## <sup>1</sup> Control of the Cell Structure of UV-induced

- <sup>2</sup> Chemically Blown Nanocellular Foams by Self-
- 3 Assembled Block Copolymer Morphology

4 Podchara Rattanakawin<sup>1</sup>, Kenji Yoshimoto<sup>1</sup>, Yuta Hikima<sup>1</sup>, Shinsuke Nagamine<sup>1</sup>, Yuhan Jiang<sup>2</sup>,

5 Masatoshi Tosaka<sup>2</sup>, Shigeru Yamago<sup>2</sup> and Masahiro Ohshima<sup>1\*</sup>

<sup>6</sup> <sup>1</sup> Department of Chemical Engineering, Kyoto University, Kyoto 615-8510, Japan

- <sup>7</sup> <sup>2</sup> Institute for Chemical Research, Kyoto University, Kyoto 611-0011, Japan
- 8 KEYWORDS Nanocellular foam, chemical foaming, block-copolymer self-assembly



9 10

For Table of Contents use only

ABSTRACT A method to fabricate highly ordered nanocellular foam by incorporating the UV-11 12 induced chemical foaming technique with self-assembly of a block copolymer, poly(methyl 13 methacrylate-block-tert-butyl acrylate) (PMMA-b-PtBA) was reported in our previous 14 communication [Rattanakawin, P. ACS Macro Lett. 2020, 9(10), 1433-1438]. Cells with a size of 15 a few tens of nanometers were successfully generated within the cylindrical PtBA-rich domains 16 by heating the UV-irradiated self-assembled PMMA-b-PtBA. Here, we show how other self-17 assembled morphologies of PMMA-b-PtBA, such as lamellae and PMMA-rich cylinders, affect 18 the formation of nanocellular foams. It is demonstrated that cells generated from the lamella 19 templates are largely expandable compared to those from the cylindrical templates, mainly due to 20 the increase in gas amount produced within the PtBA-rich domains. Meanwhile, the lamellar

1 framework is no longer maintained and transformed into a microcellular structure when the 2 foaming temperature is increased near the glass transition temperature of PMMA. We show that 3 such a drastic change in cell structure may be mitigated by increasing the molecular weight of 4 PMMA.

## 5 1. Introduction

6 Currently, the usage of polymer foams is extremely widespread and incorporates all aspects of our daily life, including the automotive,<sup>1,2</sup> packaging,<sup>3</sup> consumer products<sup>4</sup> and construction<sup>5-9</sup> 7 8 sectors. Because of their technical relevance and industrial applications, much focus has been 9 shown on developing advanced polymer foams with enhanced properties. These properties include 10 super-insulating materials with thermal conductivities less than air or equivalent to aerogel and mechanical properties comparable to or higher than that of the non-foamed polymer.<sup>10,11</sup> One of 11 the major strategies to achieve this is cell size reduction to the nanometer scale. The foams with a 12 cell size less than 100 nm and cell density  $10^{15}$ - $10^{16}$  cells/cm<sup>3</sup> are called nanocellular foams. By 13 14 creating highly dense nanosized cells, nanocellular foams have exhibited superior mechanical strength,<sup>12–15</sup> thermal insulation,<sup>16–19</sup> and optical properties<sup>20,21</sup> compared to foams with larger cell 15 16 sizes.

17 The cell structuring and ordering of the nanocellular foams have been shown to broadly impact the mechanical,<sup>12,13,15,19</sup> thermal,<sup>10,11,19</sup> and optical properties<sup>20–24</sup> of polymer foams. In 18 19 order to create nanocellular foams suitable for different applications, various strategies have been 20 developed to control the cell structure of nanocellular foams produced by conventional foaming methods, referred to as the physical foaming process. In this process, CO<sub>2</sub> is dissolved at a high 21 pressure into the polymer; then, by releasing the pressure quickly, numerous cells are nucleated 22 23 and expanded. The cell structure formation can be controlled by two major methods: adding bubble 24 nucleating agents or using self-assembled block copolymer templates. By adding bubble 25 nucleating agents, such as during the foaming process, the number density of bubble (cell) formed after the depressurization process significantly increases,<sup>11,15,25–28</sup> which will increase the cell 26 27 density and decrease the cell size of the foam. Using self-assembled block copolymers with CO<sub>2</sub>philic blocks is another strategy to control the cell structure. During the gas saturation process, the 28 gas will selectively swell the CO<sub>2</sub>-philic blocks.<sup>29–33</sup> This property enables the nucleation to be 29

1 controlled in the CO<sub>2</sub>-philic domains and increases the number density of bubble (cells) during the depressurization process. Using this method, Li et al.<sup>34</sup> demonstrated the production of highly 2 dense nanocellular foams with cell sizes and densities of 15-25 nm and  $6-15 \times 10^{10}$  cells/cm<sup>3</sup>. 3 4 respectively. However, due to the structural reconstruction of the self-assembly during CO<sub>2</sub> 5 swelling and depressurization, cell ordering was not maintained through the foaming process. The 6 concept of selective swelling has also been applied to blends of a homopolymer and a block 7 copolymer and those of immiscible polymers, where a unique nanoporous structure was fabricated.35-37 8

An alternative method to create nanocellular foam is chemical foaming. Conventionally, the chemical foaming process involves mixing a blowing agent, such as azodicarbonamide and sodium hydrogen carbonate, into a polymer matrix. The blowing agent decomposes and generates gaseous compounds upon heating at a high temperature. The gas fills and expands the space originally occupied by the blowing agent. Since the particle size of the blowing agent is typically on the order of  $1-10 \,\mu\text{m}$ ,<sup>38,39</sup> it remains challenging to create nanocellular foams by conventional chemical foaming processes.<sup>40</sup>

16 Recently, we demonstrated new chemical foaming processes that enable the generation of nanocellular foams from UV-induced chemical reactions.41,42 In the UV-induced chemical 17 18 foaming process, which was originally proposed by Kojima et al., <sup>43</sup> a copolymer containing a tert-19 butyl ester functionalized polymer such as poly(tert-butyl acrylate) (PtBA) is mixed with a small 20 amount of photoacid generators (PAGs). By irradiating the polymer film with UV light, acids are 21 produced from the PAG and spread throughout the film upon heating. As a result, isobutene is 22 generated from the tert-butyl ester deprotection reaction of PtBA, as shown in Scheme 1(a). The 23 isobutene gas expands the polymer matrix softened by heating. In the case of a random copolymer, 24 poly(methyl methacrylate-r-tert-butyl acrylate) (PMMA-r-PtBA), nanocellular foams generated from UV-induced chemical foaming have cell sizes of 100-200 nm.<sup>41</sup> 25

To enhance the cell ordering, we incorporated UV-induced chemical foaming with selfassembly of the block copolymer.<sup>42</sup> As shown in Scheme 1(b), this process involves two major steps: (1) creating a self-assembled block copolymer template with a periodic structure of the gasproducible minor domains and (2) controlling the gas generation and expansion within the minor domains. Using the proposed method, we generated highly ordered spherical nanocellular foams from self-assembled PMMA-b-PtBA, where the cylindrical PtBA-rich domains are hexagonally packed in a PMMA-rich matrix.<sup>42</sup> The formation of spherical cells from the cylindrical PtBA-rich domains was speculated to be a result of the limited amount of gas produced within the cylindrical domains.

6 In this study, we applied the UV-induced chemical foaming technique to different self-7 assembled morphologies of PMMA-b-PtBA to elucidate their influence on the formation of 8 nanocellular foam. By adjusting the weight fraction of the PtBA block ( $\phi_{PtBA}$ ) or the molecular 9 weight  $(M_n)$  of PMMA-b-PtBA, we generate cylindrical and lamellar PtBA-rich domains and 10 short-range ordered PMMA-rich domains. The cell structure created by producing gas within the 11 PtBA-rich domains largely depends on the self-assembled morphology of PMMA-b-PtBA. The 12 difference in cell structure is explained based on a balance between the amount of gas produced in 13 the PtBA-rich domains and the stability of PMMA-rich domains. We also investigated the relation 14 between the size of PtBA-rich domains and the expansion of resulting cells by using the lamellar 15 morphology generated from symmetric PMMA-b-PtBA with different  $M_n$  values. Interestingly, 16 even if more gas is generated within the PtBA-rich domains at higher  $M_{\rm n}$ , the cell expansion may 17 be limited due to a sharp increase in viscosity of PMMA-rich domains. The results in this study 18 are expected to provide insight to control the size, shape, and ordering of nanocellular foams 19 generated from the UV-induced chemical foaming process with self-assembled block copolymer 20 templates.

21

22

Scheme 1. (a) Acid-catalyzed tert-butyl ester deprotection reaction and (b) UV-induced chemical
 foaming of self-assembled block copolymer process flow.



## 2 **2. Experimental Section**

## 3 2.1 Materials

The specifications of PMMA-b-PtBA are summarized in Table 1, which includes two sets of samples: three different PtBA weight fractions (Samples 1-3) and four different molecular weights (Samples 4-7). Samples 1-3 were purchased and used as received from Polymer Source Inc. (Canada). Samples 4-7 were synthesized by organotellurium-mediated free radical polymerization,<sup>44-49</sup> whose detailed procedures and results are summarized in the Supporting Information. A photoacid generator (PAG), BBI-109, was purchased from Midori Kagaku Co., Ltd. (Japan). The maximum absorption wavelength of the PAG was 254 nm.

1 Table 1. Specification of PMMA-b-PtBA with different molecular weights and PtBA weight

## 2 fractions ( $\phi_{PtBA}$ ).

Sample <sup>[a]</sup>	M <sub>n</sub> (g/mol)	φ <sub>PtBA</sub> (wt%)	Đ	Casting Conditions
1	59000	30.5	1.20	CHCl <sub>3</sub> , room temp. for 5 days
2	56500	52.2	1.20	THF, 40 °C for 10 days
3	57000	66.7	1.20	THF, 40 °C for 10 days
4	25500	58.9	1.28	CHCl <sub>3</sub> , 40 °C for 7 days
5	73800	56.6	1.32	CHCl <sub>3</sub> , 40 °C for 7 days
6	117300	55.1	1.29	CHCl <sub>3</sub> , 40 °C for 7 days
7	233200	56.6	1.34	CHCl <sub>3</sub> , 40 °C for 7 days

3 <sup>[a]</sup> Samples 1-3 were purchased from Polymer Source, whereas Samples 4-7 were synthesized by TERP emulsion

4 polymerization (detailed synthesis procedures summarized in the Supporting Information).

## 5 2.2 UV-induced chemical foaming of the PMMA-b-PtBA film

6 PMMA-b-PtBA films were prepared by solution casting [Scheme 2]. For all samples, the 7 polymer solution was prepared by dissolving 0.20 g of PMMA-b-PtBA and 0.01 g of PAG in 20 8 g of solvent. Different solvents and casting conditions were selected to form a homogenous film 9 (refer to Table 1). Two types of solvents were used here: THF for Samples 2 and 3 and CHCl<sub>3</sub> for 10 the others. The polymer solution was cast on a 50-ml glass vial, and the solvent was removed either 11 under ambient conditions (Sample 1) or by heating at 40 °C (Samples 2-7). For the latter samples, 12 the speed of the solvent evaporation was slowed down by loosely covering the glass vial with a 13 cap. After several days of solvent removal, the resulting film was further dried in vacuum for 24 14 hours. The films were then removed from the glass vial in liquid nitrogen and then dried in a 15 vacuum for 24 hours, resulting in PMMA-b-PtBA films with a thickness of 150 µm.

Scheme 2. PMMA-b-PtBA solution casting process. The thickness of the PMMA-b-PtBA film
 was estimated from the cross-sectional SEM image of the as-cast sample.



3

The PMMA-b-PtBA film was foamed by the UV-induced chemical foaming method as previously reported.<sup>41–43</sup> The film was first exposed to UV light to generate acids from the PAG. UV irradiation was conducted with a UV lamp (UVGL-58, UVP, U.K.), whose wavelength, intensity, and dosage were set at 254 nm, ~1 mW/cm<sup>2</sup> and 3600 mJ/cm<sup>2</sup>, respectively. Immediately after UV irradiation, the sample was heated on a hotplate at 80-100 °C for 5 minutes to accelerate acid diffusion. The cells were created with the isobutene gas generated from the deprotection reaction of PtBA, and they were expanded in the polymer matrix softened by heating.

## 11 **2.3 Characterization**

12 The self-assembled morphology of PMMA-b-PtBA was characterized by small-angle X-13 ray scattering (SAXS) (NANO-Viewer, Rigaku Corp., Japan) and transmission electron 14 microscopy (TEM) (JEM-2100F, JEOL, Ltd., Japan). In the SAXS measurements, an incident X-15 ray beam (Cu K $\alpha$ ,  $\lambda$ =0.15418 nm) was irradiated through the bulk PMMA-b-PtBA for 6 hours. 16 The TEM samples were prepared using an ultramicrotome (Ultracut E, Reichert-Jung Inc., USA) 17 as thin films of ~80 nm in thickness and placed on a TEM grid. TEM experiments were conducted 18 at an acceleration voltage of 200 kV.

1 The porous structure of the foamed PMMA-b-PtBA film was observed using scanning 2 electron microscopy (SEM) (SU8000, Hitachi High Technologies Corp., Japan) with an 3 acceleration voltage of 10 kV. The foamed samples were cut into thin slices with an 4 ultramicrotome and placed on a silicon wafer. If the cell size was over the micrometer range, the 5 entire sample was directly observed by SEM after removing the film surface by the ultramicrotome. 6 Prior to the SEM observation, the sample surface was covered with  $\sim$ 1-nm-thick platinum by 7 sputtering to avoid charging effects. The cell size was estimated from the SEM images using ImageJ software (National Institutes of Health, U.S.A.).<sup>50,51</sup> 8

9 The density  $(\rho)$  of the as-cast and the foamed samples were estimated by a flotation method.<sup>52</sup> The samples were immersed in a liquid mixture of ethanol, water, and glycerol. The 10 fraction of ethanol, water, and glycerol was adjusted to make the liquid density a value in the range 11 12 of 0.79 to 1.26 g/cm<sup>3</sup>. The sample density was determined from the liquid density in which neither sinking nor floating of the sample occurred. Note that the density measurement was conducted 13 14 only for the nanocellular foam samples since the density of the microcellular foam samples was 15 lower than the density of pure ethanol. The expansion ratio ( $\Phi$ ) and porosity ( $f_g$ ) can be estimated 16 from Equations (1) and (2), where  $\rho_s$  and  $\rho_f$  are the densities of the solid and foamed sample, 17 respectively.

$$\Phi = \frac{\rho_s}{\rho_f} \tag{1}$$

$$f_{\rm g} = 1 - \frac{\rho_f}{\rho_s} \times 100\% \tag{2}$$

18 The thermal decomposition of PMMA-b-PtBA was measured by isothermal 19 thermogravimetric analysis (TGA) (DTG-60H, Shimadzu Corp., Japan) at 80-100 °C. The TGA 20 samples were prepared by casting 200  $\mu$ l of a polymer solution containing PMMA-b-PtBA (5 21 wt%) and PAG (0.025 wt%) in chloroform on a 4-cm<sup>2</sup> silicon wafer. The solvent was allowed to 22 evaporate for 12 hours under ambient conditions, followed by vacuum drying for 12 hours to 23 ensure complete solvent removal. Prior to the TGA measurements, acids were generated within 24 the PMMA-b-PtBA films by UV irradiation at 254 nm and a dosage of 3600 mJ/cm<sup>2</sup>.

## **3. Results and discussion**

2

## 3.1 Effect of self-assembled morphology on the cell structure

3 The PMMA-b-PtBA film containing a small amount of PAG was prepared by solution 4 casting, where the solvent was gradually removed by evaporation. Figures 1(a-c) show the TEM 5 images of the PMMA-b-PtBA films obtained from the solvent casting of Samples 1-3. All samples have similar  $M_{\rm n}$  of 56500-59000 g/mol but different weight fractions of PtBA ( $\phi_{\rm PtBA}$ ), i.e., 31, 52, 6 7 and 67 wt%. At  $\phi_{PtBA} = 31$  wt%, stripe patterns coexist with hexagonally packed darker dots [Figure 8 1(a)]. PtBA is the minor domain here, and the darker color corresponds to the PtBA-rich phase. 9 The SAXS profile exhibits the first Bragg peak at a scattering vector ( $q^*$ ) of 0.19 nm<sup>-1</sup> and the second and third peaks at scattering vectors (q) of 0.38 nm<sup>-1</sup> ( $q/q^* = 2.00$ ) and 0.50 nm<sup>-1</sup> ( $q/q^* = 2.00$ ) 10 11 2.63), respectively [Figure 1(d)], which is essentially consistent with the theoretical profile of hexagonally packed cylindrical morphology, i.e.,  $q/q^* = 1$ :  $\sqrt{3}$ : 2:  $\sqrt{7}$ . <sup>53,54</sup> The peaks missed at 12  $q/q^* = \sqrt{3}$  and weakened at  $q/q^* = 2$  can be due to the domain form-factor of the self-assembled 13 structure.<sup>53,54</sup> At  $\phi_{PtBA} = 52$  wt%, only stripe patterns are observed [Figure 1(b)], and the SAXS 14 profile is composed of the peaks appearing at  $q/q^* = 1:2:3$  with  $q^*$  of 0.219 nm<sup>-1</sup> [Figure 1(d)]. 15 16 The weak peak at  $q/q^* = 2$  may indicate that the thickness of PtBA-rich domains is almost equal to that of PMMA-rich domains.<sup>55,56</sup> These observations show that symmetric PMMA-b-PtBA 17 forms a lamellar morphology with an  $l_0$  of 29 nm. At  $\phi_{PtBA} = 67$  wt%, short segments of phase-18 19 separated domains are observed [Figure 1(c)]. Since the brighter domains cover ~39% of the total 20 area in Figure 1(c), they may correspond to PMMA-rich domains. The SAXS profile shows peaks at  $q/q^* = 1$ : 1.76 ( $\sqrt{3}$ ): 2.66 ( $\sqrt{7}$ ) with  $q^*$  of 0.170 nm<sup>-1</sup> [Figure 1(d)], which indicates the 21 formation of cylindrical PMMA-rich domains with  $l_0$  of 37 nm. It is speculated that the self-22 23 assembled structure may be kinetically trapped during solvent evaporation<sup>57,58</sup>, so the ordering of 24 cylindrical PMMA-rich domains may be limited to a short range.



1

**Figure 1.** Self-assembled morphology of PMMA-b-PtBA at different PtBA weight fractions ( $\phi_{PtBA}$ ). (a-c) TEM images of PMMA-b-PtBA at  $\phi_{PtBA} =$  (a) 31, (b) 52, and (c) 67 wt%. (d) SAXS profile of the self-assembled PMMA-b-PtBA. The bright and dark domains in the TEM image correspond to the PMMA- and PtBA-rich domains, respectively. In the SAXS profile, the scattering intensity (*I*) is plotted against the scattering vector (*q*), and the positions of scattering peaks are marked by black triangles. The scattering vectors of the first peak (*q*\*) are 0.190, 0.219, and 0.170 nm<sup>-1</sup> at  $\phi_{PtBA} = 31$ , 52, and 67 wt%, respectively.

9 Figure 2 illustrates the cell structures obtained by foaming the self-assembled PMMA-b-PtBA films at 80-100 °C for 5 minutes. From the cylindrical PtBA-rich domains, highly ordered 10 spherical cells are formed [Figures 2(a-c)], similar to those reported in our previous work.<sup>42</sup> The 11 resulting cell sizes are 17, 25, and 26 nm at foaming temperatures of 80, 90, and 100 °C, 12 13 respectively. In the case of the lamellar morphology, many small cells are formed in the PtBA-rich domains by foaming at 80 °C [Figure 2(d)]. These cells merged along the PtBA-rich domains and 14 expanded against the PMMA-rich domains at 90 °C [Figure 2(e)]. The width of the PMMA-rich 15 16 domains remains almost unchanged, i.e., ~35-40 nm. At 100 °C, the cell size abruptly expands to 17 hundreds of micrometers, which results in the formation of a microcellular structure [Figure 2(f)].

Table 2 lists the expansion ratio of the foamed films calculated with Equation (1). The densities of the as-cast and the foamed samples were measured with floatation method. The PMMA-b-PtBA at  $\phi_{PtBA}$  = 31 wt.% exhibits a limited expansion ratio in the range from 1.01 (80 °C) to 1.10 (100 °C), whereas that at  $\phi_{PtBA}$  = 52 wt.% shows a larger expansion ratio, i.e., 1.21 (80 °C) and 1.48 (90 °C). Note that the expansion ratio of the sample of  $\phi_{PtBA}$  = 52 wt.% foamed at 100 °C could not be accurately determined with the floatation method because the density of the microcellular foam [Figure 2(f)] was much lower than the density of pure ethanol.

8 There are two major factors for a significant increase of expansion ratio and a drastic 9 change of cell morphology observed at the film of  $\phi_{PtBA}$  52 wt.%. First, increasing the ratio of the 10 PtBA-rich domains produces more amount of isobutene gas. According to the isothermal TGA 11 measurements of PtBA-b-PMMA samples [Figure 3], the gas amount produced by heating the sample of  $\phi_{PtBA} = 52$  wt.% for 5 minutes is 11, 13, and 15 wt.% at 80, 90, and 100 °C, respectively. 12 13 These values are approximately 37-50% higher than those generated from the sample of  $\phi_{PtBA}$  = 14 31 wt.%, i.e., 8, 9, and 10 wt.% at 80, 90, and 100 °C, respectively. The second factor influencing 15 the cell structure and the expansion ratio is the mechanical stability of PMMA-rich domains. At 16  $\phi_{PtBA} = 31$  wt.%, the cylindrical PtBA-rich domains are surrounded by the PMMA-rich matrix. On 17 the other hand, at  $\phi_{PtBA} = 52$  wt.%, the planar PtBA-rich domains are sandwiched between the thin 18 PMMA-rich layers. The latter case is mechanically less stable than the cylindrical domain case. It 19 is speculated that the softened PMMA-rich lamellar domains may be collapsed at 100 °C with the 20 increased amount of gas.

For the short-range-ordered cylindrical PMMA morphology, microcellular foams have been created at 80 °C [Figure 2(g)], and their size is further increased at higher temperatures [Figure 2(h,i)]. Therefore, to maintain the framework of self-assembled morphology during the foaming process, it is essential that a continuous matrix is made of the PMMA-rich phase and foamable domains are sufficiently isolated from one another.



Figure 2. SEM images of foamed PMMA-b-PtBA with different PtBA weight fractions (φ<sub>PtBA</sub>):
(a-c) 31 wt% (Sample 1), (d-f) 52 wt% (Sample 2) and (g-i) 66 wt% (Sample 3). Foaming was
conducted at (a, d, g) 80, (b, e, h) 90 and (c, f, i) 100 °C for 5 minutes.

**Table 2.** Change in density, expansion ratio, and porosities of PMMA-b-PtBA with  $\phi_{PtBA} = 31$ 

and 52 wt.% foamed at 80-100 °C for 5 minutes. The density measurements were only conducted
 for the as-cast and the nanocellular foams.

$\phi_{ m PtBA}$ (wt%)	Conditions	Density (g/cm <sup>3</sup> )	Expansion Ratio	Porosity (%)
	As-Cast	1.26	-	-
21	80 °C 5 min	1.25	1.01	1.0
51	90 °C 5 min	1.17	1.08	7.4
	100 °C 5 min	1.14	1.10	9.1
	As-Cast	1.26	-	-
52	80 °C 5 min	1.04	1.21	17.3
	90 °C 5 min	1.03	1.48	32.4



Figure 3. Isothermal TGA thermographs of PMMA-b-PtBA after UV irradiation of PMMA-b-PtBA with (a)  $\phi_{PtBA} = 31$  wt.%, (b)  $\phi_{PtBA} = 51$  wt.% and (a)  $\phi_{PtBA} = 67$  wt.% at 80-100 °C. The measurements were conducted at three different temperatures: 80 °C (black line), 90 °C (red), and 100 °C (blue)

## 6 **3.2 Effect of the molecular weight on the cell structure**

1

7 The self-assembled morphology of symmetric PMMA-b-PtBA is shown in Figure 4, where 8 the molecular weight is varied from 25500 to 233200. No self-assembled morphology is observed 9 at  $M_n = 25500$  g/mol [Figure 4(a)], whereas a lamellar structure is formed at a larger  $M_n$  [Figures 4(b-d)]. A transition from disorder to an ordered phase is expected to occur at  $\chi N = 10.5^{59,60}$ , where 10  $\gamma$  and N denote the Flory-Huggins interactive parameter and degree of polymerization, respectively. 11 For PMMA-b-PtBA, the estimated value of  $\chi N$  is ~18 at  $M_n = 25500$  g/mol (see Supporting 12 13 Information for the detailed calculations), which is larger than the theoretical limit. It is speculated 14 that such a discrepancy may be caused by an overestimation of Flory-Huggins parameter for solvent annealing <sup>61,62</sup> and by no consideration of thermal fluctuation effects on phase 15 separation.63,64 16

17 At  $M_n > 25500$  g/mol, the size of lamellae becomes larger with increasing  $M_n$  [Figures 5(b-18 d)]. The minimum periodicity of lamellae ( $l_0$ ), which is estimated from the first peak of the SAXS 19 profile [Figure 5(a)], is 44, 70, and 130 nm at  $M_n = 73800$ , 117300, and 233200 g/mol, respectively. 20 This result yields a power law relationship, i.e.,  $l_0 \propto M_n^{\alpha}$ , with an exponent  $\alpha$  of 0.92 [Figure 5(b)]. 21 The resulting value of  $\alpha$  largely deviates from the theoretical prediction, i.e., 2/3,<sup>55,65,66</sup> which 22 indicates a potential for insufficient equilibration of the self-assembled morphology. Indeed, the 23 width of lamellae varies within the TEM images at larger  $M_n$  [Figures 5(c,d)]. Nonetheless, the

- 1 three lamellae morphologies are sufficiently distinct to investigate the effects of the lamella size
- 2 on cell expansion.



4 Figure 4. TEM images of the self-assembled morphology of symmetric PMMA-b-PtBA with  $M_n$ 

5 of (a) 25500, (b) 73800, (c) 117300, and (d) 233200 g/mol. The bright and dark domains in the

6 TEM image correspond to the PMMA and PtBA-rich domains, respectively.





**Figure 5.** Characterization of the lamella morphology. (a) SAXS profiles of symmetric PMMAb-PtBA with four different  $M_n$  values: 25500, 73800, 117300, and 233200 g/mol. The scattering vectors of the first peak (q\*) are 0.259, 0.142, 0.090, and 0.048 nm<sup>-1</sup> at  $M_n = 25500$ , 73800, 117300, and 233200 g/mol, respectively. (b) Estimated lamella  $l_0$  from the SAXS profile as a function of  $M_n$ .

1 UV-induced chemical foaming experiments were conducted at three different 2 temperatures: 80, 90, and 100 °C for the four templates shown in Figure 4. The resulting cell 3 structures are summarized in Figure 6. From the disordered template ( $M_n = 25500$  g/mol), cells are sparsely generated with a size of a few tens of nanometers at 80 °C [Figure 6(a)]. It is speculated 4 5 that the cell nucleation and the cell expansion were not promoted with the disordered template 6 because the cells were created within homogeneous PtBA and PMMA phases, rather than the 7 PtBA-rich domain. As a result, the cells were relatively small and sparse, the density of the sample 8 foamed at 80 °C remained unchanged when compared to the as-cast sample [Table 3]. On the other 9 hand, at higher foaming temperatures, the homogeneous PtBA and PMMA phases became soft 10 enough to allow further cell expansion, resulting in microcellular foams [Figures 6(b,c)].

11 In contrast, the lamellar templates ( $M_n > 25500$  g/mol) effectively control the location and size of cells. Figure 6 shows that darker stripes widen when the foaming temperature is increased 12 13 from 80 °C to 90 °C. These darker stripes correspond to trenches observed in the cross-sectional 14 SEM image of the foamed sample at 90 °C [Figure 7]. Table 3 summarizes the cell widths 15 estimated from the SEM images in Figure 6, together with the density, expansion ratio, and 16 porosity measured by the flotation method. Based on the density reduction of the foamed samples 17 shown in Table 3, it is confirmed that the nano-sized hollow structures were indeed formed within 18 the lamellar PtBA-rich domain foamed at 80 °C. As the foaming temperature increases to 90 °C 19 further decrease in the material density indicates that the gas in the hollow expands and pushes off 20 the surrounding polymers. Since the cells are created directly from the PtBA-rich domains, the 21 larger self-assembled domains in higher molecular weight PMMA-b-PtBA results in larger cell 22 sizes [Table 3].

23 From Table 3, a decreasing trend of the expansion ratio with the increase of molecular 24 weight of symmetric PMMA-b-PtBA was observed regardless of the foaming temperature. For 25 instance, in the case of PMMA-b-PtBA foamed at 90 °C, the expansion ratios were 1.41, 1.38, and 26 1.22 for  $M_{\rm n}$  = 73800, 117300, and 233200 g/mol, respectively. This trend and the observation that the lamellar morphology is maintained at 100 °C only for the largest  $M_n$ , may stem from the 27 28 viscosity of the PMMA-rich matrix. The zero-shear viscosity ( $\eta_0$ ) of PMMA with different  $M_n$  can be estimated by Flory-Fox equation, where  $\eta_0 \propto M_n^{3.4}$ .<sup>67</sup> Indeed,  $\eta_0$  for PMMA-b-PtBA at  $M_n =$ 29 117300 and 233200 g/mol is expected to be approximately 5 and 50 times that of  $M_n = 73800$ 30

g/mol, which suggests that the viscosity may be a major factor that controls the cell expansion. A
 similar relationship between the viscosity and the nanocellular foam formation was previously
 reported for the nanocellular foams created by physical foaming.<sup>68–70</sup>







6 f) 73800 (Sample 5), (g-i) 117300 (Sample 6) and (j-l) 233200. Foaming was conducted at (a, d,

7 g, j) 80, (b, e, h, k) 90 and (c, f, i, l) 100  $^{\circ}$ C for 5 minutes.



- 2 Figure 7. (a) SEM images of the cell morphology at the edge of the microtome sample for PMMA-
- 3 b-PtBA with  $M_n = 117300$  g/mol foamed at 90 °C for 5 minutes; (b) Schematic image of SEM
- 4 observation.

5 **Table 3.** Change in cell width, density, expansion ratio and porosity of PMMA-b-PtBA with 6 various  $M_n$  foamed at a temperature in the range of 80-100 °C for 5 minutes.

M <sub>n</sub> (g/mol)	Conditions	Cell width (nm)	Density (g/cm <sup>3</sup> )	Expansion Ratio	Porosity (%)
	As-cast	-	1.23	-	-
25500	80 °C 5 min	-	1.23	1	0.0
25500	90 °C 5 min	Microcellular	-		-
	100 °C 5 min	Microcellular	-	-	-
	As-cast	-	1.25	-	-
72800	80 °C 5 min	$17\pm3$	1.06	1.17	14.5
/3800	90 °C 5 min	43±13	0.88	1.41	29.1
	100 °C 5 min	Microcellular	-	-	-
	As-cast	-	1.26	-	-
117200	80 °C 5 min	$29\pm4$	1.10	1.14	12.2
11/300	90 °C 5 min	$61 \pm 20$	0.91	1.38	27.5
	100 °C 5 min	Microcellular	-	-	-
	As-cast	-	1.26	-	-
222200	80 °C 5 min	$42\pm7$	1.12	1.13	11.5
233200	90 °C 5 min	$76 \pm 21$	1.04	1.22	18.0
	100 °C 5 min	$\overline{109 \pm 15}$	0.92	1.36	26.5

# 3.3 Comparison to nanocellular foams produced by physical foaming with self-assembled block copolymers

3 The use of self-assembled block copolymers as a template in creating nanocellular foams 4 has been studied extensively for physical foaming. In physical foaming, one side of the block 5 copolymer chain is designed to be CO<sub>2</sub>-philic, e.g., poly(perfluorooctylethyl methacrylate),<sup>30,32,34,71,72</sup> poly(1,1,2,2-tetrahydroperfluorodecyl acrylate)<sup>73</sup> and poly(ethylene 6 glycol).<sup>33,74,75</sup> During the foaming process, supercritical CO<sub>2</sub> is selectively dissolved into the self-7 8 assembled CO<sub>2</sub>-philic domains under a high temperature and a high pressure, and it is expanded 9 by releasing the physical constraints. The cell size can be controlled by adjusting some process 10 parameters, such as gas saturation pressure and foaming temperature. However, during the gas 11 saturation and foaming processes, the self-assembled morphology may be reconstructed and/or significantly softened due to the supercritical CO<sub>2</sub>.<sup>29,32,33,72</sup> Therefore, it remains challenging to 12 13 maintain the framework of a self-assembled template and enhance the ordering of cells through 14 the physical foaming process.

15 In contrast to physical foaming, UV-induced chemical foaming techniques do not require 16 harsh process conditions or large-scale equipment. Similar to the conventional chemical foaming 17 process, one can generate cells and expand them by heating the self-assembled PMMA-b-PtBA. 18 As shown in this study, the cell size and the expansion ratio of our nanocellular foams ranged from 19 17-109 nm and 1.01-1.48, respectively. These are comparable to the nanocellular foams produced by the physical foaming of the self-assembled block copolymers. <sup>11,30,34,71,76</sup> One of the benefits 20 21 of the proposed chemical foaming method is the capability of preparing a micrometer order thin 22 nanocellular foamed film. The physical foaming with N<sub>2</sub> and CO<sub>2</sub> cannot prepare the thin foamed 23 film because of the formation of non-foamed layers (skin layers)  $50 - 200 \,\mu\text{m}$  in thickness on the 24 foam surface. However, this would become a disadvantage of the proposed method. It would not 25 be easy to make thick nanocellular foam. The UV penetration depth limits the maximum thickness 26 of the preparable nanocellular foams. By conducting UV-penetration experiments with a thicker 27 PMMA-b-PtBA sample 450 µm in thickness, the UV-penetration depth was approximately 345 28 µm [Supporting Information Figures S6 and S7]. By conducting the UV-irradiation from both 29 sides of the as-cast film, the maximum thickness of the nanocellular foam was approximately 790 30 μm.

1 Using the UV-Vis spectroscopy ((V-730, Jasco Corp, Japan), the attenuation coefficients of the polymer 2 films [Supporting Information Figure S8]. Interestingly, the PMMA-b-PtBA film with 5wt.% PAG 3 has higher UV light attenuation while the PMMA-b-PtBA film with 0 wt.% PAG has a lower light 4 attenuation. PAG in film significantly absorbs the UV light. PAG was converted to acids in the 5 proposed chemical foaming method by reacting to the UV light, and UV light penetrated further 6 in the polymer film. Namely, the absorption coefficient of the polymer film with PAG would 7 dynamically change during the reaction process, which causes the discrepancy between the 8 attenuation coefficient measured by UV-Vis spectroscopy and UV-penetration depth observed by 9 SEM. Further investigation is needed to control the penetration depth of UV in the film with PAG.

Besides the UV-penetration depth control, the thickness of the foam can be tuned by the process
parameters such as PAG concentration and UV dosage<sup>41</sup>, or by direct gas generation from
thermally liable functional groups, such as tert-butoxycarbonyloxy<sup>77–79</sup>, 2-hydroxyethyl acrylate<sup>80</sup>
and p-toluenesulfonylhydrazide<sup>81</sup>.

Apart from the physical and chemical foaming processes, nanosized cells in the thin film can also be created from self-assembled block copolymer templates through selective etching, where one of the blocks is decomposed and removed by either a wet or dry etching process.<sup>82–86</sup> The cell structure and size in the process are predetermined from the original self-assembled morphology of the block copolymer, and they are hardly changed by further processing.

## 19 4. Conclusions

20 In this study, we investigated the effects of the self-assembled PMMA-b-PtBA morphology 21 on the cell structure generated from UV-induced chemical foaming. Highly ordered spherical cells 22 were created from the hexagonally packed cylindrical morphology, whereas nanocellular trenches 23 were generated within the PtBA-rich domains in the lamellar morphology. In the latter case, a 24 sufficient amount of gas was contained within the lamellar PtBA-rich domains; the cells were 25 widened as the foaming temperature was raised. In the case of  $M_n = 73800$  g/mol, the cell width was increased from 16.7 nm to 42.8 nm with increasing foaming temperature from 80 °C to 90 °C. 26 27 The cell expansion was found to decrease with increasing  $M_n$ , which may result from a sharp 28 increase in viscosity. The importance of the stiffness of the PMMA-rich matrix was signified at 29 100 °C. The lamellar framework with smaller M<sub>n</sub>, i.e., 73800 and 117300 g/mol, was not

1 sufficiently stiff to keep the gas within the PtBA-rich domains, and they were transformed into 2 microcellular foams. These fundamental relationships between the self-assembled PMMA-b-PtBA 3 morphology and the cell structure generated from UV-induced chemical foaming are expected to 4 provide useful guidelines to control the size, shape, and ordering of nanocellular foams.

### 5 ASSOCIATED CONTENT

### 6 **Supporting Information**

7 The supporting information includes the following: detailed TERP polymerization procedures and

8 results (Cases 4-7), DSC thermographs of PMMA-b-PtBA, detailed calculation for  $\chi N$ , SEM

- 9 images of as-cast PMMA-b-PtBA, low magnification SEM image of foamed PMMA-b-PtBA, and
- 10 UV-penetration experiments. (PDF)

### 11 AUTHOR INFORMATION

### 12 **Corresponding Author**

- \* Masahiro Ohshima 13
- 14 Department of Chemical Engineering, Kyoto University, Katsura Campus Kyoto 615-8510, Japan
- 15 E-mail: ohshima.masahiro.2w@kyoto-u.ac.jp

### 16 **Author Contributions**

- 17 P.R. performed the experiments and data analysis. K.Y. and M.O. coordinated the project and
- 18 interpreted the data. P.R., Y. J and S.Y. synthesized PMMA-b-PtBA and conducted the intrinsic
- 19 viscosity measurement. M.T. assisted with the SAXS measurement. Y. H assisted with the DSC
- 20 characterization. S.N. assisted with the TEM measurements. P.R., K.Y. and M.O. prepared the
- 21 initial manuscript with input from Y.H., S.N., Y.J., M.T. and S.Y. All authors discussed the results
- 22 and contributed to the manuscript.

### 23 ACKNOWLEDGMENT

24 This work was partly supported by the Japan Society for the Promotion of Science (JSPS), 25

KAKENHI Grant Number 17H03453 (to M.O.) and 21H05027 (to S.Y.). P.R. was supported by

1 the Japanese Government (Monbukagakusho: MEXT) Scholarship. P.R. and K.Y. would also like

2 to thank technical staff at NanoHub, Kyoto University for support with the SEM characterization.

## **3** ABBREVIATIONS

4 CHCl<sub>3</sub>, chloroform; *D*, dispersity; *I*, scattering intensity;  $l_0$ , periodicity of the self-assembled 5 domains;  $M_n$ , number average molecular weight; PAG, photoacid generator; PMMA, poly(methyl 6 methacrylate); PMMA-b-PtBA, poly(methyl methacrylate-block-tert-butyl acrylate); PtBA, 7 poly(tert-butyl acrylate); *q*, scattering vector;  $q^*$ , first-order Bragg peak position; SAXS, small-8 angle X-ray scattering; SEM, scanning electron microscopy; TEM, transmission electron 9 microscopy;  $T_g$ , glass transition temperature; THF, tetrahydrofuran;  $\phi_{PtBA}$ , weight fraction of 9 PtBA;  $\eta$ , intrinsic viscosity;  $\eta_0$ , zero-shear viscosity.

11

## 12 REFERENCES

- Pop-Iliev, R.; Liu, F.; Liu, G.; Park, C. B. Rotational Foam Molding of Polypropylene with
   Control of Melt Strength. *Adv. Polym. Technol.* 2003, *22* (4), 280–296.
   https://doi.org/10.1002/adv.10056.
- 16 Bao, J. B.; Nyantakyi Junior, A.; Weng, G. S.; Wang, J.; Fang, Y. W.; Hu, G. H. Tensile (2)and Impact Properties of Microcellular Isotactic Polypropylene (PP) Foams Obtained by 17 18 Supercritical Carbon Dioxide. 2016. 111. J. Supercrit. Fluids 63-73. 19 https://doi.org/10.1016/j.supflu.2016.01.016.
- 20 (3) Bernardo, V.; Martín-de León, J.; Rodríguez-Pérez, M. Á. Production of PMMA-Based
  21 Nanocellular Polymers Using Low Demanding Saturation Conditions. *Mater. Lett.* 2019,
  22 255, 126551. https://doi.org/10.1016/j.matlet.2019.126551.
- 23 (4) Jin, F.-L. L.; Zhao, M.; Park, M.; Park, S.-J. J.; Jin, F.-L. L.; Zhao, M.; Park, M.; Park, S.24 J. J. Recent Trends of Foaming in Polymer Processing: A Review. *Polymers (Basel)*. 2019,
  25 *11* (6), 953. https://doi.org/10.3390/polym11060953.
- 26 (5) Chen, W.; Hao, H.; Hughes, D.; Shi, Y.; Cui, J.; Li, Z. X. Static and Dynamic Mechanical

- 1
   Properties
   of
   Expanded
   Polystyrene.
   Mater.
   Des.
   2015,
   69,
   170–180.

   2
   https://doi.org/10.1016/j.matdes.2014.12.024.
- 3 (6) Ramli Sulong, N. H.; Mustapa, S. A. S.; Abdul Rashid, M. K. Application of Expanded
  4 Polystyrene (EPS) in Buildings and Constructions: A Review. J. Appl. Polym. Sci. 2019,
  5 136 (20), 47529. https://doi.org/10.1002/app.47529.
- 6 (7) Raps, D.; Hossieny, N.; Park, C. B.; Altstädt, V. Past and Present Developments in Polymer
  7 Bead Foams and Bead Foaming Technology. *Polymer (Guildf)*. 2015, 56, 5–19.
  8 https://doi.org/10.1016/j.polymer.2014.10.078.
- 9 (8) Koo, M. S.; Chung, K.; Youn, J. R. Reaction Injection Molding of Polyurethane Foam for
  10 Improved Thermal Insulation. *Polym. Eng. Sci.* 2001, *41* (7), 1177–1186.
  11 https://doi.org/10.1002/pen.10819.
- 12 (9) Ma, X.; Tu, R.; Cheng, X.; Zhu, S.; Ma, J.; Fang, T. Experimental Study of Thermal 13 Behavior of Insulation Material Rigid Polyurethane in Parallel, Symmetric, and Adjacent 14 Facade Constructions. *Polymers* (Basel). 2018, 10 (10), 1104. Building 15 https://doi.org/10.3390/polym10101104.
- (10) Cuadra-Rodriguez, D.; Barroso-Solares, S.; Pinto, J. Advanced Nanocellular Foams:
   Perspectives on the Current Knowledge and Challenges. *Nanomaterials* 2021, *11* (3), 621.
   https://doi.org/10.3390/NANO11030621.
- (11) Costeux, S. CO 2 -Blown Nanocellular Foams. J. Appl. Polym. Sci. 2014, 131 (23), 41293.
   https://doi.org/10.1002/app.41293.

(12) Miller, D.; Kumar, V. Microcellular and Nanocellular Solid-State Polyetherimide (PEI)
 Foams Using Sub-Critical Carbon Dioxide II. Tensile and Impact Properties. *Polymer* (*Guildf*). 2011, 52 (13), 2910–2919. https://doi.org/10.1016/j.polymer.2011.04.049.

(13) Notario, B.; Pinto, J.; Rodríguez-Pérez, M. A. Towards a New Generation of Polymeric
Foams: PMMA Nanocellular Foams with Enhanced Physical Properties. *Polymer (Guildf)*.
2015, 63, 116–126. https://doi.org/10.1016/j.polymer.2015.03.003.

1	(14)	Wang, G.; Zhao, J.; Wang, G.; Mark, L. H.; Park, C. B.; Zhao, G. Low-Density and
2		Structure-Tunable Microcellular PMMA Foams with Improved Thermal-Insulation and
3		Compressive Mechanical Properties. Eur. Polym. J. 2017, 95, 382-393.
4		https://doi.org/10.1016/j.eurpolymj.2017.08.025.
5	(15)	Yeh, SK. K.; Liu, YC. C.; Chu, CC. C.; Chang, KC. C.; Wang, SF. F. Mechanical
6		Properties of Microcellular and Nanocellular Thermoplastic Polyurethane Nanocomposite
7		Foams Created Using Supercritical Carbon Dioxide. Ind. Eng. Chem. Res. 2017, 56 (30),
8		8499-8507. https://doi.org/10.1021/acs.iecr.7b00942.
9	(16)	Notario, B.; Pinto, J.; Solorzano, E.; De Saja, J. A.; Dumon, M.; Rodríguez-Pérez, M. A.
10		Experimental Validation of the Knudsen Effect in Nanocellular Polymeric Foams. Polymer
11		(Guildf). 2015, 56, 57–67. https://doi.org/10.1016/j.polymer.2014.10.006.
12	(17)	Liu, S.; Duvigneau, J.; Vancso, G. J. Nanocellular Polymer Foams as Promising High
13		Performance Thermal Insulation Materials. Eur. Polym. J. 2015, 65, 33-45.
14		https://doi.org/10.1016/J.EURPOLYMJ.2015.01.039.
15	(18)	Sundarram, S. S.; Li, W. On Thermal Conductivity of Micro- and Nanocellular Polymer
16		Foams. Polym. Eng. Sci. 2013, 53 (9), 1901–1909. https://doi.org/10.1002/pen.23452.
17	(19)	Wang, G.; Zhao, J.; Howe Mark, L.; Wang, G.; Yu, K.; Wang, C.; Park, C. B.; Zhao, G.
18		Ultra-Tough and Super Thermal-Insulation Nanocellular PMMA/TPU. Chem. Eng. J. 2017,
19		325, 632-646. https://doi.org/10.1016/j.cej.2017.05.116.
20	(20)	Martín-de León, J.; Pura, J. L.; Bernardo, V.; Rodríguez-Pérez, M. Á. Transparent
21		Nanocellular PMMA: Characterization and Modeling of the Optical Properties. Polymer
22		(Guildf). 2019, 170, 16–23. https://doi.org/10.1016/j.polymer.2019.03.010.
23	(21)	Pérez-Tamarit, S.; Notario, B.; Solórzano, E.; Rodriguez-Perez, M. A. Light Transmission
24		in Nanocellular Polymers: Are Semi-Transparent Cellular Polymers Possible? Mater. Lett.
25		2018, 210, 39–41. https://doi.org/10.1016/j.matlet.2017.08.109.
26	(22)	Feng, X.; Nejati, S.; Cowan, M. G.; Tousley, M. E.; Wiesenauer, B. R.; Noble, R. D.;
27		Elimelech, M.; Gin, D. L.; Osuji, C. O. Thin Polymer Films with Continuous Vertically

Aligned 1 Nm Pores Fabricated by Soft Confinement. ACS Nano 2019, 10 (1), 150–158.
 https://doi.org/10.1021/acsnano.5b06130.

- Vertically Aligned Nanopores in Sustainably Derived Polymer Membranes by Molecular
   Templating. ACS Nano 2017, 11 (4), 3911–3921. https://doi.org/10.1021/acsnano.7b00304.
- 6 (24) Feng, X.; Tousley, M. E.; Cowan, M. G.; Wiesenauer, B. R.; Nejati, S.; Choo, Y.; Noble,
  7 R. D.; Elimelech, M.; Gin, D. L.; Osuji, C. O. Scalable Fabrication of Polymer Membranes
  8 with Vertically Aligned 1 Nm Pores by Magnetic Field Directed Self-Assembly. *ACS Nano*9 2014, 8 (12), 11977–11986. https://doi.org/10.1021/nn505037b.
- (25) Azdast, T.; Hasanzadeh, R. Increasing Cell Density/Decreasing Cell Size to Produce
   Microcellular and Nanocellular Thermoplastic Foams: A Review. J. Cell. Plast. 2020, 57
   (5), 769–797. https://doi.org/10.1177/0021955X20959301.
- 13 (26) Sarver, J. A.; Kiran, E. Foaming of Polymers with Carbon Dioxide The Year-in-Review
  14 2019. J. Supercrit. Fluids 2021, 173, 105166.
  15 https://doi.org/10.1016/j.supflu.2021.105166.
- 16 (27)Lee, Y. H.; Park, C. B.; Wang, K. H.; Lee, M. H. HDPE-Clay Nanocomposite Foams Blown 17 with Supercritical CO2. J. Cell. Plast. 2005, 41 (5), 487-502. https://doi.org/10.1177/0021955X05056964. 18
- 19 Bernardo, V.; Loock, F.; Martin-de Leon, J.; Fleck, N. A.; Rodriguez-Perez, M. A. (28)20 Mechanical Properties of PMMA-Sepiolite Nanocellular Materials with a Bimodal Cellular 21 Structure. Macromol. Mater. Eng. 2019, 304 (7),1900041. 22 https://doi.org/10.1002/mame.201900041.
- (29) Yokoyama, H.; Sugiyama, K. Nanocellular Structures in Block Copolymers with CO 2Philic Blocks Using CO 2 as a Blowing Agent: Crossover from Micro-to Nanocellular
  Structures with Depressurization Temperature. *Macromolecules* 2005, *38* (25), 10516–
  10522. https://doi.org/10.1021/ma051757j.
- 27 (30) Yokoyama, H.; Li, L.; Nemoto, T.; Sugiyama, K. Tunable Nanocellular Polymeric

1 Monoliths Using Fluorinated Block Copolymer Templates and Supercritical Carbon 2 Dioxide. Adv. Mater. 2004, 16 (17), 1542–1546. https://doi.org/10.1002/adma.200400072. 3 (31) Zhang, R.; Yokoyama, H. Fabrication of Nanoporous Structures in Block Copolymer Using 4 Selective Solvent Assisted with Compressed Carbon Dioxide. Macromolecules 2009, 42 5 (10), 3559–3564. https://doi.org/10.1021/MA900123E. 6 (32) Shinkai, T.; Sugiyama, K.; Ito, K.; Yokoyama, H. Nanoporous Fabrication of Block 7 Copolymers via Carbon Dioxide Swelling: Difference between CO2-Swollen and 8 Nanoporous Block Copolymers. Polymer (Guildf). 2016, 100. 19-27. 9 https://doi.org/10.1016/j.polymer.2016.08.011. 10 Xu, Y.; Liu, T.; Yuan, W.-K.; Zhao, L. Influence of Microphase Morphology and Long-(33) 11 Range Ordering on Foaming Behavior of PE-b-PEO Diblock Copolymers. Ind. Eng. Chem. 12 *Res.* **2015**, *54* (28), 7113–7121. https://doi.org/10.1021/acs.iecr.5b01014. 13 (34) Li, L.; Nemoto, T.; Sugiyama, K.; Yokoyama, H. CO 2 Foaming in Thin Films of Block 14 Copolymer Containing Fluorinated Blocks. Macromolecules 2006, 39 (14), 4746-4755. 15 https://doi.org/10.1021/ma0603251. 16 (35) Bernardo, V.; Martin-de Leon, J.; Sanchez-Calderon, I.; Laguna-Gutierrez, E.; Rodriguez-17 Perez, M. A. Nanocellular Polymers with a Gradient Cellular Structure Based on 18 Poly(Methyl Methacrylate)/Thermoplastic Polyurethane Blends Produced by Gas 19 Dissolution Macromol. 2020, 305 (1), 1900428. Foaming. Mater. Eng. 20 https://doi.org/10.1002/mame.201900428. 21 Bernardo, V.; Martin-de Leon, J.; Pinto, J.; Catelani, T.; Athanassiou, A.; Rodriguez-Perez, (36) 22 M. A. Low-Density PMMA/MAM Nanocellular Polymers Using Low MAM Contents: 23 Production Characterization. (Guildf). 2019. 163. 115-124. and Polymer 24 https://doi.org/10.1016/J.POLYMER.2018.12.057. 25 Nemoto, T.; Takagi, J.; Ohshima, M. Control of Bubble Size and Location in Nano-(37) 26 /Microscale Cellular Poly(Propylene)/Rubber Blend Foams. Macromol. Mater. Eng. 2008, 27 293 (7), 574–580. https://doi.org/10.1002/mame.200800015.

1	(38)	Petchwattana, N.; Covavisaruch, S. Influences of Particle Sizes and Contents of Chemical
2		Blowing Agents on Foaming Wood Plastic Composites Prepared from Poly(Vinyl Chloride)
3		and Rice Hull. Mater. Des. 2011, 32 (5), 2844–2850.
4		https://doi.org/10.1016/j.matdes.2010.12.044.
5	(39)	Michaeli, W.; Sitz, S. Analysis of the Expansion Behaviour of Rubber Compounds with
6		Chemical Blowing Agents. Cell. Polym. 2010, 29 (4), 227–236.
7		https://doi.org/10.1177/026248931002900402.
8	(40)	Reglero Ruiz, J. A.; Vincent, M.; Agassant, JF.; Sadik, T.; Pillon, C.; Carrot, C. Polymer
9		Foaming with Chemical Blowing Agents: Experiment and Modeling. Polym. Eng. Sci. 2015,
10		55 (9), 2018–2029. https://doi.org/10.1002/pen.24044.
11	(41)	Rattanakawin, P.; Yamamura, K.; Yoshimoto, K.; Ohshima, M. Development and
12		Optimization of UV-Induced Chemical Foaming Process. J. Photopolym. Sci. Technol.
13		<b>2019</b> , <i>32</i> (5), 693–698. https://doi.org/10.2494/photopolymer.32.693.
14	(42)	Rattanakawin, P.; Yoshimoto, K.; Hikima, Y.; Chandra, A.; Hayakawa, T.; Tosaka, M.;
15		Yamago, S.; Ohshima, M. Highly Ordered Nanocellular Polymeric Foams Generated by
16		UV-Induced Chemical Foaming. ACS Macro Lett. 2020, 9 (10), 1433–1438.
17		https://doi.org/10.1021/acsmacrolett.0c00475.
18	(43)	Kojima, J.; Takada, T.; Jinno, F. Thin Microcellular Plastic Sheet Incorporating Designed
19		Foaming Patterns Made by Photochemical Foaming Technology. J. Cell. Plast. 2007, 43
20		(2), 103–109. https://doi.org/10.1177/0021955X06076573.
21	(44)	Fan, W.; Nakamura, Y.; Yamago, S. Synthesis of Multivalent Organotellurium Chain-
22		Transfer Agents by Post-Modification and Their Applications in Living Radical
23		Polymerization. Chem. – A Eur. J. 2016, 22 (47), 17006–17010.
24		https://doi.org/10.1002/CHEM.201603682.
25	(45)	Fan, W.; Tosaka, M.; Yamago, S.; Cunningham, M. F. Living Ab Initio Emulsion
26		Polymerization of Methyl Methacrylate in Water Using a Water-Soluble Organotellurium
27		Chain Transfer Agent under Thermal and Photochemical Conditions. Angew. Chemie Int.

- 1 *Ed.* **2018**, *57* (4), 962–966. https://doi.org/10.1002/ANIE.201710754.
- (46) Fan, W.; Yamago, S. Synthesis of Poly(N-Vinylamide)s and Poly(Vinylamine)s and Their
   Block Copolymers by Organotellurium-Mediated Radical Polymerization. *Angew. Chemie Int. Ed.* 2019, *58* (21), 7113–7116. https://doi.org/10.1002/ANIE.201902940.
- 5 (47) Rattanakawin, P.; Fan, W.; Yamago, S.; Yoshimoto, K.; Ohshima, M. Synthesis of
  6 Photocleavable Block Copolymers for UV Induced Foaming. *J. Photopolym. Sci. Technol.*7 2018, *31* (5), 647–650. https://doi.org/10.2494/photopolymer.31.647.
- 8 Yamago, S. Precision Polymer Synthesis by Degenerative Transfer Controlled/Living (48)9 Radical Polymerization Using Organotellurium, Organostibine, and Organobismuthine 10 Rev. 2009, 109 (11), Chain-Transfer Agents. Chem. 5051-5068. https://doi.org/10.1021/CR9001269. 11
- (49) 12 Jiang, Y.; Fan, W.; Tosaka, M.; Cunningham, M. F.; Yamago, S. Fabrication of Structurally 13 Controlled Poly(n-Butyl Acrylate) Particles by Ab Initio Emulsion Organotellurium-14 Mediated Radical Polymerization. Synthesis of High Molecular Weight Homo and Block 15 Copolymers. Macromolecules 54 10691-10699. 2021, (23),https://doi.org/https://doi.org/10.1021/acs.macromol.1c02037. 16
- 17 Wang, L.; Hikima, Y.; Ishihara, S.; Ohshima, M. Fabrication of Lightweight Microcellular (50)18 Foams in Injection-Molded Polypropylene Using the Synergy of Long-Chain Branches and 19 2017, 128. 119–127. Crystal Nucleating Agents. Polymer (Guildf). 20 https://doi.org/10.1016/j.polymer.2017.09.025.
- (51) Xu, H.; Xiao, H.; Ellison, C. J.; Mahanthappa, M. K. Flexible Nanoporous Materials by
   Matrix Removal from Cylinder-Forming Diblock Copolymers. *Nano Lett.* 2021, *21* (18),
   7587–7594. https://doi.org/10.1021/ACS.NANOLETT.1C02097.
- (52) Andreev, G. A.; Hartmanoá, M. Flotation Method of Precise Density Measurements. *Phys. status solidi* 1989, *116* (2), 457–468. https://doi.org/10.1002/PSSA.2211160203.
- (53) Hamley, I.; Castelletto, V. Small-Angle Scattering of Block Copolymers. In *Soft Matter Characterization*; Springer Netherlands, 2008; pp 1021–1081. https://doi.org/10.1007/978-

1 1-4020-4465-6\_20.

- (54) Förster, S.; Timmann, A.; Konrad, M.; Schellbach, C.; Meyer, A.; Funari, S. S.; Mulvaney,
  P.; Knott, R. Scattering Curves of Ordered Mesoscopic Materials. *J. Phys. Chem. B* 2005, *109* (4), 1347–1360. https://doi.org/10.1021/jp0467494.
- (55) Matsushita, Y.; Mori, K.; Saguchi, R.; Nakao, Y.; Noda, I.; Nagasawa, M. Molecular
   Weight Dependence of Lamellar Domain Spacing of Diblock Copolymers in Bulk.
   *Macromolecules* 2002, 23 (19), 4313–4316. https://doi.org/10.1021/MA00221A019.
- 8 (56) Hasegawa, H.; Hashimoto, T.; Kawai, H.; Lodge, T. P.; Amis, E. J.; Glinka, C. J.; Han, C.
  9 C. SANS and SAXS Studies on Molecular Conformation of a Block Polymer in
  10 Microdomain Space. *Macromolecules* 1985, 18 (1), 67–78.
  11 https://doi.org/10.1021/MA00143A011.
- 12 (57) Leolukman, M.; La, Y.-H.; Li, X.; Gopalan, P. Morphology Development in Asymmetric
  13 Poly(Styrene-b-Tert-Butylacrylate) Thin Films by Solvent Annealing. *Polym. J.* 2008, 40
  14 (9), 825–831. https://doi.org/10.1295/polymj.PJ2008014.
- 15 Tong, J. D.; Leclère, P.; Doneux, C.; Brédas, J. L.; Lazzaroni, R.; Jérôme, R. Morphology (58) 16 and Mechanical Properties of Poly(Methylmethacrylate)-b-Poly(Alkylacrylate)-b-17 Poly(Methylmethacrylate). Polymer (Guildf). 2001. 42 (8), 3503-3514. https://doi.org/10.1016/S0032-3861(00)00759-X. 18
- 19 (59) Feng, H.; Lu, X.; Wang, W.; Kang, N.-G.; Mays, J. W. Block Copolymers: Synthesis, Self20 Assembly, and Applications. *Polymers (Basel)*. 2017, 9 (10), 494.
  21 https://doi.org/10.3390/POLYM9100494.
- (60) Yoshimura, Y.; Chandra, A.; Nabae, Y.; Hayakawa, T. Chemically Tailored High- χ Block
   Copolymers for Perpendicular Lamellae via Thermal Annealing. *Soft Matter* 2019, *15*,
   3497–3506. https://doi.org/10.1039/c9sm00128j.
- (61) F. Hannon, A.; W. Bai; A. Alexander-Katz; A. Ross, C. Simulation Methods for Solvent
  Vapor Annealing of Block Copolymer Thin Films. *Soft Matter* 2015, *11* (19), 3794–3805.
  https://doi.org/10.1039/C5SM00324E.

1	(62)	Hagita, K.; Aoyagi, T.; Abe, Y.; Genda, S.; Honda, T. Deep Learning-Based Estimation of
2		Flory-Huggins Parameter of A-B Block Copolymers from Cross-Sectional Images of
3		Phase-Separated Structures. Sci. Reports 2021 111 2021, 11 (1), 1–16.
4		https://doi.org/10.1038/s41598-021-91761-8.
5	(63)	Kim, S.; Li, W.; Fredrickson, G. H.; Hawker, C. J.; Kramer, E. J. Order–Disorder Transition
6		in Thin Films of Horizontally-Oriented Cylinder-Forming Block Copolymers: Thermal
7		Fluctuations vs. Preferential Wetting. Soft Matter 2016, 12 (27), 5915–5925.
8		https://doi.org/10.1039/C6SM00739B.
9	(64)	Gronheid, R.; Nealey, P. F. Directed Self-Assembly of Block Co-Polymers for Nano-
10		Manufacturing, 1st ed.; Elsevier: Amsterdam, Netherlands, 2015.
11		https://doi.org/10.1016/c2014-0-03748-3.
12	(65)	Goodson, A. D.; Troxler, J. E.; Rick, M. S.; Ashbaugh, H. S.; Albert, J. N. L. Impact of
13		Cyclic Block Copolymer Chain Architecture and Degree of Polymerization on Nanoscale
14		Domain Spacing: A Simulation and Scaling Theory Analysis. Macromolecules 2019, 52
15		(23), 9389-9397. https://doi.org/10.1021/ACS.MACROMOL.9B02015.
16	(66)	Semenov, A. N. Theory of Block Copolymer Interfaces in the Strong Segregation Limit.
17		Macromolecules 2002, 26 (24), 6617–6621. https://doi.org/10.1021/MA00076A047.
18	(67)	Fuchs, K.; Friedrich, C.; Weese, J. Viscoelastic Properties of Narrow-Distribution
19		Poly(Methyl Methacrylates). <i>Macromolecules</i> <b>1996</b> , <i>29</i> (18), 5893–5901.
20		https://doi.org/10.1021/MA951385M.
21	(68)	Yeh, S. K.; Liao, Z. E.; Wang, K. C.; Ho, Y. T.; Kurniawan, V.; Tseng, P. C.; Tseng, T. W.
22		Effect of Molecular Weight to the Structure of Nanocellular Foams: Phase Separation
23		Approach.Polymer(Guildf).2020,191,122275.
24		https://doi.org/10.1016/j.polymer.2020.122275.
25	(69)	Forest, C.; Chaumont, P.; Cassagnau, P.; Swoboda, B.; Sonntag, P. Nanofoaming of PMMA
26		Using a Batch CO2 Process: Influence of the PMMA Viscoelastic Behaviour. Polymer
27		(Guildf). 2015, 77, 1-9. https://doi.org/10.1016/J.POLYMER.2015.09.011.

1	(70)	Costeux, S.; Khan, I.; Bunker, S. P.; Jeon, H. K. Experimental Study and Modeling of
2		Nanofoams Formation from Single Phase Acrylic Copolymers. J. Cell. Plast. 2015, 51 (2),
3		197-221. https://doi.org/10.1177/0021955X14531972.
4	(71)	Yokoyama, H.; Li, L.; Dutriez, C.; Iwakura, Y.; Sugiyama, K.; Masunaga, H.; Sasaki, S.;
5		Okuda, H. Horizontally and Vertically Aligned Polymeric Nanosheets: CO2-Induced
6		Morphological Changes of Block Copolymer Thin Films. Macromolecules 2008, 41 (22),
7		8626-8631. https://doi.org/10.1021/MA801487A.
8	(72)	Yokoyama, H. Small Angle X-Ray Scattering Studies of Nanocellular and Nanoporous
9		Structures. Polym. J. 2013, 45 (1), 3-9. https://doi.org/10.1038/pj.2012.205.
10	(73)	Ruiz, J. A. R.; Cloutet, E.; Dumon, M. Investigation of the Nanocellular Foaming of
11		Polystyrene in Supercritical CO2 by Adding a CO2-Philic Perfluorinated Block Copolymer.
12		J. Appl. Polym. Sci. 2012, 126 (1), 38-45. https://doi.org/10.1002/APP.36455.
13	(74)	Zhang, W.; Chen, B.; Zhao, H.; Yu, P.; Fu, D.; Wen, J.; Peng, X. Processing and
14		Characterization of Supercritical CO2 Batch Foamed Poly(Lactic Acid)/Poly(Ethylene
15		Glycol) Scaffold for Tissue Engineering Application. J. Appl. Polym. Sci. 2013, 130 (5),
16		3066-3073. https://doi.org/10.1002/APP.39523.
17	(75)	Taki, K.; Nitta, K.; Kihara, SI.; Ohshima, M. CO2 Foaming of Poly(Ethylene
18		Glycol)/Polystyrene Blends: Relationship of the Blend Morphology, CO2 Mass Transfer,
19		and Cellular Structure. J. Appl. Polym. Sci. 2005, 97 (5), 1899–1906.
20		https://doi.org/10.1002/APP.21930.
21	(76)	Dutriez, C.; Satoh, K.; Kamigaito, M.; Yokoyama, H. Nanocellular Foaming of Fluorine
22		Containing Block Copolymers in Carbon Dioxide: The Role of Glass Transition in Carbon
23		Dioxide. RSC Adv. 2012, 2 (7), 2821–2827. https://doi.org/10.1039/C2RA01268E.
24	(77)	Ito, H. Solid-State Thermolysis of Poly(p-t-Butoxycarbonyloxystyrene) Catalyzed by
25		Polymeric Phenol: Effect of Phase Separation. J. Polym. Sci. Part A Polym. Chem. 1986,
26		24 (11), 2971–2980. https://doi.org/10.1002/pola.1986.080241124.
27	(78)	Jing, C.; Suzuki, Y.; Matsumoto, A. Thermal Decomposition of Methacrylate Polymers

Containing Tert-Butoxycarbonyl Moiety. *Polym. Degrad. Stab.* 2019, *166*, 145–154.
 https://doi.org/10.1016/j.polymdegradstab.2019.05.027.

(79) Qi, D.; Zhao, C.; Zhang, L.; Li, X.; Li, G.; Na, H. Novel in Situ-Foaming Materials Derived

- from a Naphthalene-Based Poly(Arylene Ether Ketone) Containing Thermally Labile
  Groups. *Polym. Chem.* 2015, 6 (28), 5125–5132. https://doi.org/10.1039/c5py00768b.
- 6 (80) Iseki, M.; Suzuki, Y.; Tachi, H.; Matsumoto, A. Design of a High-Performance
  7 Dismantlable Adhesion System Using Pressure-Sensitive Adhesive Copolymers of 28 Hydroxyethyl Acrylate Protected with Tert-Butoxycarbonyl Group in the Presence of
  9 Cross-Linker and Lewis Acid. ACS Omega 2018, 3 (11), 16357–16368.
  10 https://doi.org/10.1021/acsomega.8b02371.
- (81) Jeong, J.; Yang, J.; Ha, C. S.; Cho, W. J.; Chung, I. Synthesis and Characterization of
   Polymeric Foaming Agent Containing Sulfonyl Hydrazide Moiety. *Polym. Bull.* 2012, 68
   (5), 1227–1238. https://doi.org/10.1007/s00289-011-0600-2.
- 14 (82) Ahn, H.; Park, S.; Kim, S.-W.; Yoo, P. J.; Yeol Ryu, D.; Russell, T. P. Nanoporous Block
  15 Copolymer Membranes for Ultrafiltration: A Simple Approach to Size Tunability. ACS
  16 Nano 2014, 8 (11), 11745–11752. https://doi.org/10.1021/nn505234v.
- 17 (83) Park, S.; Jun, T.; Yoon, H. R.; Jo, S.; Kim, J. H.; Ryu, C. Y.; Ryu, D. Y. Nanoporous
  18 Structures from PS-b-PMMA-b-PtBA Triblock Copolymer and Selective Modification for
  19 Ultrafiltration Membranes. *ACS Appl. Polym. Mater.* 2019, *1* (3), 584–592.
  20 https://doi.org/10.1021/acsapm.9b00050.
- (84) Thurn-Albrecht, T.; Steiner, R.; DeRouchey, J.; Stafford, C. M.; Huang, E.; Bal, M.;
   Tuominen, M.; Hawker, C. J.; Russell, T. P. Nanoscopic Templates from Oriented Block
   Copolymer Films. *Adv. Mater.* 2000, *12* (11), 787–791. https://doi.org/10.1002/(SICI)1521 4095(200006)12:11<787::AID-ADMA787>3.0.CO;2-1.
- (85) Chan, V. Z. H.; Hoffman, J.; Lee, V. Y.; Iatrou, H.; Avgeropoulos, A.; Hadjichristidis, N.;
  Miller, R. D.; Thomas, E. L. Ordered Bicontinuous Nanoporous and Nanorelief Ceramic
  Films from Serf Assembling Polymer Precursors. *Science (80-. ).* 1999, 286 (5445), 1716–

- 1 1719. https://doi.org/10.1126/science.286.5445.1716.
- (86) Hsueh, H. Y.; Yao, C. T.; Ho, R. M. Well-Ordered Nanohybrids and Nanoporous Materials
  from Gyroid Block Copolymer Templates. *Chem. Soc. Rev.* 2015, *44* (7), 1974–2018.
  https://doi.org/10.1039/c4cs00424h.
- 5