ij} as $P^*_{ij} = \xi_{ij}\sqrt{P^*_i P^*_j}$. The parameter ξ_{ij} is determined to reproduce the phase behavior of the system. The dimensionless interaction parameter, χ_{ij}, is related as $\chi_{ij} = \beta \Delta P^*_{ij} v_0$ where $\Delta P^*_{ij} \equiv P^*_i + P^*_j - 2P^*_{ij}$[2,3]. The conventional form of the SL-EOS is $\tilde{\rho}^2 + \tilde{P} + \tilde{T}[\ln(1-\tilde{\rho}) + \tilde{\rho}] = 0$, where $\tilde{\rho}$ ($\equiv \rho/\rho^*$), $\tilde{P}$ ($\equiv P/P^*$), and $\tilde{T}$ ($\equiv T/T^*$) are the dimensionless mass density, pressure, and temperature, respectively. This EOS can be rewritten by using the valuables in the SCF theory as follows:

$$P = \frac{k_{\mathrm{B}}T}{v_0}\left\{ -\ln\bar{\phi}_{\mathrm{v}} - (1-\bar{\phi}_{\mathrm{v}}) + [\chi_{\mathrm{AB}} f(1-f) - \chi_{\mathrm{Av}} f - \chi_{\mathrm{Bv}}(1-f)](1-\bar{\phi}_{\mathrm{v}})^2 \right\} \tag{13}$$

At given T and P, $\bar{\phi}_{\mathrm{v}}$ can be calculated by Equation (13).

2 Extension of the Compressible SCF Theory to Multi-Component Systems

The compressible SCF theory based on the lattice vacancy model can straightforwardly introduce additional polymer and solvent species. For example, let us consider an additional component of a gas pressure medium (g) absorbed into the polymer phase. Let n_{g} be the number of gas solvents, and let N_{g} be the number of segments of each solvent. In this case, the average segment number density is written as $\rho_0 = (n_{\mathrm{d}} N_{\mathrm{d}} + n_{\mathrm{g}} N_{\mathrm{g}} + n_{\mathrm{v}})/V$ where V is the system volume. The partition function $\mathcal{Z}$ is modified as

$$\mathcal{Z} = \int \prod_i (\mathcal{D}\phi_i \mathcal{D}\omega_i)\mathcal{D}\xi \prod_k \left(\frac{\mathcal{Q}_k^{n_k}}{n_k!}\right) \exp\left\{ -\frac{\rho_0}{N_{\mathrm{d}}} \int d\boldsymbol{r} \left[\frac{1}{2}\sum_{i,j} \chi_{ij} N_{\mathrm{d}} \phi_i \phi_j - \sum_i \omega_i \phi_i - \xi\left(1 - \sum_i \phi_i\right) \right] \right\} \tag{14}$$

where $i, j = \mathrm{A}, \mathrm{B}, \mathrm{g}, \mathrm{v}$, $k = \mathrm{d}, \mathrm{g}, \mathrm{v}$, and $\mathcal{Q}_{\mathrm{g}}$ is the partition functions for a single molecule of the gas. This partition function $\mathcal{Z}$ yields the following free energy and SCF equations:

$$\frac{N_{\mathrm{d}} F}{\rho_0 k_{\mathrm{B}} T V} = -\sum_k \left[\frac{N_{\mathrm{d}}}{N_k} \bar{\phi}_k \ln\left(\frac{N_k \mathcal{Q}_k}{N_{\mathrm{d}} \bar{\phi}_k V} \right) \right] + \frac{1}{V}\int d\boldsymbol{r} \left[\frac{1}{2}\sum_{i,j} \chi_{ij} N_{\mathrm{d}} \phi_i \phi_j - \sum_i \omega_i \phi_i - \xi\left(1 - \sum_i \phi_i\right) \right] \tag{15}$$

$$\omega_i(\boldsymbol{r}) = \sum_j \chi_{ij} N_{\mathrm{d}} \phi_j(\boldsymbol{r}) + \xi(\boldsymbol{r}) \tag{16}$$

$$\sum_i \phi_i(\boldsymbol{r}) = 1 \tag{17}$$

$$\phi_{\mathrm{A}}(\boldsymbol{r}) = \frac{\bar{\phi}_{\mathrm{d}} V}{\mathcal{Q}_{\mathrm{d}}} \int_0^f ds\ q(\boldsymbol{r}, s) q^\dagger(\boldsymbol{r}, s) \tag{18}$$

$$\phi_{\mathrm{B}}(\boldsymbol{r}) = \frac{\bar{\phi}_{\mathrm{d}} V}{\mathcal{Q}_{\mathrm{d}}} \int_f^1 ds\ q(\boldsymbol{r}, s) q^\dagger(\boldsymbol{r}, s) \tag{19}$$

$$\phi_{\mathrm{g}}(\boldsymbol{r}) = \frac{\bar{\phi}_{\mathrm{g}} V}{\mathcal{Q}_{\mathrm{g}}} \exp\left[-\frac{N_{\mathrm{g}}}{N_{\mathrm{d}}} \omega_{\mathrm{g}}(\boldsymbol{r}) \right] \tag{20}$$

$$\phi_{\mathrm{v}}(\boldsymbol{r}) = \frac{\bar{\phi}_{\mathrm{v}} V}{\mathcal{Q}_{\mathrm{v}}} \exp\left[-\frac{1}{N_{\mathrm{d}}} \omega_{\mathrm{v}}(\boldsymbol{r}) \right] \tag{21}$$

where

$$\mathcal{Q}_{\mathrm{g}} = \int d\boldsymbol{r}\ \exp\left[-\frac{N_{\mathrm{g}}}{N_{\mathrm{d}}}\omega_{\mathrm{g}}(\boldsymbol{r})\right] \tag{22}$$

When little gas is absorbed into the polymer phase, we can approximate the combining rules for SL-EOS by those of pure diblock copolymers. Henry's law determines the absorption amount of gases with applied pressure: $w_{\mathrm{g}} = HP$ where w_{g} is the weight fraction of the gas absorbed by the polymer and H is the Henry's law constant. According to the SL-EOS theory, the Henry's law constant of diblock copolymer solutions is given by[14]

$$H = \frac{M_{\mathrm{g}}}{RT\rho^*}\exp\left\{(1-\bar{\phi}_{\mathrm{v}})\frac{M_{\mathrm{g}}}{\rho_{\mathrm{g}}^* k_{\mathrm{B}}T}[P_{\mathrm{g}}^* - f\Delta P_{\mathrm{Ag}}^* - (1-f)\Delta P_{\mathrm{Bg}}^* + f(1-f)\Delta P_{\mathrm{AB}}^*] - N_{\mathrm{g}}\left[1+\frac{\bar{\phi}_{\mathrm{v}}}{1-\bar{\phi}_{\mathrm{v}}}\ln\bar{\phi}_{\mathrm{v}}\right]\right\} \tag{23}$$

where N_{g} is the number of segments of the gas molecules. From obtained w_{g}, we can calculate the average gas volume fraction as[2,3]

$$\bar{\phi}_{\mathrm{g}} = \frac{w_{\mathrm{g}}/\rho_{\mathrm{g}}^*}{w_{\mathrm{g}}/\rho_{\mathrm{g}}^* + (1-w_{\mathrm{g}})/\rho^*}(1-\bar{\phi}_{\mathrm{v}}) \tag{24}$$

3 Determination of Equation-of-State Parameters

Table S1: SL-EOS Parameters of Polymers and Gases

Parameters	PS	PnPMA	PMMA	N_2	He
P_i^* [MPa]$^{a)}$	366.9	324.8	366.6	617.3	31.8
T_i^* [K]$^{a)}$	773.0	684.4	772.4	162.2	7.8
ρ_i^* [g/cm^3]$^{a)}$	1.0928	1.0560	1.2373	1.8943	0.5300
$\xi_{\mathrm{PS},i}$		1.00154$^{b)}$	0.99735$^{c)}$	0.75$^{b)}$	0.80$^{b)}$
$\xi_{\mathrm{PnPMA},i}$	1.00154$^{b)}$			1.05$^{b)}$	1.25$^{b)}$

a) Literature values for PS[15], N_2[16], and He[16], and determined values by fitting literature *PVT* data for PnPMA[16] and PMMA[17]. b) Determined to reproduce the literature data[16,18]. c) Determined to reproduce the literature data[19].

We determined the equation-of-state (EOS) parameters from the *PVT* data and the phase behavior in references as shown in Table S1. We referred to the literature values of pure-component parameters of PS[15], N_2[16], and He[16]. We determined the parameters of PnPMA and PMMA by fitting literature value at 468 K[16] and at 398 K[17], assuming the fixed segment volume identical to the segment volume of PS (17.52 cm^3/mol) as shown in Figure S1 and S3, respectively. In this paper, we investigate PS-*b*-PnPMA of $N_{\mathrm{d}} \simeq 2600$ and $f = 0.5$ at $T = 468$ K, which corresponds to the original experimental data for PS-*b*-PnPMA with a molecular weight of $M_{\mathrm{w}} = 48700$[16]. We adjusted the parameter $\xi_{\mathrm{PS,PnPMA}}$ to reproduce the experimental phase behavior at 468 K (P_{ODT}: 3–4 MPa)[16,18]. We also investigate PS-*b*-PMMA of $N_{\mathrm{d}} \simeq 1100$ ($M_{\mathrm{n}} = 22160$) and $f = 0.5$ at $T = 393$ K and adjusted $\xi_{\mathrm{PS,PMMA}}$ to reproduce the phase behavior at 393 K ($P_{\mathrm{ODT}} = 0.1$ MPa)[19]. The parameters for PS-*b*-PnPMA/He, $\xi_{\mathrm{PS,He}}$ and $\xi_{\mathrm{PnPMA,He}}$, are adjusted to reproduce $P_{\mathrm{ODT}} \simeq 4$ MPa at 468 K[16]. The parameters for PS-*b*-PnPMA/N_2, $\xi_{\mathrm{PS,N_2}}$ and $\xi_{\mathrm{PnPMA,N_2}}$ are chosen to reproduce the non-baroplastic (barotropic) phase behavior at 468 K[16]. In this work, we have considered baroplastic BCPs in a narrow temperature-pressure window. The equation-of-state parameters may have different values in the other temperature-pressure window. A complex temperature and pressure dependence of interaction parameters in a large temperature-pressure window is crucial for future research endeavors.

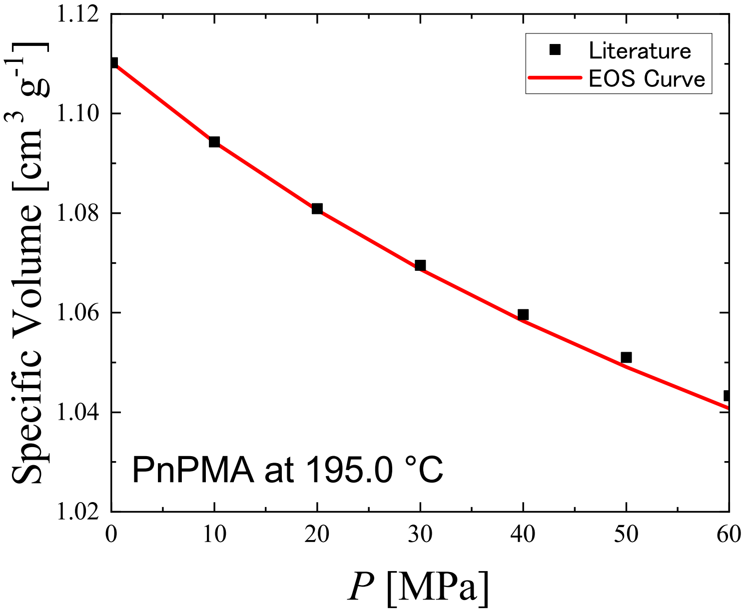

Figure S1: SL-EOS curve fitting to the literature data[16] of PnPMA at 195.0 °C (468 K).

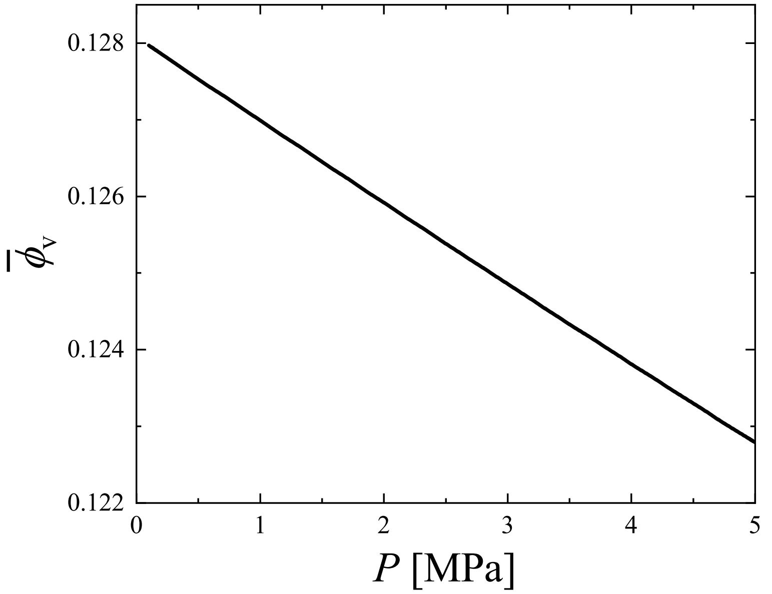

Figure S2: SL-EOS curve of PS-b-PnPMA at 468 K ($N_{\mathrm{d}} \simeq 2600$, $f = 0.5$).

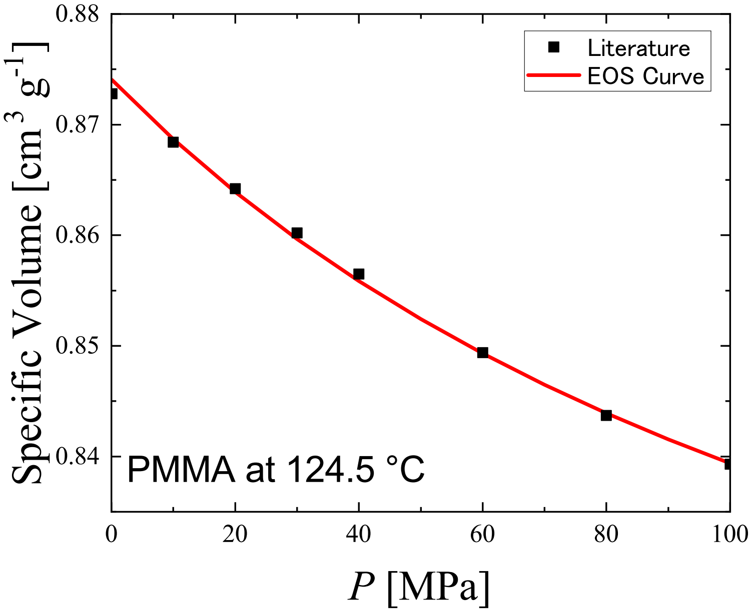

Figure S3: SL-EOS curve fitting to the literature data[17] of PMMA at 124.5 °C (398 K).

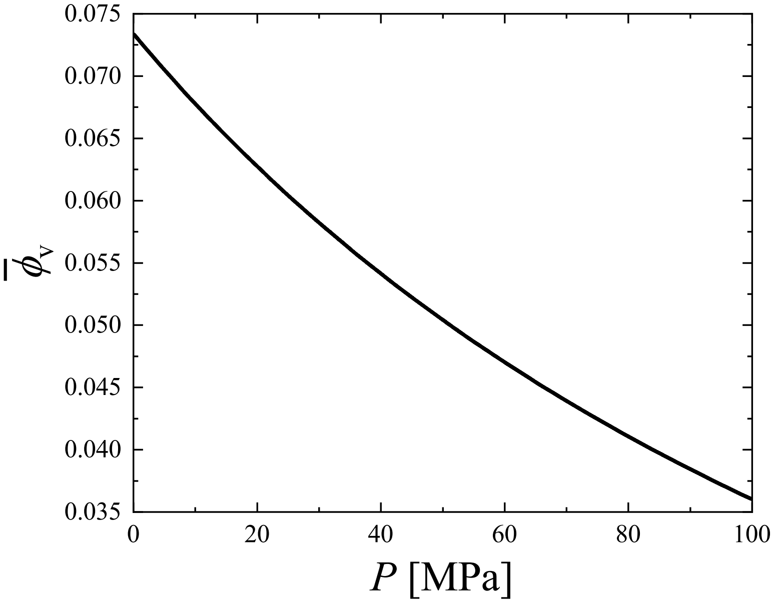

Figure S4: SL-EOS curve of PS-b-PMMA at 393 K ($N_\mathrm{d} \simeq 1100$, $f = 0.5$).

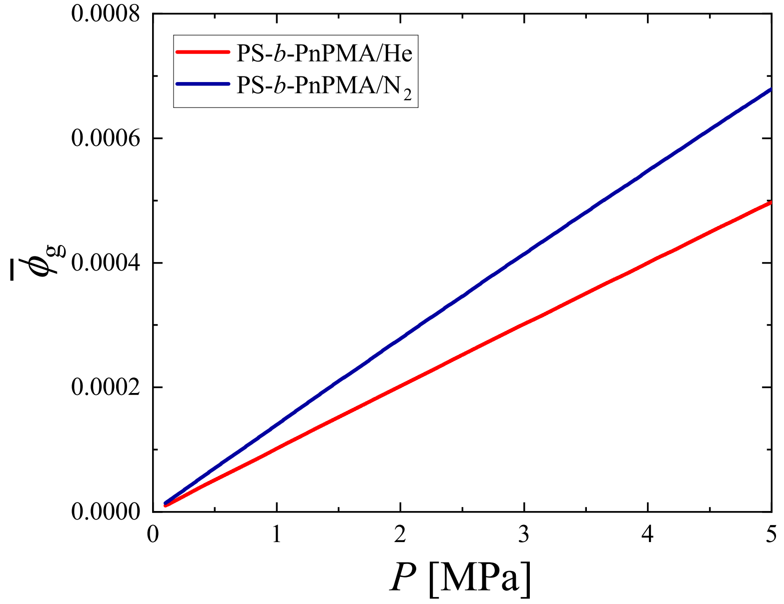

Figure S5: The volume fraction of gases absorbed into PS-b-PnPMA as a function of pressure ($N_\mathrm{d} \simeq 2600$, $f = 0.5$, $T = 468$ K).

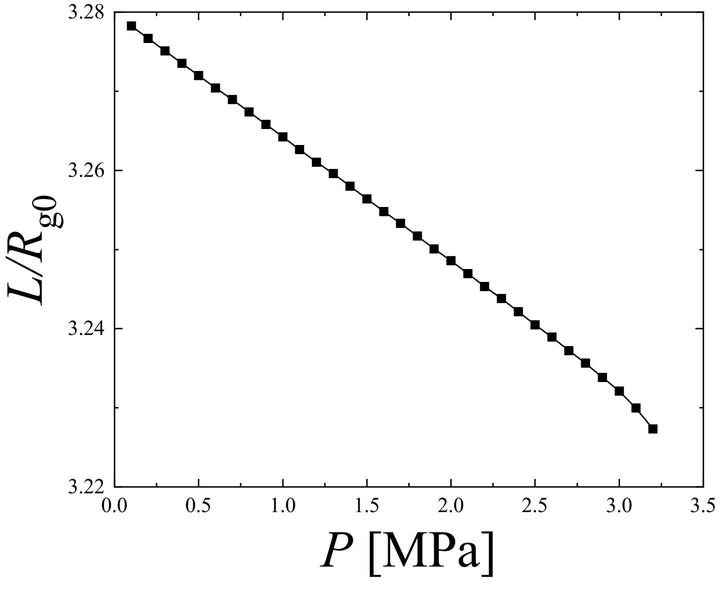

Figure S6: PS-b-PnPMA lamellar period as a function of pressure at 468 K ($N_\mathrm{d} \simeq 2600$, $f = 0.5$). The length is scaled by the radius of gyration of an ideal chain, R_g0.

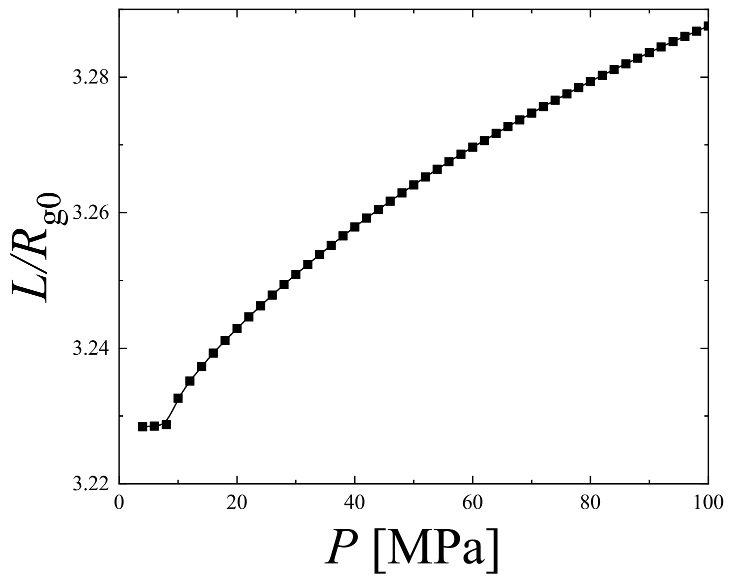

Figure S7: PS-b-PMMA lamellar period as a function of pressure at 393 K ($N_{\mathrm{d}} \simeq 1100$, $f = 0.5$). The length is scaled by the radius of gyration of an ideal chain, R_{g0}.

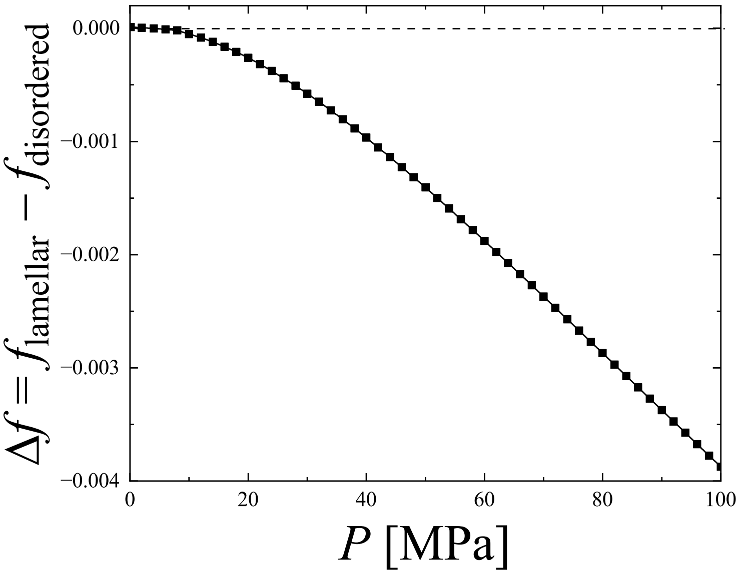

Figure S8: Pressure dependence of Δf ($= f_{\mathrm{lamellar}} - f_{\mathrm{disordered}}$) of PS-$b$-PMMA ($N_{\mathrm{d}} \simeq 1100$, $f = 0.5$, $T = 393$ K).

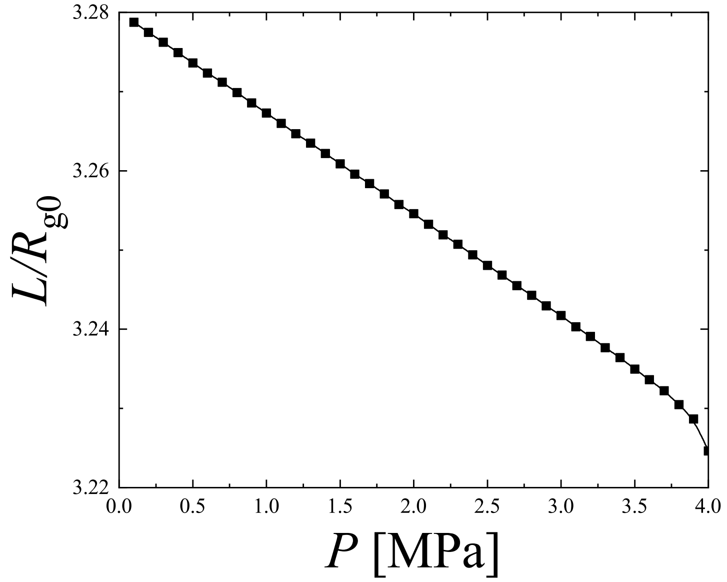

Figure S9: PS-b-PnPMA/He lamellar period as a function of pressure at 468 K ($N_{\rm d} \simeq 2600$, $f = 0.5$). The length is scaled by the radius of gyration of an ideal chain, $R_{\rm g0}$.

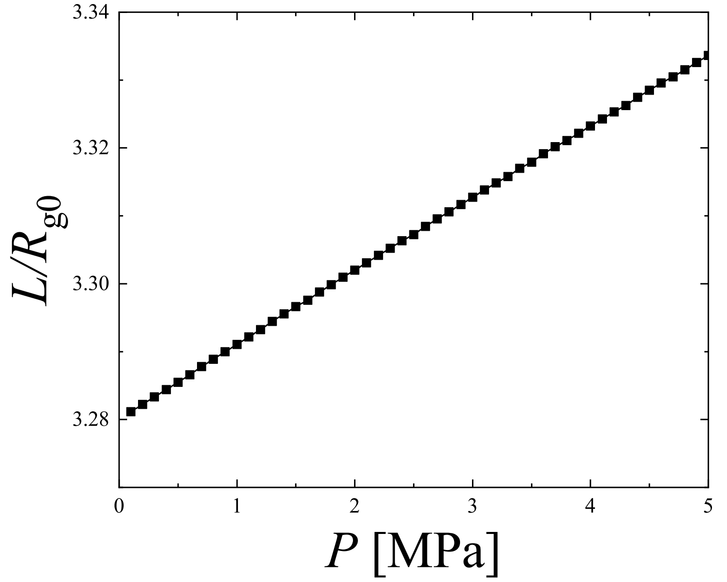

Figure S10: PS-b-PnPMA/N_2 lamellar period as a function of pressure at 468 K ($N_{\rm d} \simeq 2600$, $f = 0.5$). The length is scaled by the radius of gyration of an ideal chain, $R_{\rm g0}$.

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