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## I. Introduction

It is known that hierarchical morphologies of semicrystalline polymers at different length scales (*i.e.*, a well-ordered crystalline state, a long-range-correlated repeated lamellar stacking grain, and a subsequent two- or three-dimensionally propagated spherocrystal) play crucial roles in mechanical properties, transport characteristics, and optical features of the polymer

- <sup>a</sup>Department of Materials Science and Engineering, Stony Brook University, Stony Brook, New York 11794-2275, USA. E-mail: tadanori.koga@stonybrook.edu; maya. koga@stonybrook.edu
- <sup>b</sup>Kurashiki Research Center, Kuraray Co., Ltd., 2045-1 Sakazu, Kurashiki, Okayama 710-0801, Japan
- <sup>c</sup>Chemical and Molecular Engineering Program, Stony Brook University, Stony Brook, New York 11794-2275, USA
- <sup>d</sup>Department of Chemistry, Stony Brook University, Stony Brook, New York 11794-3400, USA
- <sup>e</sup>Condensed Matter Physics and Materials Science Department, Brookhaven National Laboratory, Upton, NY 11973, USA
- Photon Sciences Directorate, Brookhaven National Laboratory, Upton, New York, 11973, USA
- <sup>s</sup>Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899, USA

<sup>h</sup>Department of Chemistry, Bogazici Universitesi, Kimya Bolumu Bebek, 34342, Istanbul, Turkey

# Melt crystallization/dewetting of ultrathin PEO films *via* carbon dioxide annealing: the effects of polymer adsorbed layers

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Mitsunori Asada,<sup>ab</sup> Naisheng Jiang,<sup>a</sup> Levent Sendogdular,<sup>a</sup> Jonathan Sokolov,<sup>a</sup> Maya K. Endoh,<sup>\*a</sup> Tadanori Koga,<sup>\*acd</sup> Masafumi Fukuto,<sup>ef</sup> Lin Yang,<sup>f</sup> Bulent Akgun,<sup>gh</sup> Michael Dimitriou<sup>g</sup> and Sushil Satija<sup>g</sup>

The effects of CO<sub>2</sub> annealing on the melting and subsequent melt crystallization processes of spin-cast poly(ethylene oxide) (PEO) ultrathin films (20–100 nm in thickness) prepared on Si substrates were investigated. By using *in situ* neutron reflectivity, we found that all the PEO thin films show melting at a pressure as low as P = 2.9 MPa and at T = 48 °C which is below the bulk melting temperature ( $T_m$ ). The films were then subjected to quick depressurization to atmospheric pressure, resulting in the non-equilibrium swollen state, and the melt crystallization (and/or dewetting) process was carried out in air *via* subsequent annealing at given temperatures below  $T_m$ . Detailed structural characterization using grazing incidence X-ray diffraction, atomic force microscopy, and polarized optical microscopy revealed two unique aspects of the CO<sub>2</sub>-treated PEO films: (i) a flat-on lamellar orientation, where the molecular chains stand normal to the film surface, is formed within the entire film regardless of the original film thickness and the annealing temperature; and (ii) the dewetting kinetics for the 20 nm thick film is much slower than that for the thicker films. The key to these phenomena is the formation of irreversibly adsorbed layers on the substrates during the CO<sub>2</sub> annealing: the limited plasticization effect of CO<sub>2</sub> at the polymer–substrate interface promotes polymer adsorption rather than melting. Here we explain the mechanisms of the melt crystallization and dewetting processes where the adsorbed layers play vital roles.

bulk.1 Owing to emerging advanced technologies, such as organic photovoltaics,<sup>2</sup> organic transistors,<sup>3</sup> and organic lightemitting diodes,<sup>4</sup> a challenge is to manipulate such crystalline morphologies within spatially confined polymer films where the rate of crystallization, crystal orientation, and density of nucleation sites are quite different from those of the bulk.<sup>5-12</sup> The main reason for these deviations is the interplay between two interfaces: the polymer-air interface and polymer-substrate interface.13 For instance, the crystallization kinetics at the topmost polymer surface is faster than that of the rest of the film.<sup>14</sup> This is mainly attributed to the presence of the "surface mobile layer"15-17 or the "surface reduced viscosity layer"18,19 where the glass transition temperature  $(T_g)$  or viscosity is much lower than that of the bulk or film interior. On the other hand, the chain dynamics near the substrate-polymer interface is retarded by the formation of semicrystalline polymer adsorbed layers<sup>20-23</sup> at the polymer melt-substrate interface. It is proposed that these opposing effects then propagate into the film interior through chain entanglements,24 resulting in heterogeneities in the crystalline structures within polymer thin films.12,22 However, a comprehensive understanding of the crystallization process in nanoconfined geometries is still lacking.

In this paper, by using compressed CO<sub>2</sub> gas ( $T_c = 31.3$  °C and  $P_c = 7.38$  MPa), we aim to explore the melt crystallization and

#### Paper

dewetting processes from the non-equilibrium swollen amorphous state under nanoconfinement. It is known that CO<sub>2</sub> molecules absorbed into polymers play a role as diluent or plasticizer for glassy/semicrystalline polymers, lowering  $T_{g}$  and melting temperature  $(T_m)$  significantly and hence enhancing the chain mobility.<sup>25-28</sup> Especially, it was previously reported that the excess sorption of CO2 molecules near the critical point of CO<sub>2</sub> takes place at the free surface as well as the substrate interface, resulting in the excess swelling of supported polymer thin films regardless of the choice of polymer.<sup>29-37</sup> So far, the detailed mechanism considering both the CO<sub>2</sub> sorption and nanoconfinement effects has yet to be rationalized.21 To achieve our objective, we chose poly(ethylene oxide) (PEO) ultrathin films spun-cast on Si substrates as a model since the melting/ crystallization behavior in CO2 has been well characterized in bulk<sup>38,39</sup> as well as in thin films.<sup>34</sup> Firstly, we performed highpressure neutron reflectivity experiments to investigate the plasticization effect of CO2 on the PEO ultrathin films. The results indicate that the CO<sub>2</sub> induced the transition from the crystalline state to the amorphous state at a pressure as low as P = 2.9 MPa and at T = 48 °C which is below the bulk  $T_{\rm m}$ . Subsequent rapid quench to atmospheric pressure allowed us to create the non-equilibrium swollen state of the exposed PEO films. The polymer films were then transferred to a temperature-controlled stage (set temperatures ranging from 10 °C to 60 °C), permitting us to study the melt crystallization or dewetting process toward equilibrium at the given temperatures. The structural developments were characterized by using various surface-sensitive experimental techniques including X-ray reflectivity, grazing incidence X-ray diffraction, polarized optical microscopy, and atomic force microscopy. Finally, we discuss the formation of the adsorbed layer on the substrate via the CO<sub>2</sub> annealing, which plays crucial roles in the observed melt crystallization and dewetting processes.

### II. Experimental section

#### II-1. Sample preparation

Poly(ethylene oxide) (PEO, average  $M_{\rm n} = 20\ 000\ {\rm g\ mol^{-1}}$ , Sigma-Aldrich, product no. 83100) was used without any further purification. The bulk melting temperature  $(T_m)$  of PEO was determined to be 64  $^\circ \mathrm{C}$  by differential scanning calorimetry (DSC) (Perkin Elmer DSC 7). Si substrates were cleaned by immersion in a hot piranha solution (i.e., a mixture of H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub>: caution: the piranha solution is highly corrosive upon contact with the skin or eyes and is an explosion hazard when mixed with organic chemicals/materials; extreme care should be taken when handing it) for 15 min, subsequently rinsed with deionized water thoroughly, and followed by submersion in an aqueous solution of hydrogen fluoride to remove a native oxide (SiO<sub>2</sub>) layer. However, as will be discussed later, we confirmed that the SiO<sub>2</sub> layer of about 1.3 nm in thickness was re-formed even just after hydrofluoric acid etching, due to atmospheric oxygen and moisture, as reported previously.40 PEO thin films with average thicknesses of 20 nm, 50 nm, and 100 nm were prepared by spin-coating PEO-toluene solutions onto hydrogenpassivated Si (H-Si) substrates with a rotation speed of 2500

rpm. The thicknesses of the spin-cast PEO thin films were measured by an ellipsometer (Rudolf Auto EL-II) with a fixed refractive index of 1.455. The surface tension of PEO is 42.9 mJ  $m^{-2}$  (the dispersion part is 30.9 mJ  $m^{-2}$  and the polar part is 12.0 mJ m<sup>-2</sup>). The interfacial energy ( $\gamma$ ) between the polymer and the substrate is then estimated to be 2.7 mJ  $m^{-2}$  at room temperature and atmospheric pressure based on the Owens-Wendt-Kaelble equation<sup>41</sup> with the dispersion part (48.71 mJ  $m^{-2}$ ) and polar part (3.98 mJ  $m^{-2}$ ) of the surface tension of H-Si.<sup>11</sup> Hence, it is reasonable to categorize the PEO/H-Si as an attractive interacting system. All the spin-cast films were dried under vacuum at 25 °C for 2 h before CO2 processing and directly placed into the high-pressure cell. Note that this drying condition is not long enough to equilibrate the adsorption process of PEO chains: the adsorption time for PEO at 25 °C is at least 2 months.

#### II-2. In situ neutron reflectivity (NR)

With a large penetration depth, neutron reflectivity (NR) is an ideal tool to determine the in situ thickness, composition, and interfacial structure of polymer thin films immersed in fluids or gases, under high pressure in thick-walled vessels.32,42 The in situ swelling behavior of the PEO thin films in CO2 was measured by NR. Deuterated PEO (d-PEO,  $M_{\rm w} = 21 \ 400 \ {\rm g \ mol}^{-1}$ ,  $M_{\rm w}/M_{\rm n} = 1.09$ , Polymer Source Inc.) was used to enhance the scattering contrast. The d-PEO thin films with average thicknesses of 16 nm, 28 nm and 78 nm were prepared on 3-inch H-Si wafers. Specular NR measurements were performed at the NG-7 reflectometer of the National Institute of Standards and Technology Center for Neutron Research. The wavelength  $(\lambda_N)$ of the neutron beams was 0.47 nm with  $\Delta \lambda_N / \lambda_N = 2.5\%$ . The details of the high-pressure NR experiments and high-pressure cell are described elsewhere.32 The NR experiments were conducted under the isothermal condition  $(T = 48 \degree C)$  with elevated pressures up to P = 17.5 MPa. Temperature and pressure stabilities during the NR measurements were within an accuracy of  $\pm 0.1$  °C and  $\pm 0.2\%$ , respectively. The d-PEO thin films were exposed to CO<sub>2</sub> for up to 4 h prior to data acquisition to ensure the swelling process reached equilibrium. The scattering length density (SLD) values of  $CO_2$ , which vary from 0.0004  $\times$  $10^{-4}$  to  $2.5 \times 10^{-4}$  nm<sup>-2</sup> in the pressure range of 0.1 MPa < P < 17.5 MPa at T = 48 °C, were calculated based on the density of CO2 obtained by the equation of state.43 The NR data were obtained by successively increasing the pressure and then slowly decreasing the pressure. Since the background scattering from a pure CO<sub>2</sub> phase increases dramatically near the critical point,<sup>29,32</sup> we measured the scattering from the pure fluid phase (*i.e.*, the long-range density fluctuations) for the respective pressure conditions. The NR data corrected for the background scattering were analyzed by comparing the observed reflectivity curves with the calculated ones based on model SLD profiles having three fitting parameters for each layer: film thickness, SLD, and roughness between the CO<sub>2</sub> and polymer layers represented as a Gaussian function.44 The SLD profiles were subsequently converted into the corresponding polymer volume fraction profiles. Assuming that the concentration of the

mixture is homogeneous through the entire film, the SLD value of the polymer-CO<sub>2</sub> system is defined by

$$SLD_{mix} = SLD_{p} \times \phi(z) + SLD_{CO} \times (1 - \phi(z))$$
(1)

where SLD<sub>mix</sub> is the SLD value of the CO<sub>2</sub>-polymer mixture at a distance z from the substrate,  $SLD_p$  and  $SLD_{CO}$  are the pure component SLD values of the polymer and CO<sub>2</sub>, respectively, and  $\phi(z)$  is the volume fraction of the polymer at a distance z from the substrate. In order to calculate the SLD<sub>CO</sub> of the CO<sub>2</sub> dissolved in the polymer, the reported density of 0.956 g  $\rm cm^{-3}$ for CO<sub>2</sub> gas dissolved in a polymer was used.<sup>45</sup> We confirmed that the repeated pressurization and depressurization processes exhibit the same swelling behavior after the first pressurization process. Hence, it is reasonable to conclude that the polymer does not dissolve in the pure CO2 phase during the NR experiments, which is consistent with the bulk PEO solubility in CO2.46 To ensure conservation of the mass of the polymer for the NR data fitting, the volume fraction profiles were calculated such that the amount of polymer chains remained the same at all solvent concentrations including in the dry state (i.e., before CO<sub>2</sub> exposure).

#### II-3. Recrystallization via CO<sub>2</sub> Treatment

Based on the NR experiments, we found that CO<sub>2</sub> exposure at P = 9.7 MPa and T = 48 °C for 1 h is satisfactory to achieve an amorphous state in the PEO. After the CO<sub>2</sub> exposure, the chamber was rapidly quenched to atmospheric pressure within 10 s. As will be discussed later, the PEO films were still expanded just after the depressurization, resulting in the nonequilibrium swollen state. The swollen polymer films were then transferred quickly to a temperature-controlled sample stage (set temperatures ranging from 10 °C to 60 °C), and the kinetics of the melt crystallization/dewetting at the given temperature  $(T_{\rm cr})$  was studied. Goel and Beckman used a similar CO<sub>2</sub> process to establish a foaming method in which the bulk polymer is saturated with supercritical CO<sub>2</sub> followed by rapid depressurization.47,48 However, we confirmed, by using small-angle X-ray scattering experiments with a reflection geometry,49 that the CO2 process used in the present study generates only molecularscale porosity (average size of 0.8 nm) with a relatively broad size distribution, which is consistent with a previous result on semicrystalline poly(phenylene vinylene) films treated with the same CO<sub>2</sub> process.<sup>49</sup> The lack of large voids in the PEO films after the CO<sub>2</sub> process may be due to the short diffusion path for residual CO<sub>2</sub>, the high diffusivity of CO<sub>2</sub> in the rubbery PEO matrix, and the low storage modulus of PEO.50 It should also be noted that, as we previously reported for another semicrystalline polymer,<sup>51</sup> a slow depressurization process (with a quenching rate of *ca.* 0.15 MPa min<sup>-1</sup>) under the same  $CO_2$ conditions provokes more highly ordered crystalline structures with larger grain sizes. However, due to experimental difficulties in characterizing/visualizing the structural changes via the slow quench in the high-pressure cell, we here focus on only the rapid quench that allows us partly to preserve the swollen structures and then perform a suite of ex situ structural characterizations during the melt crystallization/dewetting

processes from the non-equilibrium swollen state. At the same time, as controls, we treated PEO thin films *via* a conventional high-temperature annealing at 85 °C ( $>T_{\rm m}$ ) for 2 h, followed by rapid quench to the required temperatures (between 10 and 60 °C) by transferring to the temperature-controlled sample stage.

#### II-4. Atomic force microscopy (AFM) measurements

The crystalline morphologies of the PEO thin films were observed by atomic force microscopy (AFM) (Digital Nanoscope III and Bruker Bioscope Catalyst). Both contact mode and standard tapping mode were conducted in air using a cantilever with a spring constant of  $0.06 \text{ N m}^{-1}$  and  $40 \text{ N m}^{-1}$ , respectively. The scan rate was 0.5 Hz or 1.0 Hz with a scanning density of 256 or 512 lines per frame.

#### II-5. Polarized optical microscopy (POM) measurements

Polarized optical microscopy (POM) measurements were conducted by using reflected light under an Olympus BHT microscope equipped with a differential interference contrast attachment for incident light after Nomarski (NIC Model). POM images were captured by a digital camera under polarized light at room temperature.

#### II-6. Grazing incidence X-ray diffraction (GID)

Grazing incidence X-ray diffraction (GID) measurements of the  $CO_2$ -treated and thermally annealed PEO thin films were carried out at the X22B beamline at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL). Twodimensional diffraction patterns were measured with a CCD camera (Princeton Instruments) with an incident X-ray angle of  $0.2^\circ$ , which is above the critical angle of PEO, hence illuminating the entire PEO films. The X-ray wavelength was 0.15 nm and the exposure time for all the measurements was 400 s. As will be discussed later, the adsorbed layers on the substrates after a solvent-leaching process were measured at two undulator beamlines (the X9 beamline (NSLS) and the BL03XU at SPring-8), since the diffraction peaks were too weak to be detected at the bending magnet beamline.

#### II-7. X-ray reflectivity (XR) measurements

X-ray reflectivity (XR) measurements were conducted at the X10B beamline (NSLS, BNL) to measure the film thickness of the adsorbed polymer layers on the H–Si substrates after the solvent-leaching process. The specular reflectivity was measured as a function of the scattering vector in the perpendicular direction to the film surface:  $q_z = (4\pi \sin \theta)/\lambda$ , where  $\theta$  is the incident angle and  $\lambda$  is the X-ray wavelength (0.087 nm). The XR data were fitted by using a standard multilayer fitting routine for a dispersion value ( $\delta$  in the X-ray refractive index) in conjunction with a Fourier method, a powerful tool to obtain detailed structures for low X-ray contrast polymer multilayers.<sup>52,53</sup> Note that  $\delta$  is proportional to the density of a film. The  $\delta$  value of the bulk PEO with the X-ray energy at X10B (14.2 keV) is calculated to be  $\delta_{\text{bulk}} = 1.34 \times 10^{-6}$  with a density of 1.2 g cm<sup>-3</sup>.

#### III. Results

#### III-1. In situ NR results

Fig. 1(a) shows representative NR profiles for the 16 nm thick d-PEO film at four different pressures and T = 48 °C. The solid lines correspond to the best fits to the data based on the volume fraction profiles of the polymer,  $\phi(z)$ , shown in Fig. 1(b). The thickness of the layer, which was initially 16 nm, increased to 20 nm at P = 2.9 MPa and further increased to 23 nm upon compression up to P = 9.7 MPa. It should be noted that the contribution from the density fluctuations of the pure CO<sub>2</sub> phase becomes significant near the ridge condition (P = 9.7MPa at  $T = 48 \,^{\circ}\text{C}$  and overwhelms the observed intensity at  $q_z >$ 0.1  $\text{\AA}^{-1}$ .<sup>29,32</sup> This situation makes it difficult to quantitatively discuss the presence of the adsorbed layer within the swollen PEO thin films or a CO<sub>2</sub> concentration gradient within polymer films.<sup>35,54</sup> Fig. 2 shows the linear dilation  $(S_f)$  of the 16 nm thick film during the pressurization and depressurization processes. The  $S_{\rm f}$  values were calculated by the equation  $S_{\rm f} = (L_1 - L_0)/L_0$ , where  $L_1$  and  $L_0$  are the measured thicknesses of the swollen and unswollen film, respectively. In the pressurization process, there are two distinctive features: (i) the large jump in  $S_{\rm f}$  from 0.05 to 0.25 at P = 2.9 MPa, implying a transition from the crystalline state to the amorphous state at T = 48 °C; and (ii) the anomalous peak in  $S_{\rm f}$  near P = 10 MPa that is attributed to



Fig. 1 (a) Representative NR profiles for a 16 nm thick d-PEO film at four different pressures and T = 48 °C. The solid lines correspond to the best fits to the data based on the corresponding concentration profiles shown in (b).



Fig. 2 Pressure dependence of the linear dilation ( $S_f$ ) for a 16 nm thick d-PEO film at T = 48 °C during the pressurization and depressurization processes. In the inset, the pressure dependence of the surface roughness (the pressurization process) is plotted.

the excess sorption of CO2 molecules at the "density fluctuation ridge"29-37 where the density inhomogeneity of CO2 molecules becomes maximum.55 We also found that the overall swelling isotherms of the 28 nm and 78 nm thick films including the excess swelling are nearly identical to that of the 16 nm thick film (data not shown). This thickness independence of the excess swelling is consistent with previous experimental data of rubbery polybutadiene thin films in CO<sub>2</sub> with a reduced thickness scaled by the radius of polymer gyration ( $R_{\rm g} = 5.1$  nm for the d-PEO used) of larger than  $L_0/R_g = 3.^{32}$  In the inset of Fig. 2, we also plot the pressure dependence of the root-mean-square (rms) roughness ( $\sigma$ ) obtained from the best fits. From the Figure, it is clear that the roughness decreases to a minimum value of 0.5 nm at P = 2.9 MPa and then increases with increasing pressure. This indicates that melting occurs at P =2.9 MPa, resulting in a much smoother surface, and the increase in the roughness at P > 2.9 MPa is attributed to the improvement of the solvent quality of CO<sub>2</sub> with increasing pressure for the amorphous polymer.34 It should be emphasized that this melting pressure of 2.9 MPa is lower than those of bulk PEO films (4.8-10.7 MPa)38,39 under the same isothermal condition. Intriguingly, in the depressurization process, the sharp change in  $S_f$  at P = 2.9 MPa disappeared, and the  $S_f$  value decreased gradually to 0.15 at P = 0.1 MPa. Based on the fact that the roughness after complete depressurization to atmospheric pressure is only 0.5 nm, which is nearly identical to that at the transition point (P = 2.9 MPa), we postulate that the swollen PEO thin film just after the depressurization is in the non-equilibrium amorphous state. Hence, the subsequent thermal annealing at the given temperature  $T_{\rm cr}$  prompts the equilibration (i.e., crystallization or dewetting) of the PEO thin films whose chain conformations are unfavorably stretched in air. We also confirmed that the repeated pressurization and depressurization processes exhibit the same swelling behavior as that of the first depressurization process. Hence, we conclude that the swelling isotherms after the first pressurization are in equilibrium as sole functions of temperature and pressure.

#### III-2. Crystalline structures via melt crystallization

Fig. 3 shows typical AFM and POM images of the PEO thin films after the CO<sub>2</sub> process and subsequent thermal annealing as functions of the film thickness and  $T_{cr}$ . The surface of the 20 nm thick film is depicted with AFM images, while the surfaces of the 50 nm and 100 nm thick films are depicted with POM images because the structures grew too large for AFM to capture. The surface morphologies are strongly dependent on the film thickness, as previously reported in CO<sub>2</sub> treated polycarbonate thin films:<sup>21</sup> for the 50 nm and 100 nm thick films, the main folded-chain crystals grow into quasi-two-dimensional spherulites with an average radius of a few hundred micrometers; for the 20 nm thick film, the polymer crystallized into finger-like seaweed patterns with an average width of a few micrometers, grown *via* the so-called "diffusion limited aggregation" (DLA) process.<sup>7,56,57</sup>

Fig. 4(a) and (b) display representative GID patterns of the 20 nm and 50 nm CO<sub>2</sub>-treated PEO thin films crystallized at  $T_{\rm cr} = 25$  °C. All the GID patterns show discrete diffraction peaks, indicating the formation of highly ordered crystalline structures, in contrast to broad ring patterns for the thermally annealed PEO thin films (Fig. 5(d)). To clarify the crystal orientation, we simulated diffraction patterns for different lamellar geometries with crystallographic *a*, *b*, or *c* axis being in the direction normal to the film surface. The details of the simulation are described elsewhere.<sup>22</sup> Note that the Herman-Stein orientation factor<sup>58</sup> to define the orientation along the standing axis was fixed to be 0.99, and only strong diffraction peaks were considered for the analysis. For identification it was possible to use the 120 diffraction peak at *q* = 13.6 nm<sup>-1</sup> that is located along the *q*<sub>xy</sub> axis for all three CO<sub>2</sub>-treated PEO films



Fig. 3 AFM topographic images (left column) and POM images (center and right columns) of the CO<sub>2</sub>-treated PEO thin films crystallized as functions of the film thickness and  $T_{cr}$ . The height scale for the AFM images is 0–20 nm.



**Fig. 4** Two-dimensional GID images of the CO<sub>2</sub>-treated PEO thin films crystallized at  $T_{cr} = 25$  °C: (a) 20 nm; (b) 50 nm thick films. The simulated diffraction patterns described in the text are shown (c) for crystallographic *c*-axis standing (a flat-on lamellar orientation) and (d) for crystallographic *a*-axis standing (*i.e.*, an edge-on lamellar orientation).



Fig. 5 AFM topographic images of the thermally annealed PEO thin films crystallized at  $T_{\rm cr} = 25$  °C: (a) 20 nm; (b) 50 nm thick film. The height scale for the AFM images is 0–20 nm. The corresponding two-dimensional GID results are shown in (c) for the 20 nm thick film and (d) for the 50 nm thick film.

(indicated by the arrow shown in Fig. 4(a)). A comparison of the simulated (Fig. 4(c) for flat-on and Fig. 4(d) for edge-on) and experimental results elucidated that the lamellar orientation is

assigned to be that geometry with the c axis standing (i.e., a flaton lamellar orientation where the lamellar layers run parallel to the surface and the molecular chains stand normal to the film surface). Consequently, we draw the conclusion that the highly oriented flat-on lamellar structure is formed in the PEO films after the  $CO_2$  process regardless of  $T_{cr}$  and the film thickness. We also used the different CO<sub>2</sub> pressures ranging from 2.9 to 15 MPa at T = 48 °C, where the polymer is in the amorphous state, to investigate the effect of the excess sorption at the density fluctuation ridge on the resultant crystal morphologies. The GID results revealed that the flat-on lamellar orientation occurs regardless of the CO2 pressure, while the size of the crystal grain (observed by POM) is the largest at P = 9.7 MPa (*i.e.*, the ridge). This can be explained by the fact that the amount of residue CO<sub>2</sub> molecules after the rapid depressurization is the highest at the ridge condition such that the melt crystallization proceeds at the slowest rate. Hence, the anomalous plasticization effect near the density fluctuation ridge<sup>30,49,51</sup> is not crucial for the resultant crystal orientation.

To highlight the uniqueness of the CO<sub>2</sub>-induced crystallized structures, we also studied the structures crystallized via a conventional thermal annealing process (*i.e.*, without the CO<sub>2</sub> process). Fig. 5(a) and (b) show representative AFM height images of the thermally annealed PEO thin films (20 nm and 50 nm thick) crystallized at  $T_{\rm cr} = 25$  °C. As previously reported, <sup>59,60</sup> flat-on lamellar structures characterized as screw dislocation nucleation sites or terrace structures are seen in the 20 nm thick film. In contrast, a sheaf-like morphology is observed for the 50 nm thick film, which is an indication of the edge-on lamellar orientation. The detailed structures were further examined by GID. Fig. 5(c) shows the GID pattern for the 20 nm film. It is obvious that the 120 diffraction peak for the 20 nm thick film is still located along the  $q_{xy}$  axis, but displays more arc. This indicates that the degree of the flat-on lamellar orientation is not so high compared to that of the  $CO_2$ -treated film. Fig. 5(d) shows the GID result for the 50 nm thick film where we can see an azimuthal ring pattern, indicating the random orientation of the edge-on lamellae. Table 1 summarizes the orientations of the lamellar structures for the melt crystallized PEO thin films after the thermal annealing processing. From the Table, we note

Table 1 Lamellar orientation and instability of the PEO thin films prepared *via* thermal annealing and  $CO_2$  annealing as functions of the film thickness and  $T_{cr}$ 

	Thermal annealing			CO <sub>2</sub> annealing		
$T_{\rm cr} (^{\circ} {\rm C})$	20 nm	50 nm	100 nm	20 nm	50 nm	100 nm
60	Dewet	Dewet	Dewet	Dewet	Dewet	Dewet
55	Flat-on <sup>a</sup>	Flat-on	Flat-on	Dewet	Dewet	Dewet
40	Flat-on	Flat-on	Flat-on	Dewet	Dewet	Dewet
35	Flat-on	Flat-on	Flat-on	Flat-on	Flat-on	Flat-on
30	Flat-on	Edge-on <sup>b</sup>	Edge-on <sup>b</sup>	Flat-on	Flat-on	Flat-on
15	Flat-on	Edge-on <sup>b</sup>	Edge-on <sup>b</sup>	Flat-on	Flat-on	Flat-on
10	Flat-on	Edge-on <sup>b</sup>	Edge-on <sup>b</sup>	Flat-on	Flat-on	Flat-on

 $^a$  Flat-on lamellar orientation.  $^b$  Coexistence with the flat-on adsorbed layer at the substrate interface.

the following observations: (i) the flat-on lamellar orientation is preferable for all thermally annealed PEO thin films crystallized at and above  $T_{\rm cr} = 35$  °C; (ii) below  $T_{\rm cr} = 35$  °C, the random orientation of the edge-on lamellae is formed in the 50 nm and 100 nm thick films, while only the flat-on lamellar orientation is found in the 20 nm thermally annealed films; and (iii) the dewetting process occurs in all the thermally treated films at  $T_{\rm cr} = 60$  °C, which is very close to the bulk  $T_{\rm m}$ . We will discuss the dewetting in detail in the next section. Hence, the thermally annealed films clearly show a thickness dependence of the orientation, in contrast to the CO<sub>2</sub>-treated PEO thin films.

Wang et al.12 reported the effects of quench depth and film thickness on lamellar orientations formed in semicrystalline polymer thin films at atmospheric pressure. They introduced the three- $T_{g}$  layered model (*i.e.*, the surface mobile layer ( $T_{g}$  <  $T_{g,bulk}$ ), the middle bulk-like layer ( $T_g = T_{g,bulk}$ ) and the adsorbed layer  $(T_g > T_{g,bulk})$ ). It is postulated that each region has a different bell-shaped overall crystallization rate curve as a function of crystallization temperature in the range between  $T_{g}$ and  $T_{\rm m}$ . As a result, the crystallization initiates, depending on the crystallization rate at a given temperature, either at the free surface (in the case of a higher  $T_{\rm cr}$ ) where the chains are highly mobile exhibiting lower  $T_{\rm g}^{15,61,62}$  and reduced viscosity,<sup>18,19</sup> or at the substrate interface (in the case of a lower  $T_{\rm cr}$ ) where the adsorbed chains are barely mobile even at  $T \gg T_{\rm g}$ .<sup>63</sup> Hence, our experimental results for the thermally annealed 50 nm and 100 nm thick films can in principle be explained by the threelayer model, but not for the 20 nm thick film. We postulate that the persistence of the flat-on lamellae in the 20 nm thick films is attributed to the effect of an irreversibly adsorbed layer. We will discuss this point later.

#### III-3. Dewetting structures

Here we focus on the dewetting behavior induced by the CO<sub>2</sub> annealing and subsequent thermal annealing at high  $T_{\rm cr}$ . It is known that dewetting is a phenomenon resulting from a breakup of thin films into droplets on substrate surfaces due to high mobility of polymer chains.<sup>64</sup> Fig. 6 shows representative POM images of the CO<sub>2</sub>-treated 50 nm thick PEO films at different  $T_{\rm cr}$ . Typical hole-shaped breakup structures<sup>65–67</sup> were observed at and above  $T_{cr} = 40$  °C (Fig. 6(a)-(c)), while the thermally annealed 50 nm thick PEO film dewetted at  $T_{\rm cr} \ge$ 60 °C. Hence, the lower limit temperature for the CO<sub>2</sub>-induced dewetting shifts to the lower temperature side (by about 15 °C) relative to that for the annealed PEO films. We found that the  ${
m CO}_2$ -induced dewetting is the most severe at  $T_{
m cr}$  = 40 °C (Fig. 6(a)), which may correspond to the transition temperature between crystallization and dewetting, as Okerberg et al. pointed out.68 The average height and the width of the rims (i.e., the hole boundary colored in light blue in Fig. 6(a)) are about 50-70 nm and 5-10 µm, respectively. Based on the AFM image shown in Fig. 6(d), we found that the polymer chains inside of the rims still crystallize into large needle-like (flat-on) patterns. Further AFM examination near the rims demonstrated that the needle-like structures are initiated from the rim and propagate into the inner region of the holes, as reported by Reiter and



**Fig. 6** Representative POM images of the CO<sub>2</sub>-treated 50 nm thick PEO thin films dried after 1 h at the following  $T_{\rm cr}$  values: (a) 40 °C; (b) 45 °C; (c) 50 °C. The AFM topographic image inside of the rims in (a) is shown in (d). The height scale for the AFM image is 0–50 nm.

Sommer.<sup>56</sup> In addition, we also confirmed that polymer chains in the matrix (non-dewetting) region crystallize as well, forming a flat-on lamellar orientation.

In order to shed light on the process, we further studied the time evolution of the dewetting structures. Fig. 7 shows the dewetting structures of the CO2-treated PEO thin films (20 nm and 50 nm in thickness) induced at  $T_{\rm cr} = 40$  °C. The results clearly show that the sizes of the dewetting structures are quite different between the 20 and 50 nm thick films in the same time period. For the 20 nm thick film, the kinetics is rather slow, and small (micron-scale) dewetting structures become evident after 12 h. On the other hand, ring-like dewetting holes of a few hundred microns in diameter were observed in the 50 nm (and 100 nm) thick films even after 1 h, and no further growth of these holes was observed in both thicker films during the course of the thermal annealing up to 12 h. These results suggest that the dewetting kinetics for the CO2-treated PEO thin films is significantly perturbed when the thickness is down to 20 nm. In order to investigate this retarded dewetting kinetics, we induced dewetting of the thermally annealed films at  $T_{\rm cr} = 60$  °C (without the  $CO_2$  process). As a result, the same trend was indicated: the slowing down of the dewetting kinetics for the thermally annealed 20 nm thick film compared to that of the thermally annealed 50 and 100 nm thick films. It is known that the dewetting velocity is independent of film thickness for "nonslipping" (sticking) films,69 while, in the case of slipping films, thinner films dewet faster than thicker ones.70-72 Since the interfacial energy of the PEO/H-Si system is very low (i.e., an attractively interacting system), the dewetting velocity would remain constant regardless of film thickness. This is at least true for the 50 nm and 100 nm thick thermally annealed PEO films. Below we show that this thickness dependence of the dewetting kinetics is a consequence of the interplay between the



Fig. 7 Time evolution of the surface morphologies of the CO<sub>2</sub>-treated PEO thin films dried at  $T_{\rm cr} = 40$  °C and for the times indicated, depicted with AFM images for the 20 nm film (left column) and POM images for the 50 nm film (right column). The height scale for the AFM images is 0–20 nm.

polymer-air interface, where the dewetting is initiated, and the polymer-substrate interface, where the adsorbed polymer layer is formed.

# IV. Discussion

Before moving into the main discussion, we briefly explain about irreversibly adsorbed polymer layers. Adsorbed polymer layers at the solid/polymer melt interface have recently been the subject of extensive study due to their strong influence on the physical and mechanical properties of polymeric materials confined at the nanometer scale.<sup>20,63,73–79</sup> Several research groups utilized the approach proposed by Guiselin,<sup>80</sup> which combines prolonged high-temperature annealing and subsequent solvent leaching,<sup>63,73,75,76</sup> and demonstrated the formation of adsorbed monolayers with a thickness of less than  $R_g$  against planar walls (substrates). The formation of adsorbed layers has also been reported for semicrystalline polymers prepared on planar substrates.<sup>20,22,81,82</sup>

We begin with the thermally annealed PEO films (50 nm thick) to investigate the adsorbed layer. PEO films annealed at 85 °C for 2 h were solvent leached in baths of fresh chlorobenzene at room temperature repeatedly. The details of the leaching process are described elsewhere.<sup>79</sup> After each leaching process, the residual layers were annealed at 85 °C for 1 h to remove any excess solvent trapped in the films. We

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measured the thickness of the residual layer by using ellipsometry and XR. A series of the leaching experiments gave rise to the residual (adsorbed) layers on H–Si substrates with different thicknesses ranging from 2.5 nm to 8.5 nm. We found that the residual layer of 2.5 nm in thickness (Fig. 8(e)) is the final adsorbed layer the thickness of which remains unchanged with any further aggressive leaching. As shown in Fig. 8, the AFM experiments for these adsorbed layers clearly show the finger-like seaweed flat-on lamellar structures, except for the 2.5 nm thick adsorbed layer. The GID experiments at the X9 beamline (NSLS) were carried out to further



Fig. 8 AFM topographic images of the PEO adsorbed layers: (a) 8.5 nm; (b) 6.5 nm; (c) 2.5 nm. The CO<sub>2</sub>-treated adsorbed layer (6.5 nm thick) is shown in (d). The XR profile (red circles) of the 2.5 nm adsorbed layer is shown in (e). The solid line corresponds to the best fit to the data based on the three-layer model (*i.e.*, PEO, SiO<sub>2</sub>, and Si layers). The thickness of the SiO<sub>2</sub> layer was determined to be about 1.3 nm from an independent XR measurement on a bare H–Si substrate. In the inset, the dispersion profile ( $\delta$  in the X-ray refractive index) obtained from the best fit is shown. The surface roughness is estimated to be 0.7  $\pm$  0.1 nm. The dotted line in the inset corresponds to the  $\delta$  value of the bulk. The formation of the high-density adsorbed layer next to a Si substrate is consistent with previous reports concerning different polymers.<sup>79,90</sup>

explore the structure of the 2.5 nm thick adsorbed layer. As compared to the GID data for the thermally annealed PEO thin film (50 nm thick, Fig. 9(a)), there are no diffraction peaks from the final adsorbed layer (Fig. 9(b)). On the other hand, GID experiments at SPring-8 clarified the 120 diffraction peak from the other adsorbed layers (Fig. 9(c)). Hence, these AFM and GID results lead to the conclusion that the chain architecture of the 2.5 nm thick final adsorbed layer prevents chain folding near the solid wall. We believe that this final layer corresponds to the "flattened" layer<sup>79</sup> with many solid/segment contacts that is composed of the early-arriving polymer chains at the substrate during the adsorption process. On the other hand, the other thicker adsorbed layers should be composed of two layers: an inner flattened layer and an outer loosely adsorbed layer that is formed by the latecoming chains during the adsorption process, which find fewer free surface areas and hence adsorb more loosely with fewer adsorbed sites.79 We previously demonstrated that loosely adsorbed polystyrene chains can be preferentially removed by optimizing solvent leaching conditions, while the flattened layer remains on the substrate.79 Therefore, it is reasonable to suppose that the loosely adsorbed polymer chains in the present study are gradually washed away during the consecutive leaching, resulting in the "transient" adsorbed layers of 4-8 nm in thickness.



**Fig. 9** Two-dimensional GID results for (a) the 50 nm thick spin-cast PEO film and (b) the 2.5 nm flattened layer. The dark spots in both images (indicated by the red arrows) correspond to the scattering contributions from the SiO<sub>2</sub> layer formed on the H–Si substrate. The one-dimensional GID results for the "transient" adsorbed layers (6.5 nm and 8.5 nm in thickness) and the flattened layer (2.5 nm in thickness) are shown in (c). The presence of the 120 diffraction peak at around q = 13.6 nm<sup>-1</sup> was used to determine the existence of the crystalline structure.

Next, we clarify the formation of the adsorbed layer in the CO<sub>2</sub>-treated films before the subsequent thermal annealing at  $T_{\rm cr}$ . With the aforementioned leaching process in conjunction with XR and AFM, we found the presence of the final flattened layer ( $\sim$ 2.5 nm in thickness) as well as the outer loosely adsorbed layer in all the CO2-treated PEO films (regardless of the film thickness and  $CO_2$  conditions). At the same time, we applied the same CO<sub>2</sub> treatment (*i.e.*, CO<sub>2</sub> exposure at T = 48 °C and P = 9.7 MPa and subsequent rapid depressurization) to the unexposed PEO adsorbed layers shown in Fig. 8(a)-(c). As shown in Fig. 8(d), the AFM result showed that the finger-like seaweed pattern of the CO2-treated adsorbed layer (original thickness of 6 nm) is slightly denser than that of the unexposed one (Fig. 8(b)). We also found that the magnitude of the swelling (obtained by ellipsometry and XR) of the CO<sub>2</sub>-treated adsorbed layer is much less ( $S_f = 0.03$ ) than that of the spin-cast PEO films after the complete depressurization to air ( $S_f = 0.15$ , Fig. 2). Hence, it is expected that the plasticization effect of  $CO_2$  at the interface is achieved to only a limited extent at the polymersubstrate interface, as compared to the rest of the spin-cast films. Consequently, we postulate that this limited plasticization effect plays a role in accelerating the polymer adsorption and chain folding rather than melting of the crystalline structures near the interface. According to a previous report by Jia and McCarthy,<sup>83</sup> CO<sub>2</sub> interacts with a hydroxyl group on a Si substrate, screening the polymer-substrate interaction. This would be the case for a polycarbonate-CO<sub>2</sub> system reported by Lan and co-workers.<sup>21</sup> However, as Jia and McCarthy also demonstrated, the screening effect is not fully achieved when a strong interaction between a polymer and Si substrate (e.g., our present system, PEO/H-Si) is present. We are currently studying various polymers with different segment/solid interactions to provide a better understanding of the adsorption mechanism in the presence of  $CO_2$ .

Based on the above results, we now propose the melt crystallization process of the PEO thin films associated with the adsorbed layer. The key is the interaction between the adsorbed layer and unadsorbed chains near the substrate interface. It has been indicated that the presence of a so-called reduced mobility interface (RMI) layer<sup>84,85</sup> (or transition zone) is required to ensure continuity in the mobility profile from the adsorbed layer to the bulk through chain entanglements.<sup>24</sup> Napolitano et al. reported that the RMI layer of poly(ethylene terephthalate) thin films prepared on aluminum substrates is about 20 nm in thickness.<sup>20</sup> While the formation/extent of the RMI layer may depend on the strength of the substrate interaction, the flexibility of polymer chains, or the thermal annealing conditions,<sup>15,84-86</sup> it is reasonable to suppose that part or the whole of the interior region of the 20 nm thick PEO films corresponds to the transition zone. For the PEO/H-Si system, the interaction is strong ("sticky") so that the adsorbed chains are predicted to adopt flat-on lamellar formation at the substrate,87 which is in good agreement with the present AFM results. If the melt crystallization from the amorphous state was initiated from the adsorbed lamellar layer (that remains unmelted even at  $T \gg T_{\rm m}$ as seen in polyethylene thin films<sup>22</sup>) as seed, the free polymer chains in the transition zone might then form the flat-on

lamellae with the same orientation as for the adsorbed lamellar layer in order to maximize the contacts, thereby stabilizing the interface.88 This would be the reason why the flat-on lamellar orientation in the presence of the adsorbed layer is favorable for the 20 nm thick films regardless of choice of  $T_{\rm cr}$  and the use of CO<sub>2</sub> annealing. It should also be noted that the melt crystallization process along with the adsorbed layer is analogous to the "self-seeding" process for replicating polymer single crystals on Si substrates.<sup>89</sup> The question is then why the flat-on lamellar orientation persists up to the topmost surface of the 100 nm thick CO<sub>2</sub>-treated film, in contrast to the thermally annealed films where the edge-on lamellar formation is dominant at the topmost surface of films of more than 50 nm in thickness at the lower  $T_{\rm cr}$  (see Table 1). This may be attributed to great reductions of both  $T_{\rm m}$  and  $T_{\rm g}$  of the swollen PEO thin films with the CO<sub>2</sub> annealing. As summarized in Table 1, the plasticization effect of  $CO_2$  shifts the film stability (*i.e.*, dewetting) to a lower temperature. Hence, with the aforementioned three-layer model,<sup>12</sup> we may conclude that the  $T_{cr}$  values used in the present study (as low as 10 °C) may not be low enough to induce the edge-on orientation at the topmost surface. As a consequence, the flat-on lamellar formation would proceed from the surfacebound flat-on lamellar layer and propagate into the film interior without emerging as independent nucleation at the top surface. Further experiments at lower  $T_{\rm cr}$  should be the subject of future work.

Finally, we look into the role of the adsorbed layer in the dewetting process. As previously reported, the loosely adsorbed polymer layer has nearly zero thermal expansion79 and is immobile<sup>63</sup> in air (or under vacuum) even at  $T \gg T_{g}$ . While the adsorbed layer swells in CO<sub>2</sub>, the degree to which it does so is extremely small. Hence, the strong hindrance of the mobility of the adsorbed chains is still sustained even in the CO<sub>2</sub>-treated PEO films. As a result, the effect of the adsorbed layer propagates into the film interior via the chain entanglements, resulting in the strongly hindered dewetting dynamics of the 20 nm thick CO<sub>2</sub>-treated film (the same mechanism should be applicable to the 20 nm thick thermally annealed film). It is important to mention that the propagation distance of the substrate effect of the CO<sub>2</sub>-treated films is limited to the region within 50 nm from the substrate interface, based on the dewetting kinetics at the topmost surfaces of the 50 nm thick and 100 nm thick films. We are currently conducting experiments to further quantify the effect of CO<sub>2</sub> on the RMI layer.

# V. Conclusion

The CO<sub>2</sub>-induced crystallization and dewetting of PEO ultrathin films were investigated by a suite of surface-sensitive experimental techniques. Spin-cast PEO films (without further hightemperature annealing) prepared on H–Si substrates were exposed to CO<sub>2</sub> at T = 48 °C and P = 9.7 MPa for 1 h to melt the polymer and then depressurized quickly to atmospheric pressure, allowing melt crystallization (and/or dewetting) from the non-equilibrium amorphous state at the given crystallization temperatures ( $T_{cr}$ ). As a result, we found that all the CO<sub>2</sub>-treated films show flat-on lamellar structures regardless of the thickness and  $T_{\rm cr}$ . This contrasts with the experimental results from the PEO thin films crystallized *via* the conventional thermal annealing process where the edge-on lamellar orientation occurs at the film surface. In addition, we found holeshaped breakup dewetting structures at the surface of the  $\rm CO_2$ -treated PEO films at and above  $T_{\rm cr} = 40$  °C, while the thermally annealed PEO film dewetted at  $T_{\rm cr} \ge 60$  °C. Interestingly, it was also found that the dewetting kinetics is severely hindered for the 20 nm thick  $\rm CO_2$ -treated film compared to that for the 50 nm and 100 nm thick  $\rm CO_2$ -treated films, while the dewetting kinetics is expected to be independent of film thickness for the attractively interacting system.<sup>69</sup>

We found that the formation of a very thin adsorbed layer during the CO<sub>2</sub> annealing plays vital roles in the observed melt crystallization and dewetting processes. After the CO<sub>2</sub> annealing, we used the solvent leaching process with chlorobenzene to extract the adsorbed layer that cannot be dissolved even in a good solvent. The systematic leaching experiments revealed the formation of a non-crystallized adsorbed layer of about 2.5 nm in thickness as well as transient crystallized adsorbed layers (of up to 8.5 nm in thickness) on the H-Si substrates. It was also found that the plasticization effect of CO<sub>2</sub> is achieved to only a limited extent at the polymer-substrate interface, as compared to the rest of the spin-cast films. Hence, this limited plasticization effect accelerates polymer adsorption and chain folding rather than the melting of the crystalline structures near the interface. We therefore postulate that the "bound" lamellar layer, which does not melt even in CO<sub>2</sub>, initiates the melt crystallization from the non-equilibrium amorphous state as a seed during the subsequent annealing process. In addition, the limited plasticization effect does not improve the inherent hindrance of the mobility of the adsorbed polymer chains either, maintaining the long-range perturbations associated with the adsorbed layer into the film interior through chain entanglements. Since the formation of the adsorbed layer would be a general phenomenon regardless of monomer-substrate interactions,<sup>20,63,73-79</sup> the present study brings new focus to the effects of the adsorbed layer on the crystallization and dewetting processes under nanoconfined geometries. Also, the present study demonstrates that the CO<sub>2</sub> solvent annealing can be used as a low-temperature, environmentally green, and more effective process to produce controlled crystalline morphologies with long-range order in place of conventional high-temperature thermal annealing.

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