Tuning Morphology and Melting Temperature in Polyethylene Films by MAPLE

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ABSTRACT: The control of structure and thermal stability in semicrystalline polymer films remains an important challenge in applications ranging from solar energy devices to packaging films. Here, we demonstrate the ability to dramatically alter the morphology and melting temperature (T_m) of low-molecular-weight linear polyethylene (PE) by employing an innovative vapor-assisted deposition process termed matrix assisted pulsed laser evaporation (MAPLE). We report the ability to tune T_m of PE films by 20 °C by simply adjusting the deposition temperature during MAPLE processing. This unique capability stems from the ability of MAPLE to exploit confined crystallization during thin film growth. In addition, we demonstrate the ability to exploit MAPLE to design PE films that exhibit the same T_m as their melt-crystallized analogues but have an ~25% higher degree of crystallinity. Our investigation offers new insights into how confinement effects in polymer crystallization can be utilized in the emerging field of polymer film fabrication by MAPLE to control structure and key material properties of semicrystalline polymer films.

INTRODUCTION

From next-generation solar energy harvesting devices to various types of plastic microelectronics, many of the polymeric materials that will enable tomorrow’s technologies are semicrystalline. Rather than comprising a single uniform phase, semicrystalline polymers are characterized by folded-chain lamellar crystals with intercalated entanglements that remain amorphous. The structure within semicrystalline polymers has a strong influence on thermal stability, i.e., the melting temperature (T_m) as well as the mechanical and electrical properties of semicrystalline polymers. The precise control of structure and T_m in polymer thin films, without the need for chemical modification or the inclusion of functional additives, remains of interest and a formidable challenge in material science.

Here, we introduce a new and promising approach to dramatically tune the structure and T_m of semicrystalline polymer films by exploiting the unique deposition capabilities of matrix assisted pulsed laser evaporation (MAPLE). In the MAPLE process, polymer films are grown by laser ablation of a frozen dilute solution of polymer and solvent, in which the solvent serves as a sacrificial matrix to transport the polymer into the gas phase and eliminate polymer degradation. MAPLE has been shown to be a promising approach to deposit functional polymer films. Via MAPLE, film growth proceeds by the deposition of nano- to micrometer-sized isolated (or confined) polymer droplets with simultaneous crystallization at a controlled substrate deposition temperature (T_dep). By exploiting this feature, we demonstrate that for low-molecular-weight linear polyethylene (PE; M_n = 3000, M_w/M_n = 1.10) T_m can be tuned by 20 °C simply by controlling T_dep during MAPLE deposition. To place these results in context, it is not practically feasible to tune T_m by more than 5 °C via melt crystallization for PE. Furthermore, we demonstrate that while PE films processed by MAPLE can be designed to exhibit the same T_m as their melt-crystallized analogues, the degree of crystallinity is always notably enhanced. This tunability in the structure of PE stems from the ability of MAPLE to confine polymer crystallization into nanoscale dimensions during film formation.

RESULTS AND DISCUSSION

Film Formation by Additive Deposition and Crystalization of Confined PE Droplets. To gain an understanding of the crystallization mechanism of PE films formed by MAPLE processing, we first investigated the impact of T_dep on crystallization during the early stages of film formation, i.e., when the film consists of isolated nano- and microsized...
droplets of PE prior to consolidation. The importance of $T_{\text{dep}}$ as a key processing parameter to control morphology, and hence properties, stems from its strong correlation to the nucleation rate of confined droplets and lamellar thickness.36

By characterizing the early stage film morphology, lamellar thicknesses and rough estimates of the critical volume ($V_{\text{crit}}$) required for self-nucleation of the confined droplets could be investigated, as previously performed in the study of MAPLE-deposited poly(ethylene oxide).36,37 To enable such a study, we deposited isolated PE droplets atop silicon substrates (Si) by MAPLE from a dilute solution target (see Supporting Information for details of the MAPLE conditions).

We first investigated the crystalline morphology formed at $T_{\text{dep}} = 116 \, ^\circ\text{C}$, which represents the typical crystallization temperature of bulk PE when $M_n = 3000$.40 Figure 1a shows an optical microscopy image of MAPLE-deposited PE (MAPLE-PE) droplets formed at $T_{\text{dep}} = 116 \, ^\circ\text{C}$. At this temperature, platelet-like monolamellar crystals (MLCs) were formed from nucleating confined droplets of volume larger than $\sim 1 \, \mu\text{m}^3$. The region marked R1 in Figure 1a indicates a MLC grown from a nucleating droplet, whose structure is provided in the inset of Figure 1a. The AFM height image in Figure 1b magnifies the MLC depicted in R1. This revealed that the MLC had a uniform thickness (lamellar thickness, $d$) of $\sim 27 \, \text{nm}$, which agreed well with the fully extended chain length of PE when considering 0.127 nm as the increment of length per CH$_2$ group. It also agrees with the observation by Ueda and Register,36 where the same PE, in bulk, formed extended chain crystals when crystallized at a similar temperature. The formation of 27 nm thick MLCs also indicated that the molecular weight of PE was well preserved during MAPLE processing.

When PE was deposited at $T_{\text{dep}} = 75 \, ^\circ\text{C}$, the MLCs were composed of folded chains with $d \sim 10 \, \text{nm}$. Interestingly, nucleating droplets with sizes down to $10^{-4} - 10^{-3} \, \mu\text{m}^3$ were composed of a single lamella or a few stacked lamellae, thus leading to the formation of PE nanocrystals. Figure 1c shows the AFM amplitude image of the PE nanocrystals while Figure 1d shows the AFM height image magnifying the region R2 in Figure 1c. The arrow in Figure 1c points to a crystal containing a screw dislocation, which represents the morphology of a few stacked lamellae. The Figure 1c inset schematically describes the structure of the PE nanocrystals. The nucleation rate for such small droplets ($10^{-4} - 10^{-3} \, \mu\text{m}^3$) is expected to be highly dependent on $T_{\text{c}}$ and the droplet size.36,41 The nucleation rate of PE confined to $\sim 10^{-3} \, \mu\text{m}^3$ was predicted to be $1, 10^{-2}$, and $10^{-3} \, \text{min}^{-1}$ at $T_{\text{c}} = 75, 80,$ and $90 \, ^\circ\text{C}$, respectively.44,45 Therefore, self-nucleation of such confined droplets was expected during the time scale of deposition ($\sim 1 \, \text{h}$) for $T_{\text{dep}}$ below 80 °C, but at $T_{\text{dep}}$ above 80 °C, only much larger droplets would be able to nucleate during deposition. When $T_{\text{dep}} = 116 \, ^\circ\text{C}$, all identified nucleating droplets with $d \sim 27 \, \text{nm}$ had a volume larger than $\sim 1 \, \mu\text{m}^3$, as shown in Figure 1a.

The above observations provided clues to PE film formation and morphology development by MAPLE. In the early stages of deposition, crystallization of PE proceeds primarily via nucleation of droplets with volumes larger than $V_{\text{crit}}$. As the film becomes consolidated, crystal lattice sites at the surface of the film promote the crystallization of subsequently deposited droplets. Meanwhile, $T_{\text{dep}}$ uniquely determines the thickness of the lamellae, as illustrated by Figure 1e, which compares the representative height profiles of MAPLE-PE MLCs formed at four different $T_{\text{dep}}$: 75, 80, 100, and 116 °C. The average MLC thickness at each $T_{\text{dep}}$ is presented in Figure 1f. It should be

Figure 1. (a) Optical microscopy image of MAPLE-PE on Si formed with 30 min of deposition from a 0.2 mg/mL solution target at $T_{\text{dep}} = 116 \, ^\circ\text{C}$. The inset shows the structure of a MLC grown from a nucleating droplet of size $\sim 1 \, \mu\text{m}^3$. (b) AFM height image magnifying the MLC in R1 in part a. (c) AFM amplitude image of MAPLE-PE formed with $T_{\text{dep}} = 75 \, ^\circ\text{C}$ showing the morphology of PE nanocrystals consisting of a single lamella or a few stacked lamellae. The white arrow indicates a crystal with a screw dislocation. The inset schematic shows the structure of the PE nanocrystals. (d) AFM height image magnifying the MLCS in R2 in part c. (e) Representative height profiles of PE MLCs formed at various $T_{\text{dep}}$. (f) Bar graph comparing MLC thicknesses of MAPLE-PE formed at various $T_{\text{dep}}$, error ranges represent the standard deviation of the height measurements on multiple isolated PE MLCs formed at each $T_{\text{dep}}$.

Figure 2. (a) Optical microscopy image of MAPLE-PE on Si, formed with 1.5 h of deposition from a 1 mg/mL solution target at $T_{\text{dep}} = 25 \, ^\circ\text{C}$. (b, c) Optical microscopy images of a flash-DSC chip where (b) shows the chip covered with a polyimide mask. The mask has a laser-machined hole of size 250 x 250 μm$^2$ in the center (indicated by arrow), which exposes the sample stage of the chip. (c) Optical image that shows the sample stage of the chip after MAPLE PE deposition. The white dashed line marks the region of the deposited film.
noted that the thicknesses at $T_{\text{dep}} = 75$, 80, and 100 °C are approximately half the extended-chain crystal thickness, indicating that some of the chains could comprise two independent crystal stems. This crystallization behavior is clearly different from typical melt crystallization, where structure formation is mostly dominated by spherulitic growth throughout the entire film that readily occurs after the onset of nucleation.

**Tuning $T_m$ of MAPLE-PE Films by Controlling $T_{\text{dep}}$.** To investigate the $T_m$ of MAPLE-PE films formed at various $T_{\text{dep}}$, we performed calorimetric analysis by directly depositing PE atop flash-calorimetry chips (flash-DSC chips). Here, we performed MAPLE with a longer deposition time and higher deposition rate compared to the conditions used to undertake the above AFM analysis of early stage film growth; these growth conditions formed a consolidated film in the investigated $T_{\text{dep}}$ range, except at $T_{\text{dep}} = 116$ °C, where dewetting of the PE film into large droplets occurred (see Figure S2 in Supporting Information). Figure 2a shows an optical microscopy image of a consolidated PE film deposited atop Si at $T_{\text{dep}} = 25$ °C. Flash-DSC chips have a sample and reference area of 500 μm diameter each. We masked the chip with a polyimide film having a laser-machined hole of size 250 × 250 μm$^2$ to exclusively expose the sample area, as shown in Figure 2b. After masking, the chip was attached to a MAPLE substrate heater for deposition. Figure 2c shows an image of the flash-DSC chip after MAPLE, where the white-dashed square indicates the deposited area.

Figure 3. (a) Plots comparing normalized flash-DSC first heating thermograms of MAPLE-PE formed with various $T_{\text{dep}}$ ranging from −2 to 116 °C. The dashed curve is the normalized heating thermogram of LN$_2$-quenched 5 mg PE, obtained using a conventional DSC. (b) Plots showing GIWAXS intensities of MAPLE-PE, formed with $T_{\text{dep}}$ from 5 to 116 °C atop Si, as a function of scattering vector, $q$. All patterns have two peaks at $q_1 = 1.54$ Å$^{-1}$ and $q_2 = 1.70$ Å$^{-1}$, which correspond to (110) and (200) reflections of orthorhombic PE, respectively. The plots were normalized to have the same intensity at $q_1 = 1.54$ Å$^{-1}$, and the individual traces were shifted along the y-axis for clarity.

**Figure 4.** (a) Normalized DSC cooling and the subsequent heating thermograms of PE. Various cooling rates were used as follows: 0.5 °C/min (blue), 5 °C/min (red), 40 °C/min (green), and $3 \times 10^3$ °C/min ($= 5000$ °C/s or 5k-quenching, black-dotted). Bulk-DSC was used for cooling rates of 0.5–40 °C/min, and flash-DSC was used for $3 \times 10^3$ °C/min. (b) Schematic describing the temperature protocol used for isothermal crystallization with flash-DSC. (c) Flash-DSC heating thermograms of PE, measured after isothermal crystallization at various temperatures ($T_c,\text{iso}$) from 90 to 116 °C. For comparison, a heating curve of the same PE crystalized by 5k-quenching is shown as the dotted-blue curve. The inset magnifies the melting regions of three isothermally crystallized samples, formed with $T_c,\text{iso} = 105, 110$, and 116 °C, which each exhibits a bimodal shape. (d) Optical microscopy images comparing the morphology of MAPLE-PE atop a flash-DSC chip before (left panel) and after (right panel) postdeposition melting at 150 °C. Here, the sample was initially prepared by MAPLE at $T_{\text{dep}} = −2$ °C.
nonisothermal cooling of bulk PE (~5 mg), even by quenching into liquid nitrogen (LN2), could only achieve a lower bound of $T_m = 126.4 \pm 4^\circ C$, as illustrated by the dashed curve in Figure 3a. The $T_m$ of finite lamellar crystallites, which consist of amorphous layers of thickness $d_a$ and crystalline layers of thickness $d_c$ ($d = d_a + d_c$), can be predicted by the Gibbs–Thomson equation:  

$$T_m = T_m^0 \left(1 - \frac{2\sigma_s \Delta H_f^\circ}{d \Delta H_f^\circ \rho}\right)$$  

where $\sigma_s$ is the amorphous (chain end or fold) surface energy, $T_m^0$ and $\Delta H_f^\circ$ are the equilibrium melting temperature and heat of fusion (energy/mass) of an infinitely thick PE lamella, respectively, and $\rho$ is the density of crystalline PE. From this relationship, the variation in $T_m$ can be attributed to a change in $d_c$. To confirm that the variation of $T_m$ was not due to a different unit cell structure, we performed grazing-incidence wide-angle X-ray scattering (GIWAXS) on MAPLE-PE films deposited atop Si. The samples all exhibited two strong peaks at $q_1 = 1.54 \text{ Å}^{-1}$ and $d_2 = 1.70 \text{ Å}^{-1}$, as shown in Figure 3b, which corresponded to the (110) (interplanar spacing of 4.11 Å) and (200) (interplanar spacing of 3.70 Å) reflections of the orthorhombic PE crystal structure, respectively.  

The $d_c$ and the corresponding $T_m$ of lamellar crystallites are known to be controlled by $T_c$, as supported by the same dependence of $d_c$ (or $T_m$) on $T_c$ between melt- and solution-crystallization. To investigate the correlation between $T_{dep}$ and $T_c$ during film formation by MAPLE, we compared the $T_{dep}-T_m$ relationship with the $T_{iso}-T_m$ relationship obtained by melt crystallization of our PE. We conducted both nonisothermal and isothermal melt-crystallization experiments using traditional DSC (bulk-DSC) and flash-DSC.  

For nonisothermal crystallization, we used various cooling rates to obtain a range of $T_c$ and the corresponding $T_m$ which were quantified as the peak temperatures during crystallization and melting, respectively. Figure 4a compares the cooling and heating thermograms of the PE between 25 and 150 °C. Bulk-DSC was used for cooling rates of 0.5–40 °C/min, and flash-DSC was used for 300 000 °C/min (5 000 °C/s, “5k-quenching”). After cooling from the 150 °C melt at various rates, subsequent heating runs were employed to measure $T_m$ and heating rates of 10 °C/min and 5000 °C/s were used for bulk- and flash-DSC, respectively. The slowest cooling rate of 0.5 °C/min resulted in the highest $T_c$ of 118.2 °C and a corresponding $T_m$ of 128.2 °C, at which our PE of $M_n = 3000 \text{ g/mol}$ is expected to form its most stable crystals, with an extended-chain conformation.  

Increasing the cooling rate to 40 °C/min with bulk-DSC merely decreased $T_c$ by ~5 °C and $T_m$ by ~1.6 °C. In comparison, 5k-quenching with flash-DSC resulted in a broad crystallization peak with the onset $T_c$ below 100 °C, and a $T_m$ around 113.5 °C on subsequent heating, significantly reducing $T_c$ and $T_m$ in comparison to those obtained from bulk-DSC with cooling rates below 40 °C/min.  

As 5k-quenching by flash-DSC can dramatically reduce the onset $T_c$, we next conducted isothermal crystallization above 90 °C to obtain a broader range of $T_c-T_m$ data. Figure 4b describes the temperature protocol used for isothermal crystallization via flash-DSC. A melt of a PE sample at 150 °C was 5k-quenched to a target crystallization temperature ($T_{c iso}$) in the range of 90–116 °C and isothermally crystallized for 10 min. This was followed by another 5k-quench down to 25 °C, and after isothermal annealing for 0.5 s the sample was heated to 150 °C at 300 000 °C/min to measure $T_m$. Figure 4c compares the flash-DSC heating thermograms of the same PE sample after isothermal crystallization at various $T_{c iso}$. The $T_m$ clearly increased with increasing $T_{c iso}$, as expected.  

Interestingly, the melting peak became bimodal at $T_{c iso}$ above 105 °C. We reason that this was due to two different sets of nucleation events: one occurring at $T_{c iso}$ and the other occurring during the subsequent 5k-quench step to 25 °C. Annealing of MAPLE-PE films at 150 °C leads to dewetting into numerous isolated liquid droplets of various sizes, as shown in Figure 4d. In such a sample geometry, each droplet must be individually nucleated; therefore, the nucleation probability of smaller PE droplets during the isothermal hold would significantly decrease as $T_{c iso}$ is increased. As a result, only larger droplets could crystallize at higher $T_{c iso}$ while smaller ones would stay liquid at $T_{c iso}$ and crystallize during the 5k-quench to 25 °C. The first melting peak of the PE samples with $T_{c iso}$ above 105 °C occurs at ~113–114 °C, which matches the $T_m$ of PE which was 5k-quenched from the melt (see Figure 4c inset). Therefore, for those samples we selected $T_m$ from the second melting peak as corresponding to crystals formed at the target $T_{c iso}$.  

Figure 5 compares the $T_m-T_{dep}$ relationship obtained from MAPLE with the $T_m-T_c$ relationship obtained from melt crystallization. Data obtained by MAPLE crystallization (MAPLE), isothermal crystallization (ISO), and nonisothermal crystallization (NIC) are plotted as green circles, blue triangles, and red squares, respectively. Above 75 °C, all three data sets reasonably fit one straight line (line 1 in Figure 5), indicating that the MAPLE-deposited PE crystallized at the deposition temperature ($T_{dep} = T_c$). At $T_c = T_{dep} = 116 °C$, however, the $T_m$ values obtained by ISO and MAPLE exhibited a difference of ~3.4 °C. We believe that this is due to the high $T_{dep}$ of 116 °C—a temperature sufficiently high that not all the PE droplets nucleate during MAPLE deposition. Uncrystallized droplets would crystallize at $T_c < 116 °C$ during the cooling step after MAPLE, which would bias the DSC melting peak toward the
lower temperature region. The linear relationship between \( T_c \) and \( T_m \) on line 1 agrees with the typical crystallization-melting behavior of metastable polymer crystals formed at a relatively low undercooling (\( \Delta T = T_m - T_c \)).\(^{50-52}\)

Interestingly, in the \( T_{\text{dep}} \) range below 75 °C, the \( T_m - T_{\text{dep}} \) data follow a different line (line 2 in Figure 5), which deviates from line 1. In this temperature range, the \( T_m - T_{\text{dep}} \) data for melt crystallization were not available due to rapid crystallization prior to reaching the target \( T_c \), even for flash-DSC. On line 2, \( T_m \) decreased by \( \sim 1.8 \) °C for every 20 °C decrease in \( T_{\text{dep}} \), which was about 3.9 times smaller than that the \( T_m \) depression rate on line 1. For MAPLE-PE formed at \( T_{\text{dep}} = -2 \) °C, the measured \( T_m \) was 19.7 °C higher than the \( T_m \) extrapolated along line 1.

While predicting the exact \( T_m - T_{\text{dep}} \) relationship in the deeply supercooled regime was beyond the scope of this study, the following factors may be relevant to the deviation observed below 75 °C. First, the Hoffman–Lauritzen model\(^ {53,54}\) could support the observation. The theoretical \( T_m - T_c \) relationship based on the Hoffman–Lauritzen model intrinsically has nonlinearity, where the change of \( T_m \) with \( T_c \) becomes smaller at lower \( T_c \) (or larger \( \Delta T \)).\(^ {50} \) Therefore, even if \( T_c = T_{\text{dep}} \), the \( T_m - T_{\text{dep}} \) plot would exhibit a decrease in slope at smaller \( T_{\text{dep}} \) values. Additionally, from the experimental viewpoint, the rapid crystallization kinetics of PE may have resulted in crystallization prior to reaching \( T_{\text{dep}} \) (\( T_c > T_{\text{dep}} \)) below \( T_{\text{dep}} \sim 75 \) °C, thus resulting in the deviation of the \( T_m - T_{\text{dep}} \) trend from line 1, where \( T_c \) is precisely known and controlled. The \( T_c = T_{\text{dep}} \) condition should pertain when the temperature of the liquid PE droplets deposited on the substrate equilibrates to \( T_{\text{dep}} \) prior to nucleation; that is, the characteristic heat conduction time (\( \tau_{\text{heat}} \)) should be much smaller than the characteristic nucleation induction time (\( \tau_{\text{nuc}} \)) of PE. As a decrease of temperature dramatically accelerates PE nucleation, \( \tau_{\text{nuc}} \) will become smaller than \( \tau_{\text{heat}} \) at a sufficiently low \( T_{\text{dep}} \). PE droplets of 0.1 and 1 μm radius are estimated to nucleate prior to thermal equilibration (\( \tau_{\text{nuc}} < \tau_{\text{heat}} \)) at \( T_{\text{dep}} \) below \( \sim 52 \) and \( \sim 63 \) °C, respectively, roughly where the data begin to deviate from line 1 (see Supporting Information for details of the calculation). In addition, the rapid crystal growth after the onset of nucleation may prevent the latent heat released upon crystallization from diffusing out of the droplet as fast as it is generated, contributing to an increase in \( T_c \).\(^ {55}\)

**Figure 6.** (a) Plots showing the crystallinity of MAPLE-PE as a function of \( T_{\text{dep}} \) determined by two methods: relative crystallinity \( (X'_c) \), left y-axis) obtained by flash-DSC analysis (red squares) and crystallinity \( (X_{\text{GIWAXS}}) \) (right y-axis) obtained by the analysis of GIWAXS patterns (blue triangles). Crystallinity of single lamellar crystals calculated from the MLC thickness and \( d = 2.5 \) nm \( (X_{\text{single}}) \), right y-axis) is marked with + signs. (b) Plots comparing \( X_c \) of MAPLE-PE (black squares) and melt-crystallized PE as a function of the corresponding \( T_m \). For melt-crystallization, ISO with \( T_{\text{iso}} = 90 \) and 95 °C (blue triangles) and NIC with cooling rates from 10 to 5000 °C/s (red circles) were used. (c, d) Illustrations showing the structure development of PE during (c) melt-crystallization and (d) MAPLE-crystallization. Note that the MAPLE-crystallized PE has a higher crystallinity due to the smaller content of intercrystallite amorphous phase.
MAPLE-PE exhibited an abnormally low $X'_c$ with a dewetted film morphology (see Figure S2). We assumed that this was due to the slow nucleation of PE at 116 °C. Dewetting of uncrystallized PE would occur during deposition at such a high temperature; therefore, the isolated liquid droplets would crystallize at $T_c < 116$ °C on cooling after MAPLE. To check the validity of the $T_{dep}$-$X'_c$ trend obtained by flash-DSC analysis, we also derived the crystallinity of MAPLE-PE from GIWAXS data (blue triangles with right y-axis in Figure 6a). From the analysis of wide-angle X-ray scattering patterns, $X'_c$ (or $X'_{GIWAXS}$) of PE could also be determined, as elaborated in the Supporting Information. With the proportionality constant of $0.642 \pm 0.020$ between $X'_c$ and $X'_{GIWAXS}$ ($0.642X'_c = X'_{GIWAXS}$), the two crystallinity vs $T_{dep}$ curves reasonably match, as expected.

From the simplified model of semicrystalline polymers, we can assume that two types of structures mainly contribute to the amorphous fraction: (i) the fold/endo group surface of lamellar crystallites and (ii) entangled PE chains that are kinetically trapped between lamellae, when the crystals are thin enough for some of the PE chains to form two stems. Because of the amorphous nature of the fold surface, even PE single lamellar crystallites exhibit semicrystallinity, with a crystallinity ($X_{c,single}$) approximately equal to $d_c/d_T^{56}$ $X'_c$ (or $X'_{GIWAXS}$) would be the same as $X_{c,single}$ if the bulk polymer consists exclusively of unconnected lamellar crystallites or smaller than $X_{c,single}$ if the polymer contains a considerable amount of entanglements kinetically trapped between lamellae. Considering the thickness of PE amorphous layers ($d_x, d_y = d - d_c$) is $\sim 2.5$ nm, $56,56,57$ the $X_{c,single}$ of our PE formed at $T_{dep} = 116, 100, 80$, and 75 °C would be 0.91, 0.84, 0.80, and 0.77, respectively (see + symbols with y-axis on the right in Figure 6a), based on the MLC thickness measurements provided in Figure 6f. The predicted $T_{dep}$-$X_{c,single}$ relationship is in reasonable agreement with the $T_{dep}$-$X'_c$ relationship, as shown in Figure 6a.

At a given $T_c$ or $X_{c,single}$, the variation in crystallinity should thus reflect differences in the extent of interlamellar entanglements. To understand how effectively MAPLE processing forms crystalline PE at a given $T_{dep}$, we compared $X'_c$ of PE processed via MAPLE and melt crystallization as a function of $T_m$ in Figure 6b; the black squares, red circles, and blue triangles represent the $X'_c$ of PE formed by MAPLE, NIC, and ISO, respectively. Cooling rates of 10–5000 °C/s (NIC10–NIC5000) were used for NIC, and $T_{clust}$ of 90 and 95 °C (ISO90C, ISO95C) were used for ISO crystallization. As $T_m$ represents the $X'_c$ of constituent lamellar crystallites, we propose that the crystallinity–$T_m$ plot provides insight into the difference in the extent of interlamellar entanglements between PE samples crystallized in different ways. Interestingly, the MAPLE-PE samples exhibited a higher crystallinity over the whole range of $T_m$.

We attribute the higher crystallinity of MAPLE-PE samples to MAPLE’s ability to generate disentangled-chain precursors for crystallization. In the case of melt-crystallization, PE chains need to disentangle from the mutually entangled melt (entanglement molecular weight of linear PE $\sim 1200$ g/mol$^{58,59}$) for crystallization. We expect that the rapid nonisothermal quenching would not provide sufficient time for disentanglement of the chains, leading to a higher content of entanglements trapped in interlamellar regions. This is schematically illustrated in Figure 6c; estimates of the characteristic times for disentanglement and crystallization for our low-molecular-weight PE (see Supporting Information) suggest that this situation should pertain at temperatures below about 100 °C, above the isothermal $T_c$ values employed in Figure 6b, as well as the $T_c$ values during nonisothermal crystallization at cooling rates above 10 °C/s. In comparison, we suspect that crystallization via MAPLE can dramatically reduce the entanglement density in the melt; since the MAPLE target consists of a frozen dilute solution, polymers are deposited as isolated chains or few-chain clusters, allowing PE chains to individually crystallize at the substrate, as depicted in Figure 6d. Hence, MAPLE offers a unique route for the deposition and control of morphology in thin polymer films, in which growth proceeds by the assembly of individual droplets under conditions where crystallization simultaneously occurs.

CONCLUSIONS

Here, we exploited MAPLE as a state-of-the-art processing technology for the deposition of PE films with control over structure and $T_m$. We demonstrated the ability to precisely tune $T_m$ over 20 °C. This range was achieved through the unique means of film formation during MAPLE, wherein polymer droplets were deposited and crystallized at a target substrate temperature. As confinement within droplets can suppress the onset of nucleation, deeply supercooled crystallization of PE could be achieved during film formation. Furthermore, MAPLE processing formed films with higher crystallinity compared to their melt-crystallized counterparts with the same $T_m$, by effectively reducing the density of chain entanglements. As such, this investigation offered new insights into how confinement effects in polymer crystallization could be utilized in film fabrication to finely control the structure of crystalline polymers. We anticipate that this approach will lay the foundation for the exploitation of MAPLE in emerging technologies where semicrystalline polymer films can play a key role.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.7b02345.

Notes

The authors declare no competing financial interest.

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