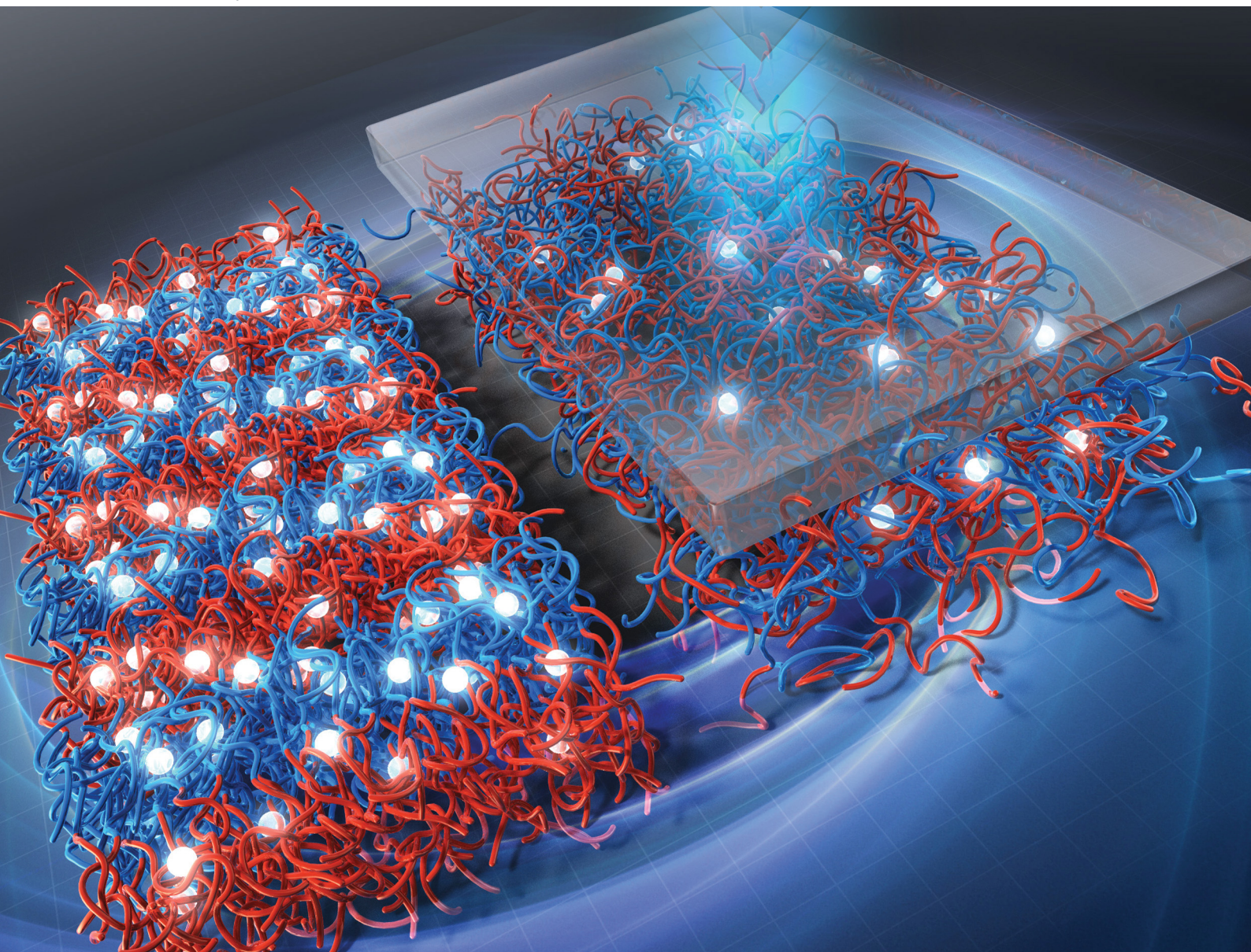


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# Critical role of lattice vacancies in pressure-induced phase transitions of baroplastic diblock copolymers†

Hiroki Degaki,<sup>id</sup> <sup>ac</sup> Ikuo Taniguchi,<sup>id</sup> <sup>bc</sup> Shigeru Deguchi<sup>id</sup> <sup>c</sup> and  
Tsuyoshi Koga<sup>id</sup> <sup>\*ac</sup>

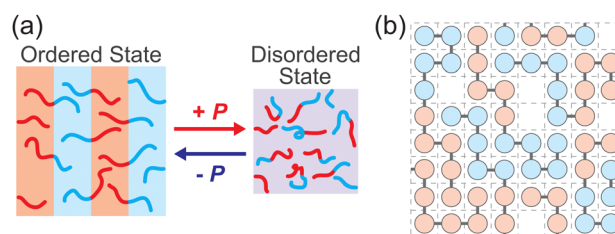
Baroplastic diblock copolymers exhibit order–disorder transitions and melt upon compression at low temperatures, in some cases even at ambient temperatures. Their unique low-temperature processability makes them promising candidates for sustainable polymeric materials. Despite their potential, however, the molecular mechanisms governing the pressure-induced phase transitions of these copolymers remain largely unexplored. This study develops a compressible self-consistent field theory for baroplastic copolymers based on a simple lattice vacancy model that explicitly incorporates voids to account for compressibility. The theory shows that the selective presence of voids in compressible domains stabilizes the ordered phase, while a reduction of voids under compression leads to the order–disorder transition. In addition, this work demonstrates for the first time the critical role of gas absorption rates in each segment in the pressure-induced order–disorder transition of baroplastic diblock copolymers. These findings have significant implications for the rational design of baroplastic polymers with tailored low-temperature processability.

Block copolymers (BCPs) have unique properties resulting from order–disorder transitions (ODTs), phase transitions between ordered phases formed by microphase separation and disordered phases.<sup>1,2</sup> Most BCPs are thermoplastic and undergo ODTs in response to temperature changes. Over the past two decades, baroplastic BCPs, which undergo phase transitions from ordered to disordered states in response to elevated

pressure, have attracted increasing interest.<sup>3</sup> Typical baroplastic BCPs are composed of a hard segment with a high glass transition temperature (high  $T_g$ ) and a soft segment with a low  $T_g$ , such as some of polystyrene-*block*-poly(*n*-alkyl methacrylates) and polystyrene-*block*-poly(*n*-alkyl acrylates).<sup>4–10</sup> Under elevated pressure, baroplastic BCPs exhibit improved miscibility and undergo ODTs, as shown in Fig. 1a.

Disordered baroplastic BCPs flow even below the  $T_g$  of a hard segment due to the presence of a soft rubbery segment. Therefore, they can be processed at much lower temperatures than thermoplastics, in some cases even at ambient temperatures.<sup>3,11,12</sup> Because of their unique low-temperature processability, baroplastic BCPs have attracted considerable attention as a new class of sustainable polymer materials that enable polymer processing with reduced energy consumption and CO<sub>2</sub> emissions. Low-temperature processing also significantly extends the life of polymers in material recycling by minimizing thermal degradation of the polymer chain. In addition, recent studies have reported the development of biodegradable baroplastics from renewable resources.<sup>13,14</sup>

Theoretical considerations have played a pivotal role in understanding pressure-induced ODTs in baroplastic BCPs. The compressible regular solution (CRS) model, which incorporates compressibility into the Flory-Huggins regular solution



**Fig. 1** (a) Pressure-induced order–disorder transition (ODT) in baroplastic diblock copolymers. (b) Lattice vacancy model of the symmetric diblock copolymer system. The vacant sites are called voids, expressing the free volume of the system.

<sup>a</sup> Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan. E-mail: koga.tsuyoshi.6m@kyoto-u.ac.jp

<sup>b</sup> Graduate School of Science and Technology, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan

<sup>c</sup> Research Center for Bioscience and Nanoscience, Japan Agency for Marine-Earth Science and Technology (JAMSTEC), 2-15 Natsushima-cho, Yokosuka 237-0061, Japan

† Electronic supplementary information (ESI) available: Details for the theory, details for determination of the equation-of-state parameters, equation-of-state calculations, gas absorption calculation, domain size calculation, and free energy calculation of PS-*b*-PMMA. See DOI: <https://doi.org/10.1039/d4sm00098f>



theory, has been successful in predicting the baroplasticity of BCPs.<sup>3,8,15,16</sup> However, the CRS model was originally developed for conventional homopolymer blends, not specifically for BCPs. Consequently, a theoretical framework based on BCP theories was needed to accurately and quantitatively describe the baroplastic BCP behavior. Cho and co-workers pioneered basic frameworks using two prominent mean-field BCP theoretical methods: the self-consistent field (SCF) theory<sup>17</sup> and the random phase approximation theory.<sup>18</sup> They elucidated the compressibility of baroplastic BCPs using the perturbed hard-sphere chain model,<sup>19</sup> revealing that the finite compressibility difference between different segments induces baroplastic behavior.

This study introduces the compressible SCF theory based on the lattice vacancy model<sup>20–22</sup> for baroplastic BCPs. Unlike Cho and co-workers' perturbed hard-sphere chain model, which accounts for compressibility using the perturbed fields for hard-sphere chains,<sup>19</sup> our model incorporates compressibility effects into the Flory-Huggins lattice model<sup>23,24</sup> by explicitly considering lattice vacancies called voids (Fig. 1b). We adopt the lattice vacancy model due to its simplicity and high extensibility to complex multi-component systems. Our theory provides a perspective on the molecular mechanisms underlying baroplastic behavior from the unique point of the lattice vacancy model, with a specific focus on voids. Furthermore, we demonstrate the extensibility of our theory by applying it to elucidate the phase behavior of baroplastic BCPs when absorbing gas pressure media.

Let us consider a compressible system of diblock copolymers under constant temperature  $T$  and isotropic pressure  $P$ . The lattice vacancy model introduces, in addition to the polymer segments, voids that express the free volume and are distributed throughout the system (Fig. 1b). Because voids are considered a hypothetical solvent species, the compressible SCF theory with voids can be formulated as straightforwardly as the incompressible SCF theory based on the mean-field approximation.<sup>25–28</sup> Although Noolandi and colleagues have previously proposed a similar method in the context of temperature-induced phase behavior,<sup>29</sup> we explicitly apply the treatment *via* voids to the field of pressure-induced phase behavior for the first time. This application is achieved by using the Sanchez-Lacombe equation of state (SL-EOS)<sup>20–22</sup> derived from the lattice vacancy model: in the present theory, the number of voids, or the system density, changes with temperature  $T$  and pressure  $P$ , obeying the SL-EOS. The lattice vacancy model allows us to apply these classical frameworks developed in the field of incompressible SCF theory and polymer EOS theory. Therefore, instead of repeating the formulation and the validity of each classical method discussed in the references, this paper focuses on discussing the calculation results. The details of the theory are provided in the ESI† together with the references. Note that applications of this compressible SCF theory to copolymer systems of more complicated structures, such as linear multiblock copolymers and starpolymers, are straightforward.<sup>26,27,30</sup>

We employ polystyrene-*block*-poly(*n*-pentyl methacrylate) (PS-*b*-PnPMA) as a model system to elucidate the molecular

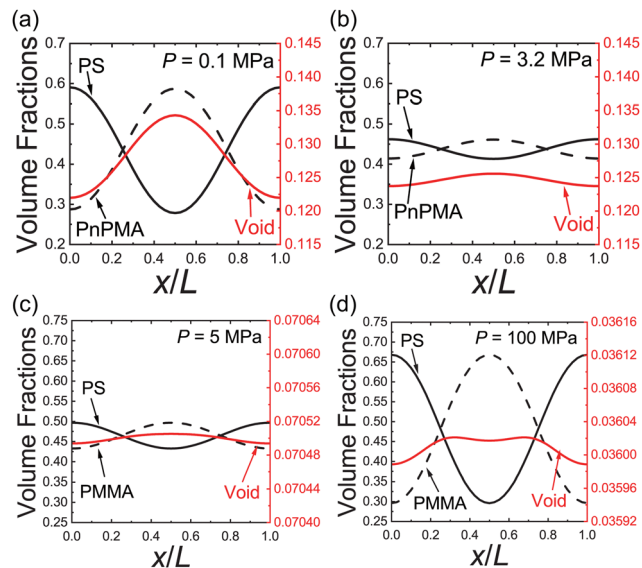


Fig. 2 (a) and (b) Normalized concentration profiles of baroplastic PS-*b*-PnPMA lamellar ( $N_d \approx 2600$ ,  $f = 0.5$ ,  $T = 468$  K) at (a) 0.1 MPa and (b) 3.2 MPa. (c) and (d) Normalized concentration profiles of non-baroplastic (barotropic) PS-*b*-PMMA lamellar ( $N_d \approx 1100$ ,  $f = 0.5$ ,  $T = 393$  K) at (c) 5 MPa and (d) 100 MPa. The  $x$ -axis is taken perpendicular to the lamellar interfaces, and  $L$  is the lamellar period.

mechanisms underlying baroplastic behavior. SL-EOS parameters of each component characterize the molecular properties. The parameters of PS and PnPMA are provided in Table S1, ESI†. Particularly, the characteristic pressure and temperature of PnPMA are smaller than those of PS. Since these parameters are proportional to the self-interaction energies of each component, this indicates that PnPMA has lower self-interaction energies and is comparatively softer, making it easier to compress. In this paper, we investigate the case of  $N_d \approx 2600$  ( $N_d$  being the degree of polymerization of the diblock copolymers) and  $f = 0.5$  ( $f$  being the block ratio) at  $T = 468$  K, which corresponds to the original experimental data for PS-*b*-PnPMA with a molecular weight of  $M_w = 48\,700$ .<sup>31</sup>

First, we investigate the pressurization of the pure copolymer system to consider the effects of voids on the phase behavior of baroplastic BCPs. Fig. 2a and b show the concentration profiles of the PS-*b*-PnPMA lamellar structure as a function of pressure. As pressure is applied, the concentration profile of the lamellar structure becomes flatter. This compatibilization of PS and PnPMA can be attributed to the influence of voids. Voids are more compatible with PnPMA because PnPMA is softer than PS resulting in significant differences in the interactions between the blocks and the voids. Therefore, at low pressure, the lamellar state, where voids are preferentially located within the soft PnPMA layer, is more stable compared to the disordered state where voids randomly interact with both the PS and PnPMA segments. However, at high pressure, the stabilization effect of the void distribution within the lamellar structure diminishes due to the reduction in the number of voids caused by compression. As a result, the disordered state, characterized by a stress-free configuration of polymer chains, becomes more favorable and stabilized.



Fig. 3a demonstrates the pressure dependence of the dimensionless free energy difference per segment between the ordered lamellar phase and the disordered phase, denoted as  $\Delta f = f_{\text{lamellar}} - f_{\text{disordered}}$ . The lamellar structure is destabilized to reach the ODT condition by pressurization. The calculated pressure-induced ODT point is determined to be 3.3 MPa, which agrees with the literature value.<sup>10,31</sup> These results suggest that the effective Flory-Huggins repulsion between the two blocks in the baroplastic system decreases with pressure. Investigating the relationship between the effective Flory-Huggins interaction parameter and pressure is an important area for our future research.

For comparison, we present calculation results for polystyrene-*block*-poly(methyl methacrylate) (PS-*b*-PMMA), a barotropic material that undergoes a transition from a disordered state to an ordered state upon compression.<sup>9,32</sup> The molecular parameters of PS and PMMA are provided in Table S1, ESI.† Our calculations in Fig. 2c and d also successfully reproduced the pressure-induced ordering of the system of  $N_d \approx 1100$  ( $M_n = 22\,160$ ) and  $f = 0.5$  at  $T = 393$  K. In this case, voids are almost uniformly distributed because there is little difference in compressibility between PS and PMMA. Uniformly distributed voids reduce contact between incompatible PS and PMMA segments and stabilize the disordered state. As the number of voids decreases with compression, the interfacial stabilizing effect of the voids also decreases, eventually forcing the system to phase separate to reduce the interfacial area. While voids exhibit a roughly uniform distribution also in the ordered state (note that the difference between the volume fractions of voids in two layers in Fig. 2d is about one thousandth smaller than that for baroplastic PS-*b*-PnMA in Fig. 2a), they preferentially exist at lamellar interfaces to prevent contact between the PS and PMMA domains (Fig. 2d) and stabilize ordered structures by suppressing the interface energy.

Next, we show the high extensibility of our theory to more complex multi-component systems. As an illustrative example, we study the pressurization of PS-*b*-PnMA by gas pressure media. When baroplastics are compressed by a gas pressure medium, the gas medium is absorbed into the polymer phase to affect the phase behavior. In fact, according to Kim and co-workers, the phase behavior of PS-*b*-PnMA changes depending on the kind of pressure medium, even if the medium is an inert gas such as nitrogen and helium.<sup>31</sup>

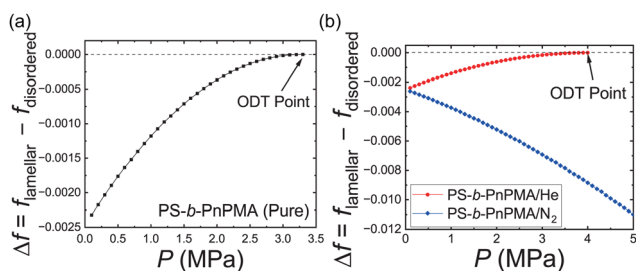


Fig. 3 Pressure dependence of  $\Delta f (= f_{\text{lamellar}} - f_{\text{disordered}})$  in the unit of  $k_B T$  and ODT points of (a) PS-*b*-PnMA, (b) PS-*b*-PnMA/He and PS-*b*-PnMA/ $N_2$  ( $N_d \approx 2600$ ,  $f = 0.5$ ,  $T = 468$  K).

Because of the simplicity of the lattice vacancy model, we can easily consider the diblock copolymer system absorbing the gas medium by a simple addition of another gas solvent species. The absorption amount of the gas with applied pressure is determined by the Henry's law:  $w_g = HP$  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 is expressed with EOS parameters.<sup>33</sup> The complete formalism of the theory for the BCP/gas systems is given in the ESI.†

We here consider the same baroplastic diblock copolymer as above: PS-*b*-PnMA of  $N_d = 2600$  and  $f = 0.5$  at  $T = 468$  K. The molecular parameters of  $N_2$  and He are shown in Table S1, ESI.† Fig. 3b shows  $\Delta f$  of PS-*b*-PnMA/gas.  $N_2$  gases invert the phase behavior of the pure PS-*b*-PnMA: the system is ordered with increasing pressure and decreasing  $\Delta f$ . In contrast, He gases have little effect on the original baroplastic behavior of PS-*b*-PnMA, and  $\Delta f$  is increased with applied pressure.

In the former case of the  $N_2$  absorption, the polymer-gas interaction difference is relatively large,  $\chi_{\text{PS},N_2} - \chi_{\text{PnMA},N_2} = 1.21$  ( $\chi_{ij}$  being the Flory interaction parameter between the  $i$ -th and the  $j$ -th components). This means that the contact of PnMA- $N_2$  is more favorable than that of PS- $N_2$ . Therefore,  $N_2$  is preferentially contained in the soft PnMA layers as seen in Fig. 4a and b. Absorbed gases behave as substitute voids because voids are decreased while gases are increased upon compression. Namely, increased  $N_2$  with applied pressure stabilizes the lamellar structure because highly selective absorption makes  $N_2$  gases behave like voids. As a result,  $N_2$  makes PS and PnMA incompatible with increasing pressure, which is the opposite behavior of the original baroplastic behavior (Fig. 3).

In contrast, in the latter case of the He absorption, the polymer-gas interaction difference is relatively small,  $\chi_{\text{PS},\text{He}} - \chi_{\text{PnMA},\text{He}} = 0.55$ , and there is little difference between the contact of PS-He and that of PnMA-He. As a result, He distributes almost uniformly as shown in Fig. 4c and d. He has little effect on the compatibility between PS and PnMA and

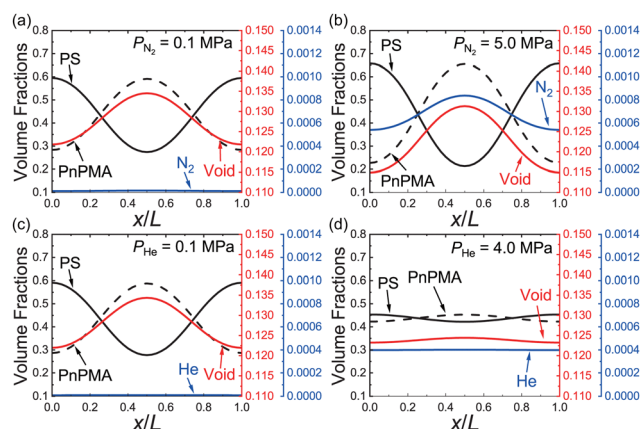


Fig. 4 (a) and (b) Normalized concentration profiles of PS-*b*-PnMA/ $N_2$  ( $N_d \approx 2600$ ,  $f = 0.5$ ,  $T = 468$  K) at (a) 0.1 MPa and (b) 5.0 MPa. (c) and (d) Normalized concentration profiles of PS-*b*-PnMA/He ( $N_d \approx 2600$ ,  $f = 0.5$ ,  $T = 468$  K) at (c) 0.1 MPa and (d) 4.0 MPa.



slightly weakens the baroplasticity of PS-*b*-PnPMA leading to the shift of the ODT point to higher pressure, 4.0 MPa (Fig. 3).

Previously, Cho and colleagues showed that differences in compressibility between hard and soft segments lead to baroplastic behavior using their perturbed hard-sphere chain model.<sup>17,18</sup> Our study further complements and reinforces their findings, with a particular focus on the role of voids. In addition, our model reveals the molecular mechanisms underlying the effect of gas-pressure-medium absorption on baroplastic behavior, taking advantage of the high extensibility to multi-component systems. The extensibility of our model, achieved through the straightforward conversion from the classical incompressible model to the compressible one by the introduction of voids, has the potential to advance theoretical considerations across a wide range of compressible polymeric materials.

## Conclusions

We have employed the compressible SCF theory based on the lattice vacancy model to investigate the pressure-induced phase behavior of BCPs. Our results have revealed a preferential distribution of voids within soft segment domains, which stabilizes the lamellar structure at low pressure. With increasing pressure, these voids gradually diminish, eventually leading to the destabilization of the lamellar structure and resulting disorder. Computational results for the actual baroplastic, PS-*b*-PnPMA, are consistent with experimental observations.<sup>31</sup> The high extensibility of our framework, facilitated by the simplicity of the lattice vacancy model, has also enabled us to examine the impact of the gas type used as the pressure medium on the baroplastic behavior. When gases are preferentially absorbed into the soft segment, they induce a shift in the baroplastic behavior, transitioning towards ordered structures at elevated pressure. This shift occurs because the absorbed gases stabilize the ordered structure under high pressure. This study provides valuable insights into the pressure-induced ODTs governing the low-temperature processability of BCPs, with a particular emphasis on the crucial role played by voids. While this work has primarily focused on baroplastic BCPs, the exploration of compressible BCP systems exhibiting various pressure-induced phase behaviors is a topic for future research.

## Conflicts of interest

There are no conflicts to declare.

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