

Semi-crystalline polymer thin films: The art of confinement and substrate effect

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ABSTRACT

The crystallization of the thin and ultra-thin polymer films has been studied by different research groups due to their importance in the development of advanced coating materials. Studies have revealed that thin and ultra-thin polymer films behave differently from their bulk counterparts; in semi-crystalline polymers, the differences include the morphology, degree of crystallinity, chain and lamellar orientation, crystallization rate and surface modulus, etc. Reiter *et al.* studied the crystallization of polyethylene oxide (PEO) in quasi-two dimensions and observed the dependence of morphology on the crystallization temperature and molecular weight; Taguchi *et al.* studied the morphology and crystallization rate of isotactic polystyrene (PS) ultra-thin films as a function of film thickness; Schönherr *et al.* used an *in situ* scanning force microscope (SFM) method which could image the growth of surface directed spherulites growth of PEO; Despotopoulou *et al.* systematically investigated the effect of confinement on the crystallinity and chain orientation of ultrathin poly(di-n-hexylsilane) films. The influence of confinement and surface interaction on the melting temperature and the crystallite orientation has only recently been studied. With the advancement of modern technology, more and more properties of the films thinner than 20 nm have been revealed and precisely measured, and

the distinct influence of these two factors can be clearly identified. With the aid of SFM and near edge X-ray absorption fine structure spectroscopy (NEXAFS), Wang *et al.* have shown that the crystal lamellae took a highly preferential orientation on strongly attractive substrate, and the orientation changes from edge-on to flat-on below the threshold thickness of 20-30 nm, while lamellar twisting occurred on weakly attractive substrate; by using the shear modulus force microscopy (SMFM), Wang *et al.* have found that the melting temperature (T_m) of the ultra-thin films on the highly attractive substrate was lower for up to 38°C than the bulk polymer, while on the weakly attractive substrate, the T_m depression of the film with the same thickness was only 12°C. Fitting with Thomson-Gibbs equation, the interfacial reaction was demonstrated to be the key factor that led to the large T_m depression.

KEYWORDS: semi-crystalline polymer, film, confinement, substrate, morphology, orientation, melting point

1. INTRODUCTION

Semi-crystalline polymer thin (thickness between 100 nm and 1,000 nm) and ultra-thin (<100 nm) films have attracted intense interest of research in the past several decades due to their increasingly important applications in the modern industries [1-5]. They exhibit unique properties which are different from their bulk counterparts in terms of the chain mobility [6, 7], preferential crystal and chain orientation [8-14], optical and mechanical

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anisotropies [15], special electronic properties [4], different thermal transition [12, 13, 16-18], all of which shed great light on the fundamental understanding of polymer physics [15]. Previous studies have shown that the diffusion coefficient of polymer chains near an attractive substrate can be up to $\sim 10^2$ smaller than that near the vacuum interface [6], demonstrating that the substrate interaction is another critical factor determining the properties of the polymer thin films. Under the interplay of the confinement and substrate interaction, the crystallization of thin and ultra-thin polymer films has been an intriguing and controversial topic. On one hand, the effect of the substrate becomes increasingly important with the diminishing film thickness, and substrate can induce the heterogeneous nucleation and orient the crystal lamellae, the crystallization is facilitated. On the other hand, the constrained geometry can prohibit the nucleation formation due to the difficulty to reach the critical nucleation size, and the little material available will cause the slower diffusion rate, the crystallization process can be slowed or inhibited [19].

The susceptibility of the semi-crystalline polymer films to the confinement and substrates also originates from their thermodynamically meta-stable nature. In a polymer melt, the chains exist in un-organized coiled states which have high conformational entropy, during the crystallization the chains transform to ordered low-entropy states [20-24]. For n-alkanes, the full stretching of chains longer than 150 $-\text{CH}_2-$ units are rarely reached under normal pressure [25], the chains thus have to take folded structure and form the crystal lamellae [24, 26]. The thickness of the lamellae of a polymer single crystal grown from dilute polymer solution is normally 10 nm. In the polymers crystallized from the melt, however, the crystals are far from ideal, there are always amorphous parts in between the crystalline parts, the chains have the potential to extend, and the resulting crystal is hence meta-stable, their lamellar thickness, morphology, degree of crystallinity, and melting temperature largely depend on many factors including the thermal history, interfacial reaction, as well as confinement [21, 27-29].

This short review is a summary of the studies of several research groups that have conducted

systematic investigations on the crystallization of thin and ultra-thin polymer films under constrained geometry or on various substrates. We focus on the effect of confinement and substrate interaction on the morphology, orientation of crystal lamellae and polymer chain, degree of crystallinity, crystallization kinetics, and melting point. We organize the review in such a way that the most closely related properties are discussed in one section, and the work of one research group may be reviewed in different sections.

2. Morphology, orientation of crystal lamellae and polymer chains

The morphology of the semi-crystalline ultra-thin polymer films has always been an area of extensive interest not only because it's the most direct property that can be observed by various microscopes, but also because it's closely related to other properties of the crystals, i.e., the mechanical and optical anisotropy, toughening mechanism, the degree of crystallinity, and sometimes it can reflect the organization of the chains. Ever since the invention of the scanning force microscopy (SFM) or atomic force microscopy (AFM), it has been a powerful tool for studying the surface properties of the materials, and it has been widely used in studying the crystallization of polymers [30, 31]. Apart from providing static images of the crystal morphology and surface viscoelastic properties, the tapping mode AFM has also been used for *in situ* observation of the morphology development during crystallization process [28, 31-36].

Spherulite is one of the most prevalent morphologies in the melt-crystallized bulk polymers. A spherulite consists of numerous crystal lamellae of nearly constant lateral dimension growing from a common center; through repeated branching, the lamellae uniformly fill up the space and form a mature spherulite [37-40]. Polymers never crystallize completely, there are always amorphous regions between the crystal lamellae, and hence they are called "semi-crystal". A spherulite can be either compact or open. A compact structure is one in which a large proportion of the material has been crystallized and the lamellae are packed closely; an open structure, on the other hand, is one in which the lamellae are separated to a

greater extent by the amorphous material [38]. In thin films, due to the confinement in the thickness dimension, the spherulites exhibit 2D feature [41]. Studies have also shown that the packing density, the thickness and orientation of the lamellae, as well as the orientation of the polymer chains are also significantly influenced by the film thickness and substrates [1, 11-13, 19, 32, 33, 42-45]. Bartczak *et al.* studied the crystallization of high density polyethylene (HDPE) either on the calcite crystals or between the layers of ethylene-octene rubber, and found a strong dependence of the morphology on the film thickness: for the films thicker than 0.4 μm , the crystal resembles the conventional spherulite, for films with smaller thickness the morphology is in sheaf-like aggregates within which the lamellae are oriented edge-on with respect to the substrates [15]. Their findings disclosed two important clues, first, the film thickness has significant influence on the morphology; second, the substrate has the capability of inducing preferential lamellar orientation. Later, Melbring *et al.* studied the spun-coated HDPE as a function of film thickness, and also found strong dependence of morphology and lamellar orientation on the film

thickness [46]. In the study of linear low density polyethylene (LLDPE), Wang *et al.* measured the orientation of crystal lamellae, the crystal lattice and polymer chains with the combination of SFM and near edge X-ray absorption fine structure (NEXAFS) spectroscopy, and clearly demonstrated that the strongly interactive substrates can induce preferential orientation of the crystal lamellae and the polymer chains, while the weakly interactive substrates don't have such ability, in which the twisted lamellae exist in the thick film (366 nm) and complete dewetting happens in the films of 180 nm or thinner [11].

Schönherr and Frank have used the *in situ* hot stage AFM to observe the growth of spun-coated PEO films on oxidized silicon, and found that in the films of 1 μm or thicker, lamellae grows preferentially in edge-on orientation, while in the films thinner than 300 nm, lamellae are in flat-on projection (Fig. 1) [33, 47]. The chain orientation within the PEO films was also studied by the combination of transmission-FTIR and grazing incidence reflectance-FTIR (GIR-FTIR). The results are fully consistent with the AFM observation, that in the 110 nm thick film, the PEO helices are oriented preferentially along the

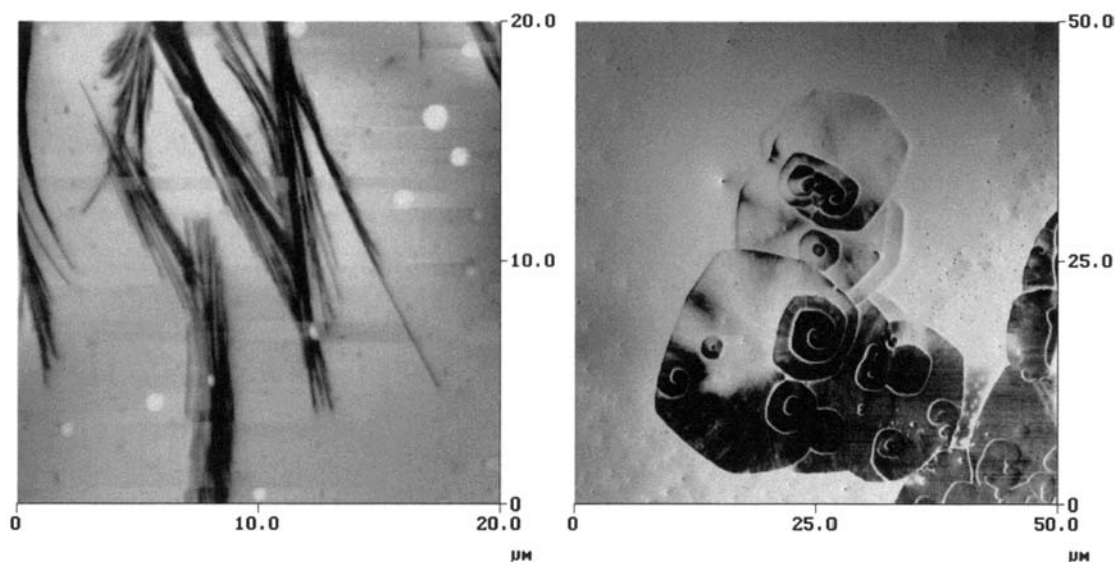


Fig. 1. TM-AFM phase images of PEOpy-49 films with various thicknesses on oxidized silicon (images were acquired *in situ* at ca. 57°C): thickness of ca. 2.5 μm (left) and 110 nm (right). In both films the featureless areas correspond to the polymer melt, which has not yet crystallized. (Reprinted with permission from Schönherr, H. and Frank, C. W. 2003, *Macromolecules*, 36, 1188-1198. Copyright (2003) American Chemical Society).

surface normal direction, indicating a flat-on lamellae, and this preference increases as the film thickness decreases [47].

In the study of the poly(ethylene-vinyl acetate) (EVA) and linear low density polyethylene (LLDPE) crystallized on HF-passivated silicon (Si) substrates by Wang *et al.*, the 2D spherulite with densely packed lamellae can only be formed in the relatively thick films, ~250 nm and above; with decreasing thickness, the crystal aggregates become more open and show larger gaps between the lamellae; for still thinner films, the boundaries of the spherulites disappear, and the lamellae fan out from the nucleation center, exhibiting a hedrite morphology; for the film of 10-15 nm thick, the crystals grow in a dendrite-like shape, with more isolated lamellae (Fig. 2) [12]. The study on the LLDPE showed that the orientation of the lamellae changes from edge-on to flat-on at a threshold thickness of 20-30 nm, [12, 13] which is much smaller than the observation by Schönherr *et al.* in the PEO study (300 nm) [33, 47]. The origin of this difference is unclear, we propose several possible causes: (1) different polymers; (2) different crystallization conditions; (3) different substrates.

The origin of the edge-on lamellae in the relatively thick films is a result of minimization of the energy for the primary nucleation formation step, while the flat-on lamellae in the very thin films dominates because the edge-on lamellae would create far more interface areas than the flat-on lamellae, which is not thermodynamically favored [12]. Moreover, Wang *et al.* found that the flat-on lamellae always grow in contact with the edge-on lamellae, which they call the “ridge”, and hence can be viewed as a result of the secondary nucleation, which agrees with the discovery by Frank *et al.*, that the nucleation process in the ultra-thin films is prohibited due to the small thickness [1]; in this case, the crystal growth is initiated from a thicker part, which was also observed by Reiter *et al.* in the crystallization of pseudo-dewetted PEO monolayers [48]. Later, Jeon *et al.* studied the morphology of the LLDPE films on HF-passivated Si substrate as a function of film thickness and crystallization temperature. For the films crystallized at 115°C, they observed a very similar trend as found in the study by

Wang *et al.*, i.e., spherulites with densely-packed edge-on lamellae in the thick films of 370 nm, and more open sheaflike structure emerges as the films are thinner; the percentage of the edge-on lamellae also decreases with the reduced film thickness, which gives way to mostly flat-on lamellae in the 30 nm thick film [49]. Similar trend of the lamellar orientation transition from edge-on to flat-on with the film thickness decrease has also been observed in other polymer systems [14, 50].

As can be seen from the above results, the spherulites can no longer be formed when the film is very thin due to the limited materials availability and the substrate-polymer interaction. Instead, the diffusion-controlled crystal growth in the ultra-thin polymer films has been reported by different researchers [44, 48, 51-53]. In the study of the crystallization of poly(ethylene terephthalate) (PET) thin films, Sakai *et al.* discovered a terrace-like structure in the peripheral of the spherulite. From the electron diffraction (ED), they concluded that the terrace consists of the single crystal several micrometers in size [44]. Since this terrace morphology only appears in the peripheral where the thickness is extremely low, they proposed that the diffusion-controlled morphology is most likely the result of the low dimensionality effect, i.e., the diffusion of each polymer chain may be restricted by the direct interaction with the substrate in the very thin region of the film [44].

Reiter, Sommer and co-workers have conducted systematic studies on the influence of the substrate on the crystallization of ultra-thin polymer films [48, 52, 54, 55].

In the study of the quasi-two dimension crystallization of poly(ethylene oxide) (PEO), they performed a pseudo-dewetting process which made an ultra-thin layer of PEO (4-6 nm thin) area in between the “dewetted” PEO droplets, and the crystallization of the ultra-thin layer was initiated from the edge of the rim or droplet [48]. This was similar to the observation in the LLDPE ultra-thin films by Wang *et al.* and in agreement with the observation by Frank *et al.* [1, 19] that nucleation is not possible for the film thinner than 10-15 nm, since the nucleation was formed at the thicker area on the droplet, before the crystals grew toward the center of the dewetting hole.

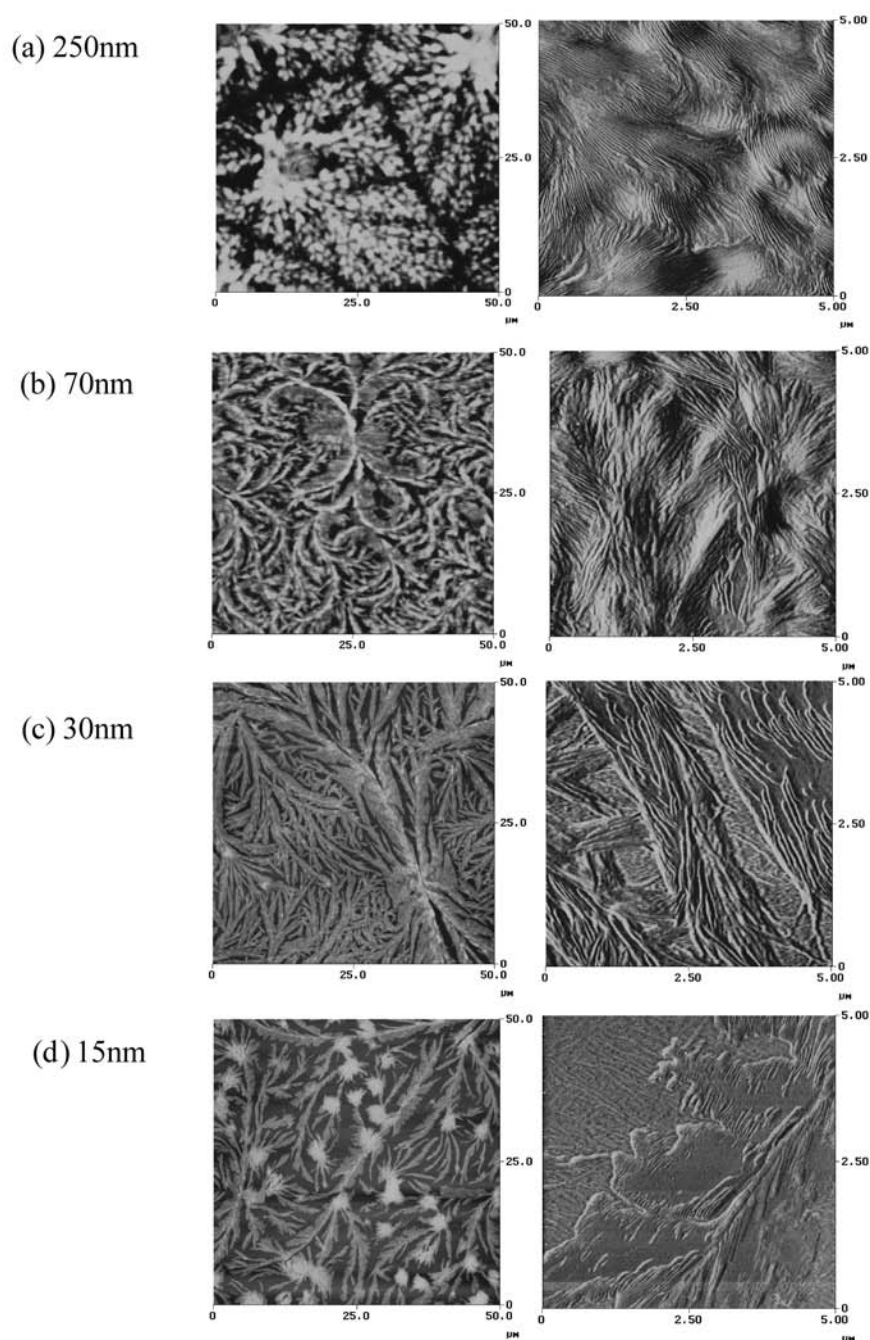


Fig. 2. SPM images of the LLDPE films with thicknesses ranging from 250 to 15 nm crystallized nonisothermally. In each figure, the left is the height image with scan size of 50 μm , and the right is the friction image with a scan size of 5 μm . (Adapted with permission from Wang, Y., Ge, S., Rafailovich, M., *et al.*, 2004, *Macromolecules*, 37, 3319-3327. Copyright (2004) American Chemical Society).

As the crystallization through this way is a diffusion-controlled process, it results in fingerlike morphology (Fig. 3). Strong temperature dependence of the crystal morphology of the ultra-thin

crystal layer was also observed, with a higher crystallization temperature resulting in a much wider finger than a lower temperature. Also, the crystallization rate of the ultra-thin layer was

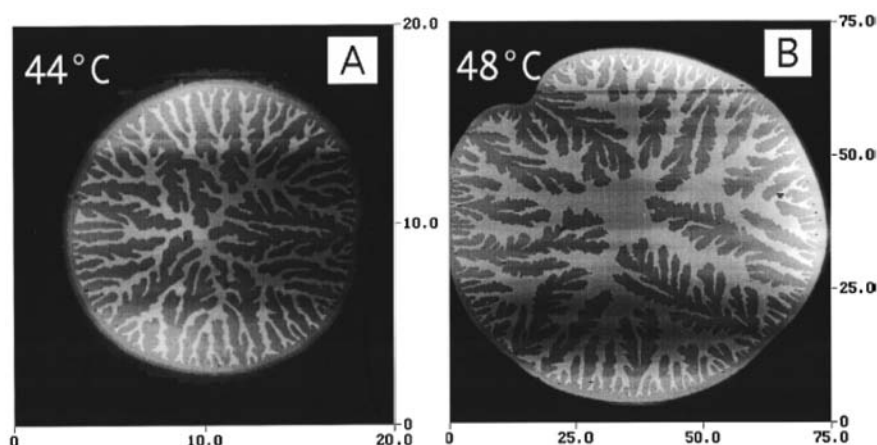


Fig. 3. Typical patterns obtained by crystallization of a monolayer of PEO 7.6k remaining in a hole created by pseudo-dewetting, measured by AFM. The samples were crystallized at (a) 44°C/880 min and (b) 48°C/1105 min, and then quenched to room temperature. They have been measured right after crystallization. Note the different sizes of the images. The area covered by the fingers is $58 \pm 1\%$ and $52 \pm 1\%$, respectively. The average height of the fingers is 8 ± 1 and 9 ± 1 nm, respectively. (Reprinted with permission from Reiter, G. and Sommer, J. U. 2000, *Journal of Chemical Physics*, 112, 4376-4383. Copyright (2000) by the American Institute of Physics).

found to be much slower than the thicker part, i.e., the droplet or rim region. Computer simulation probed the process in further detail and agreed well with the experimental results [56]. Later, Dorenbos *et al.* employed Monte Carlo simulation to predict the morphology of polymer crystals on pre-patterned surface of parallel lanes which have alternately a high and low affinity with respect to particle adsorption, and compared it to the non-patterned surface. Their results showed that while on the non-patterned substrate the crystal was thick finger-like structures, the patterned surface exhibits highly directed anisotropic needle-crystal growth in which the main branch of each crystal is located on a high affinity lane. The crystallization rate was also quite different on the two substrates, with the pre-patterned substrates guided a much faster crystallization. These simulation results demonstrated the important role the substrate can play in the crystallization kinetics and crystal morphology, and also predicted the possibility of guiding the crystal growth to obtain well-characterized novel, periodic structures on a mesoscopic scale [57].

Taguchi and co-workers, in the study of the melt-crystallized isotactic-PS (it-PS) ultra-thin films, also observed the diffusion controlled morphology for the films below the thickness of 15 nm [58]. At the same time, they showed that the morphology

has strong dependence on the film thickness and varies from dense branching morphology (DBM) to diffusion-limited aggregates (DLA) with decreasing film thickness (Fig. 4). The depleted zone, i.e., a thinner area, which they call “halo” region that surrounds the crystals in the ultra-thin films, gives a clear evidence for the diffusion-controlled crystallization; and the width of the halo increases with decreasing film thickness and eventually vanishes as a result of exhaustion of materials. Another phenomenon accompanying the diffusion-controlled crystallization is the increased width of the crystal branch as the film thickness decreases. The authors interpreted the phenomena as a result of the increase of the characteristic length of the diffusion controlled growth l_D given by $2D/G(d)$, where D is the diffusion constant of chain molecules, and $G(d)$ is the growth rate of the crystal tip. For the films thinner than the entanglement length (~ 7 nm), D should be constant with film thickness, while $G(d)$ still shows decrease with decreasing film thickness, and consequently, l increases as film becomes thinner [58].

3. Degree of crystallinity and crystallization kinetics

It has been reported by different groups that the crystallization rate of the polymer thin films

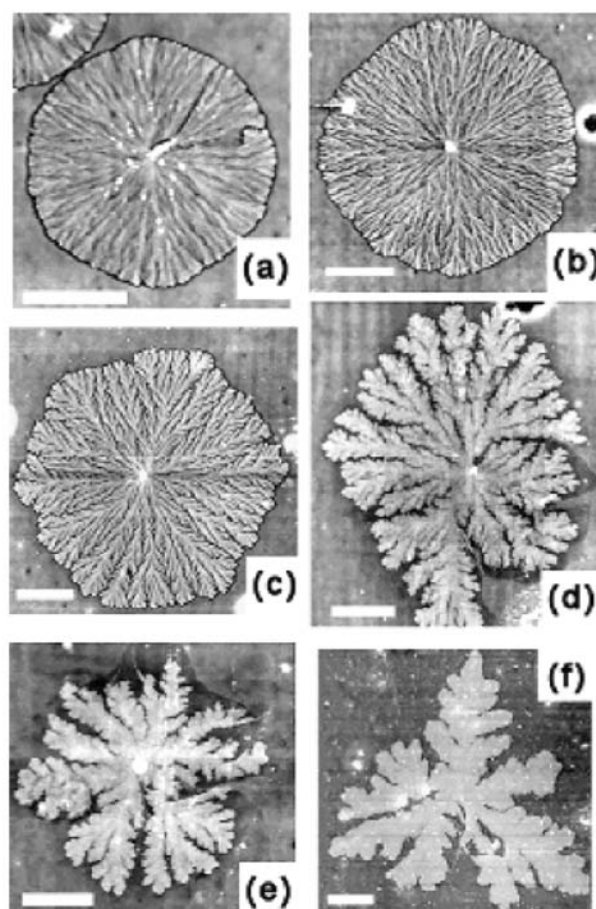


Fig. 4. AFM images of it-PS crystals grown at 180°C in ultrathin films. Each crystal is grown (a) in a film 17 nm thick for 30 min, (b) 14 nm, 1 hr, (c) 11 nm, 1 hr 30 min, (d) 9.7 nm, 3 hr 15 min, (e) 8.7 nm, 3 hr 15 min, and (f) 6.1 nm, 14 hr. Scale bars represent 5 nm. (Taguchi, K., Miyaji, H., Izumi, K. *et al.*, 2002, *Journal of Macromolecular Science-Physics*, B41, 1033-1042. Reprinted with permission from Taylor & Francis).

decreases with the decreasing film thickness [1, 19, 33, 48, 58, 59]. Despotopoulou *et al.* studied the crystallization of spun-coated poly(di-n-hexylsilane) ultra-thin films with thickness of 50-500 Å on three different substrates: (1) hydrophilic quartz; (2) octadecyltrichlorosilane (OTS) treated quartz; (3) hexamethyldisilazane (HMDS) treated quartz. The films were crystallized at various temperatures ranging from -5°C to 15°C, and then the properties were measured with the combination of UV spectroscopy, fluorescence spectroscopy and FT-IR. They discovered (1) a reduction in crystallization rate with a diminishing film

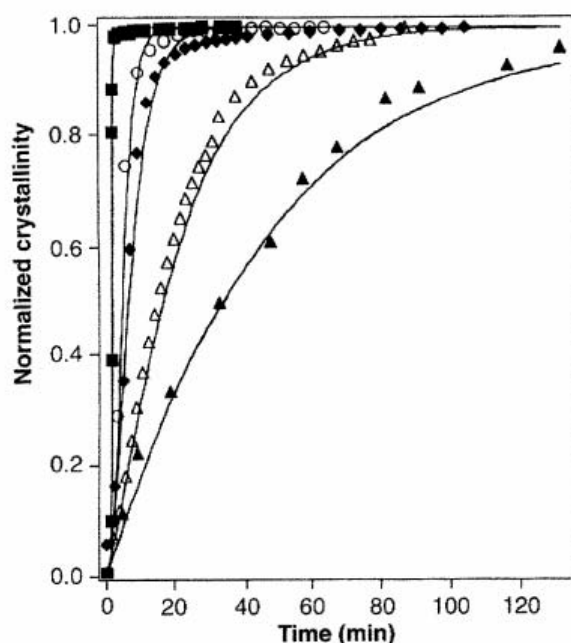


Fig. 5. Kinetics of crystallization at 0°C of spin-cast PD6S films of thickness 95 Å (solid triangles), 160 Å (open triangles), 220 Å (diamonds), 300 Å (circles), and 500 Å (squares). The solid lines are nonlinear fits of the Avrami equation to the normalized experimental crystallinity data. (Frank, C. W., Rao, V., Despotopoulou, M. M. *et al.*, 1996, *Science*, 273, 912-915. Reprinted with permission from American Association for the Advancement of Science).

thickness crystallized at the same temperature, particularly for the thicknesses <300 Å (Fig. 5); (2) a reduction in crystallization rate with a decreased supercooling; (3) an enhanced degree of crystallinity with larger supercooling for the films with the same thickness; (5) the degree of crystallinity is strongly hindered in the ultra-thin films (<500 Å), with crystallinity vanishing below about 150 Å, the films on all three substrates showed similar degree of crystallinity as a function of film thickness (Fig. 6); (6) with decreasing film thickness, the disordering of the side chains (at 2000 Å) precedes the disordering of the backbones (at 300 Å); (7) the backbone lies extended, with polymer axis and extended hexyl side chains parallel to the plane of the film and with the hexyl carbon-carbon bond plane perpendicular to the substrate. They also compared the crystallization kinetics of the ultrathin film on two different substrates, OTS-treated quartz surface and untreated

glass substrate, and found out that the process of crystallization was much faster on OTS than on the un-treated glass at the same temperature, even though the final degree of crystallinity was the same [1, 19, 43, 60].

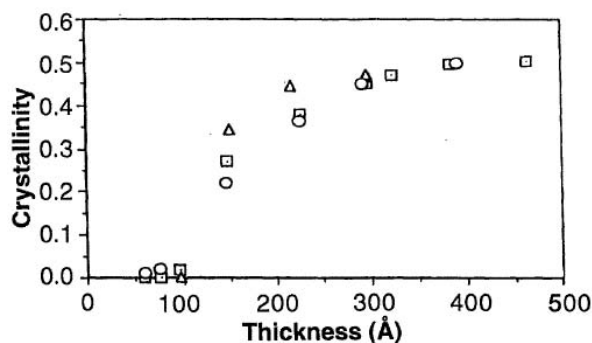


Fig. 6. Dependence of maximum attainable crystallinity, determined from UV absorption spectra, on thickness of PD6S films spin-cast on quartz (squares), hexamethyldisilazane-treated quartz (circles), or octadecyltrichlorosilane-treated quartz (triangles). (Frank, C. W., Rao, V., Despotopoulou, M. M. *et al.*, 1996, *Science*, 273, 912-915. Reprinted with permission from American Association for the Advancement of Science).

In the studies of the LLDPE films on HF-passivated silicon substrate by Wang *et al.*, the authors observed a non-diminishing crystallinity in the film as thin as 10 nm (Fig. 7), which is seemingly contradictory to the conclusion of Despoutopoulou and co-workers. But if we look at the morphology of the film of ~15 nm (Fig. 2d), we can see that the flat-on crystal always initiates from a thick edge-on lamellae (ridge), which is in agreement with the proposal by Despoutopoulou *et al.*, that the nucleation process is inhibited in the ultra-thin film. However, since Wang *et al.* used either non-isothermal crystallization in which the film was annealed at 140°C for 30 minutes before gradually cooling to room temperature in the vacuum oven overnight, or isothermal crystallized at relatively high temperature (60°C) overnight, there has been relatively long annealing time at the high temperature which has allowed these ridge areas to form and consequently the secondary nucleation from these ridge areas are possible. On the other hand, Despoutopoulou *et al.* used a different crystallization process: the films were annealed at 100°C for 15 minutes, slowly cooled to room temperature, and kept at crystallization temperature (-5°C-15°C) for at least 8 hours. The

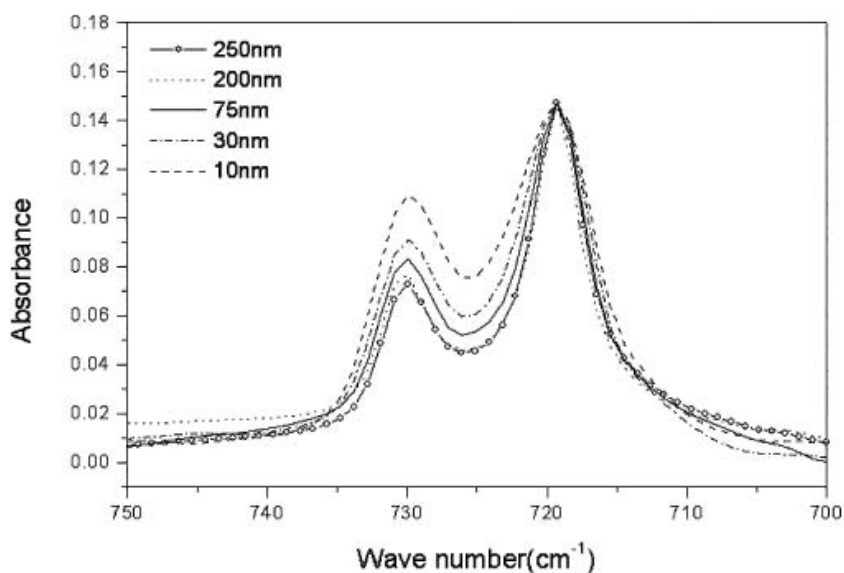


Fig. 7. ATR-FTIR spectrum of the LLDPE films with different thickness. The existence and intensity of the peak at 730 cm^{-1} is an evidence of the crystallinity. (Reprinted with permission from Wang, Y., Ge, S., Rafailovich, M. *et al.*, 2004, *Macromolecules*, 37, 3319-3327. Copyright (2004) American Chemical Society).

time at high temperature is much shorter, which may not have allowed the thick areas to form and hence the nucleation formation is prevented.

In the studies of PEO and pyrene end-labeled PEO (PEOpy) on native silicon substrate, Schönherr and Frank used the *in situ* hot stage AFM to measure the lamellar growth rate, and found that the growth rate starts to decrease at the film thickness of 200-500 nm, and drops sharply in the films of 200 nm thick or below, and to the value of 10-15% of the bulk value in the films between 15 and 100 nm thick. The authors attributed this substantial decrease in lamellar growth rate to reduction of molecular mobility of the PEO ultra-thin films on silicon oxide [33]. The slowed crystallization rate in the films of 200 nm or thinner in the same system was also revealed by the combination of FTIR and fluorescent spectroscopy measurements, as rate constant in the Avrami equation substantially decreases with film thickness decrease [47].

In the study of it-PS crystallized at 180°C, Taguchi *et al.* also investigated the crystal growth rate as a function of film thickness. By measuring the time evolution of the farthest tips from the center of the crystals, r_{tip} , they found that the growth rate of the films of 7.2 nm thick and above decreased with the decreasing film thickness according to the equation:

$$G(d) = G(\infty)(1 - a/d) \quad (1)$$

where $G(d)$ is the crystal growth rate of film with thickness d , $G(\infty)$ is the crystal growth rate of the bulk, and a is the constant of about 6 nm, independent of crystallization temperature, molecular weight and substrate materials; however, below ~8 nm, which happens to be lamellar thickness of it-PS, equation (1) does not apply anymore, the decreasing rate of G with d becomes much lower (Fig. 8). This study clearly showed that when the diffusion becomes the rate-controlling step, the G does not obey the same law as in the thicker films in which the reduced rate is attributed to the reduced mobility of the polymer chains in thin films [58]. Although the precise quantification is still to be established, it's clear that different mechanisms dominate the kinetics of the ultra-thin films.

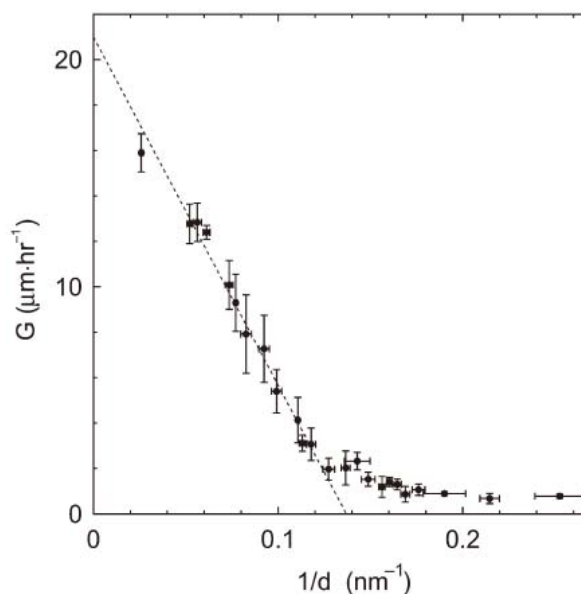


Fig. 8. Growth rate $G(d)$ vs. inverse of film thickness $1/d$ for it-PS crystals grown at 180°C in ultrathin films. The dotted line shows $G(d) = G(\infty)(1 - a/d)$ with fitting parameters $a = 7.2$ nm and $G(\infty) = 21 \mu\text{m/hr}$. (Taguchi, K., Miyaji, H., Izumi, K. *et al.*, 2002, Journal of Macromolecular Science-Physics, B41, 1033-1042. Reprinted with permission from Taylor & Francis).

4. Melting temperature

The substrate-polymer interaction can change the interdiffusion dynamics of the polymer thin films [61-64]. Zheng *et al.* has shown that the diffusion coefficient of polystyrene (PS) near the attractive substrate, SiO₂, is ~100 times smaller than that near the vacuum interfaces; moreover, the diffusion rate of deuterated polystyrene (PS) in the hydrogenated PS matrix is an order of magnitude slower than the bulk value up to $10 R_g$ (radius of gyration) from the interface [6, 7]. Since the glass transition temperature (T_g) is closely related to the chain dynamics, the effect of substrate and geometric confinement on the T_g of the polymer thin films has been intensely investigated by the researchers. It was found that the T_g of the polymer films can be increased, decreased, or unchanged with the reducing film thickness, depending of the polymer-substrate interaction [16, 17, 65]. Fryer *et al.* studied the interfacial energy (γ_{SL}) and thickness effect on the films of polystyrene (PS) and poly(methyl methacrylate) (PMMA) with thickness of 80-18 nm,

and found that at low values of γ_{SL} , T_g 's were decreased from bulk value; at high values of γ_{SL} , T_g 's were increased from bulk value; the deviation of the T_g 's from the bulk value increased with decreasing film thickness. They interpreted the T_g dependence on the interfacial energy and film thickness as consistent with the three layer model, in which the interfacial interaction changes the segmental mobility of the chains near the substrate, and the weighted average of the mobility of the layers according to the relative dimensions of the layers determines the T_g of the entire film [66, 67].

In semi-crystalline polymers, the picture is more complicated. Upon heating, unlike the glass transition of amorphous polymers which takes place within a broad temperature range, the crystal transforms from an ordered structure to liquid state within very narrow temperature window, typically one degree; and this melting temperature, T_m , is not solely determined by the chain mobility, but can be influenced by various factors. In bulk polymers, the T_m is correlated to lamellar thickness as depicted in Thomson-Gibbs Equation: [26, 68]

$$T_m = T_m^0 - \frac{2\gamma_e T_m^0}{l\Delta H_v} \quad (2)$$

where T_m^0 is the melting point of the infinitely large crystal, γ_e is the top and bottom surface energy of the crystal lamellae, ΔH_v is the melting enthalpy, and l is the lamellae thickness. In the bulk polymers, the major factor that contributes to the depression of T_m was the reduced lamellar thickness l [69, 70]. The question is: can we extrapolate the application of this equation to the scenario of thin films? In a previous study by Kim *et al.*, a reduction in T_m with the film thickness decrease was observed in the EVA films down to the thickness of ~ 25 nm [18]. In the studies of the EVA and LLDPE films crystallized on hydrophobic silicon substrate by Wang *et al.*, the authors observed a T_m depression with the film thickness decrease when the film is thinner than a threshold value, and in the thinnest film measured, 15 nm, the T_m is 38°C lower than the bulk value; yet the AFM images clearly show that the lamellar thickness does not diminish as the film goes thinner [12]. In order to explore the cause of

the large T_m depression, Wang *et al.* dug deeper into the thermodynamic origin of Thomson-Gibbs equation, and built a universal version of the equation, which can be applied to both bulk and thin films: [12]

$$T_m = T_m^0 - \frac{2\gamma_e T_m^0}{l\Delta H_v} - \frac{2\gamma_l}{\Delta H_v} \left(\frac{1}{x} + \frac{1}{y} \right) T_m^0 \quad (3)$$

where T_m^0 , γ_e , ΔH_v and l have the same physical meaning as in Equation (2), while x , y are the width and length of lamellae, respectively, γ_l is the lamellar lateral surface energy (Fig. 9a). In the bulk polymers, the x and y dimension are orders of magnitude larger than the l dimension [38], and hence contribute negligible effect on T_m , therefore the last two terms are neglected from the equation, yielding the Thomson-Gibbs equation, which is Equation (2). In the ultra-thin films, however, the film thickness is in the comparable size as lamellar thickness, and depending on the lamellar orientation, it can confine the y dimension in such a large degree that it can no longer be ignored and can exert considerable influence on T_m (Fig. 9b). Taking into account of the lamellar orientation, we calculated the T_m as a function of film thickness and reached a much smaller T_m depression than measured [12]. Thus, the geometric confinement alone is not the sole cause for the large T_m depression, the intrinsic properties such as ΔH_v could have been changed due to the polymer-substrate interaction. In a subsequent work, Wang *et al.* studied T_m as a function of film thickness on three different substrates: hydrophobic silicon (Si), aluminum (Al) and polyimide (PI), which have different affinity to the LLDPE [13]. The results have shown that T_m depression is highly dependent on the substrate that the highest attractive substrate, Si, leads to a largest T_m depression, 38°C ; whilst the least attractive substrate, PI, leads to the smallest T_m depression, 12°C (Fig. 10). This can be interpreted as result of the reduced melting enthalpy relative to the bulk value due to the adsorption of the chains to the strongly attractive substrate in the melting state, which consequently reduces T_m^0 [13].

Wang *et al.* also compared the effect of the branching concentration on the morphology and

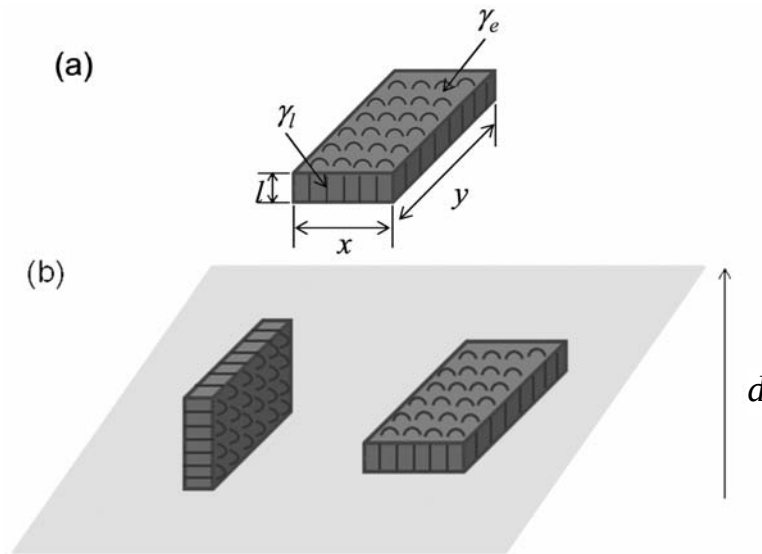


Fig. 9. (a) Schematic drawing of the crystal lamellae; (b) schematic drawing of an edge-on and a flat-on lamellae on the substrate to show the different effect thickness confinement can have on their size.

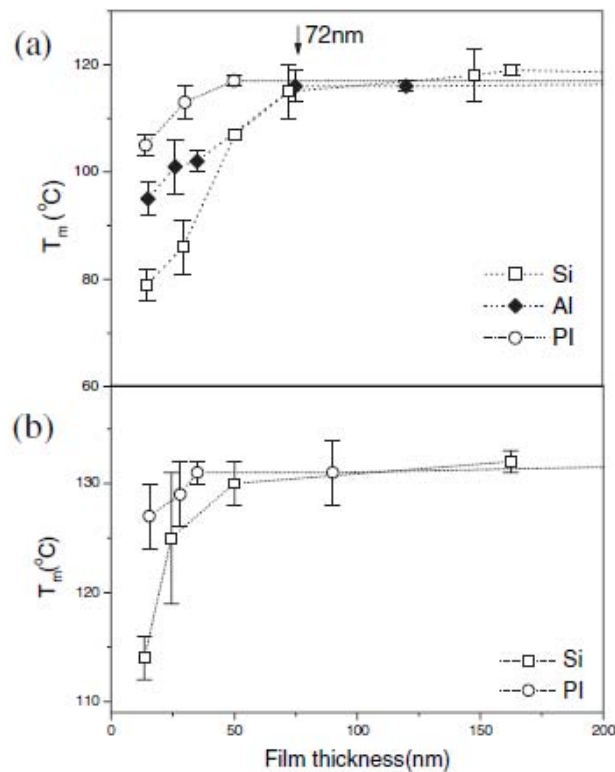


Fig. 10. (a) Melting point of B-3 vs. film thickness on silicon, aluminum, and polyimide substrates. (b) Melting point of B-5 vs. film thickness on silicon and polyimide substrates. B-3 and B-5 are LLDPE with different properties: density (B-3 = 0.92, B-5 = 0.95 g/cm³), branching ratios (20 branches for B-3 and 2.3 branches for B-5 per 1000 backbone atoms), and bulk melting points (117°C for B-3 and 132°C for B-5). (Reprinted with permission from Wang, Y., Rafailovich, M., Sokolov, J. *et al.*, 2006, Physical Review Letters, 96, 028303. Copyright (2006) by the American Physical Society).

melting temperature of the films. The authors found similar trend on morphology and T_m of the films B3 (LLDPE) and B5 (Linear medium density polyethylene) which has 20 branches and 2.3 branches per 1000 backbone atoms, respectively, although the magnitude of the largest T_m depression for B5 is much smaller, namely, 18°C on Si and 5°C on PI, as compared to 38°C on Si and 12°C on PI for B3 [13]. More systematic study is required in order to fully interpret the difference caused by the branching density.

5. CONCLUDING REMARKS AND OUTLOOK

Previous work by various research groups has clearly demonstrated the critical influence of confinement and substrate interaction on crystallization process and the final properties of the thin and ultra-thin polymer films. Contrary to the bulk crystals where the polymer-polymer interactions dominates, in the thin films, the interfacial forces between the polymer and the substrate plays an increasing vital part with diminishing film thickness. Although the behaviors of different polymers don't precisely resemble one another, several trends are universally true in all the systems reviewed in this article: (1) the strongly attractive substrates can cause preferential lamellar orientation in the thin and ultra-thin films, with decreasing film thickness, the lamellae orientation transforms from edge-on to flat-on, the threshold thickness for transition depends on polymers and thermal histories; (2) the morphology is highly dependent on the film thickness, the compact 2D spherulite in the relatively thick film is substituted by the diffusion-controlled dendrite or finger pattern in the ultra-thin film; (3) the homogeneous nucleation process is prohibited in the ultra-thin films, given appropriate annealing condition to allow the formation of "ridge" or pseudo-dewetted droplets, crystallization can initiate from the thick ridge of droplet edge; (4) crystal growth rate decreases with decreasing film thickness; (5) melting point is a strong function of both film thickness and substrate interaction, highly attractive substrate cause the largest T_m depression. Understanding the huge power that the interplay of the geometric confinement and interfacial reaction can have on altering the behaviors

of the polymer films will enable us to control the macroscopic properties of semi-crystalline polymers from the microscopic scale, and hence unveil more magic potentials in this class of classical materials.

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