Submicron Films Prepared from Aqueous Dispersions of Nanoscale Polymer Crystals

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ABSTRACT: Thin and ultrathin films of polyethylene of variable thickness are obtained from aqueous dispersions of prefabricated nanoscale crystals by spin-coating. Continuous films with a thickness of only 15 nm, up to 220 nm, homogeneous over hundreds of μm , or assembled discontinuous monolayers of flat-on lamella particles were prepared, depending on the solids content of the dispersion employed, as revealed by AFM and TEM. The morphology of melt-recrystallized films was not affected by the surfactant present. Homogeneous continuous films without undesirable dewetting were retained upon melting and recrystallization of the films upon cooling, composed of polygonal spherulites for a thicker film (220 nm), randomly grown edge-on lamella for a 40 nm film, and dominant flat-on lamella for a 15 nm thick film. Annealing below T_m resulted in lamella thickening, without changes of crystal orientation or structure of the particle assemblies for discontinuous monolayers. Surfactant adsorbed to the nanocrystals in the aqueous dispersion desorbs at least partially during formation of the nascent films, and upon annealing below the melting point surfactant migrates to the film-air interface to form aggregates, which can be removed by rinsing, during which the film stays intact and structurally unaltered as revealed, amongst others, by water contact angles. © 2009 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 47: 6420–6432, 2009

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INTRODUCTION

Thin and ultrathin polymer films are of interest both from an application oriented perspective, and for the fundamental understanding of polymer morphology and properties in confinement.^{1,2} Their structure and properties can differ substantially from bulk materials, and also the preparation of submicron films requires different techni-

ques than the melt processing most often applied to semicrystalline bulk polymers.

For the preparation of semicrystalline (ultra)-thin films, the polymer is commonly applied to a substrate in a nonordered state, usually as a dilute solution in an organic solvent and often at elevated temperatures. Formation of crystalline order occurs only upon evaporation of the solvent and cooling, which therefore pronouncedly influences the crystallization process. As a completely different approach, we have recently communicated the preparation of polyethylene (PE) ultrathin films from aqueous dispersions of prefabricated nanocrystals. Film formation occurs at room temperature, and water rather than organic

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solvents is evaporated. The nanocrystals function as mesoscopic building blocks for the film, that is well-defined crystalline order is already introduced to the film formation step.³ Efficient interaction between the monolamellar particles via the amorphous layer, in combination with their very small sizes, results in macroscopically continuous ultrathin semicrystalline PE films. Electron diffraction confirms that the nanoscale crystalline phase present in the primary PE nanocrystals is maintained in the nascent films.

We now give a full account on the nature and structure of PE films prepared from aqueous dispersions of prefabricated nanocrystals. The nascent morphologies and behavior at elevated temperature of submicron films of variable thickness are addressed, as well as the fate of surfactant, which provides colloidal stability in the original PE dispersions.

RESULTS AND DISCUSSION

The as-obtained PE dispersion contains just enough surfactant to afford colloidal stability of the particles but no free surfactant, as confirmed by a high surface tension of $>60 \text{ mN m}^{-1}$, therefore the dispersion was directly applied for the film preparation without any further treatment, such as dialysis. Detailed characterization of the dispersion has been provided elsewhere.⁴ In brief, the as-prepared PE dispersion typically contains a polymer content of about 2 wt % with particle size of about 10 nm as determined by dynamic light scattering (DLS). The particles are composed of highly linear PE with about 5 methyl branches/1000 carbon atoms and a high molecular weight of $M_n = 300 \text{ kg mol}^{-1}$ ($M_w/M_n = 1.7$). The bulk polymer melts at $T_m = 133^\circ\text{C}$ and possesses a degree of crystallinity of $\sim 55\%$ as determined by differential scanning calorimetry (DSC). Cryo-TEM illustrated the distinct anisotropic disc-like shape of the highly crystalline particles, with a thickness of about 9 nm, and lateral diameter of about 24 nm. SAXS analysis demonstrated that the disc-like particles essentially consist of one single lamella with a lamellar thickness of about 6 nm, sandwiched between two about 1 nm amorphous layers.

Nascent Crystalline Films

Directly drying the as-obtained dispersion on a substrate affords continuous films of micrometer

thickness. To reproducibly prepare microscopically smooth and uniform submicron PE films, spin-coating was applied. By varying the polymer content of the applied dispersions, and the spin-coating rotation frequency, films of variable thickness ranging from 15 nm to 300 nm were obtained. The film thickness is mainly determined by the polymer solids content of the dispersions employed. AFM images of the films prepared from the dispersion with various polymer content of 8 wt %, 0.8 wt %, and 0.2 wt % [Fig. 1(a–c)] illustrate that a sufficiently high polymer content ($>0.8 \text{ wt } \%$) is required to obtain complete coverage of the substrate on a large scale, otherwise isolated “holes” form as seen in the phase image [Supporting Information Fig. S1(b)]. AFM height and phase images show a uniform morphology and the absence of large crystalline structure, even for the thickest film studied here. This is in agreement with TEM analysis on free-standing polymer films, which were prepared by floating the films off the substrate in water and transferring onto a copper grid. TEM micrographs of about 150 nm thick film show an overall uniform structure, with minor electron density variations on a local scale [Supporting Information Fig. S1(d)].

At a low polymer content of 0.2 wt %, the particles assemble as a discontinuous monolayer on the substrate. Surprisingly, height cross sections on the assembled structures show a rather uniform thickness of 8–9 nm [Fig. 1(c-2)]. Considering the anisotropic shape of the particles, this indicates that the primary crystals orient preferentially with their lamellae laying flat on the substrate. Height cross sections on a 220 nm thick film show that even at this relatively high film thickness, the surface roughness only varies in the range of about $\pm 5 \text{ nm}$ [Fig. 1(a-2)], which implies a layer-by-layer packing of the particles in the nascent films probably is maintained even up to hundreds of nanometres.

It is noteworthy that the area marked with an arrow in Figure 1(c-1) is probably composed of surfactant (SDS) desorbed from the PE particle surface during film formation. A height cross section shows its typical thickness of 1–2 nm and rather smooth surface [Fig. 1(c-2)]. Phase images indicate its different viscoelastic properties by comparison to the surrounding area covered by PE particles and to the uncovered substrate [Supporting Information Fig. S1(c)]. Distribution of the surfactant in the nascent films, and the effect of annealing thereon will be discussed in more detail below.

Figure 1. AFM height images of (a-1) 220 nm thin film, (b) about 15 nm ultrathin film, (c-1) discontinuous monolayer, and corresponding height cross sections (a-2) and (c-2), for (a-1) and (c-1), respectively

In preparation of annealing studies (*vide infra*), the melting temperature of the films of different thicknesses was studied with a differential AC-chip calorimeter [Supporting Information Fig. S2(a)]. The melting peak temperature of about 300 nm and about 50 nm film was determined to be 131 °C and 128 °C, respectively, which shows no significant melting depression in the submicron thin films compared to the bulk material ($T_m = 133$ °C in the first heating trace of a standard DSC measurement with a heating rate of 2 K min^{-1}). A formation of large droplets induced by a conceivable dewetting during the AC calorimetry measurements can be excluded. AFM on the film previously subject to the AC-chip calorimetry experiment shows a complete coverage of the chip sensor surface by the film with a surface roughness of about 10 nm [Supporting Information Fig. S2(b)].

In the film forming approach we report here, the crystalline order already exists before film formation, thus the size and degree of perfection of the crystallites are expected to be uniform over the whole film thickness. By contrast, a depression of the melting point with decreasing film thickness has been reported in various solution cast films. The observed depression was attrib-

uted either to less perfected crystalline order in proximity to the film-air interfaces, or to strong interactions between the substrate and the polymer.⁵⁻⁷

Morphology of Films Recrystallized from the Melt

For bulk semicrystalline polymers the crystalline morphology, crystallization kinetics and the mechanical properties are closely correlated to one another, as documented by numerous studies.⁹ Pioneering studies of isolated PE crystals have been ground-breaking for understanding polymer crystallization,^{10,11} and crystal growth, reorganization phenomena and so forth are still subject to debate.¹²⁻¹⁶ Closely related, the morphology of PE thin and ultrathin films has also received considerable attention recently, amongst others in the context of understanding confinement effects on polymer crystallization.^{5,17,18} Spherulites are a common morphology of bulk crystalline polymers and micrometer thick films. However, in thin and ultrathin films, the morphological details and crystallization kinetics are significantly influenced by the confinement in one dimension, and interactions between the polymer and the substrate.¹⁹⁻²¹

Water-soluble additives, especially surfactant, can have a profound effect on the film formation process from polymer dispersions.^{22,23} Given that the SDS surfactant present in the PE dispersion remained at least partially in the nascent films, the morphology of films recrystallized from the melt by heating the nascent films once above the melting temperature was studied to elucidate the evolution of film morphologies with respect to the film thickness and any conceivable influence of surfactant molecules thereon.

The as-prepared films were heated to 160 °C and kept at this temperature for 10 min, then cooled to ambient temperature for AFM imaging (Fig. 2). Constant heating and cooling rates were applied to ensure the same thermal history of the films studied. By keeping the film above the melting temperature for 10 min, presumably the structure of the primary crystals is entirely overcome and the material subsequently crystallized from a molten state under the confinement in one dimension. Note that the crystallization event is not intervened by evaporation of any organic solvent, therefore the crystalline morphology observed here is reasonably discussed only versus previous observations on solvent-cast films which had undergone thermal treatment to remove the previous thermal history from the film preparation process.

For the continuous films with a thickness ranging from about 40 nm up to several hundreds of nanometres, in all cases spherulitic structures were observed, with varied morphological details. In the 220 nm thick film, more conventional polygonal spherulites formed with a diameter up to ~0.1 mm, and a characteristic extinction pattern can be distinctly observed by optical microscopy [crossed polarizers, Supporting Information Fig. S3(a)]. The radial growth of edge-on lamella from the nucleation center of the spherulites [Fig. 2(b)] is very similar to previous observations on the morphology of thin HDPE films.^{17,24} For film thicknesses below 200 nm, only open spherulitic structures were observed [Fig. 2(c,d) and Supporting Information Fig. S3(b,c)], probably due to limited branching of lamellae in such thin films. The growth direction of lamellae appears more random with decreasing film thickness. In a 40 nm thick film, parent lamellae can be hardly distinguished [Fig. 2(c-1)]. Notably, despite that surfactant remained in the film which could potentially promote droplet formation, even in the molten state, dewetting was not observed in annealing of the 40 nm and thicker film. The surface roughness after annealing remains within the range of

5 to 10 nm [Fig. 2(c-2)]. In 40 nm films, some areas of irregular shapes between the crystallized lamellae were revealed to be uncovered of polymer by the phase image [Fig. 2(d)], which probably resulted from a limited amount of material available to the lamellar growth front in such ultrathin films, rather than dewetting.²⁵ For the 15 nm film, and also in discontinuous monolayers, annealing at 160 °C results in obvious dewetting and the formation of large droplets. By lowering the annealing temperature to 130 °C, and applying a shorter annealing time of 3 min, flat-on lamellae form predominantly as indicated by their height and lateral size given by the line cross section profile (Fig. 2(e-1,2) and inset of an enlarged area in (e-1)).

It is interesting to note that in the melt-crystallized films of thickness ranging from 40 to 220 nm, edge-on lamellae are the preferred crystalline form. This can be better distinguished in the phase images [Fig. 2(d), inset of an enlarged area in (d) and Supporting Information Fig. S3(c)]. In the samples studied, flat-on lamellae become dominant only at a film thickness of 15 nm. The orientation of lamellae with respect to film thickness is still under debate, and subject to both theoretical²⁶ and experimental studies.^{25,27,28} It is generally agreed that the primary nuclei adopt an edge-on orientation on the substrates, which grows further along this orientation in films of sufficient thickness.²⁴ With decreasing thickness, the growing lamellae tend to change to flat-on orientation in favor of lowering the interfacial energy between the crystallized lamellae.⁵ However, the corresponding critical film thickness varies for different polymers, and the thermal history of the films. In our case we observe that the critical thickness approaches the dimension of the lamellar thickness of the primary PE crystals. Besides factors such as temperature, or polymer-substrate interactions, in our case a contribution of enhanced surface nucleation on the film surfaces enriched with impurities such as extruded surfactant, can not be excluded as well. A migration of the surfactant molecules towards the film-air interface upon heating was indicated by the annealing of ultrathin films below the melting temperature, as discussed below.

Annealing of PE Crystal Monolayer Assemblies and Ultrathin Films

For semicrystalline polymers, annealing generally can have a significant impact on their

Figure 2. AFM height images of recrystallized PE films from the melt with film thickness of (a,b) 220 ± 20 nm, (c,d) 40 ± 10 nm; and (e) 15 ± 5 nm. (c-2) and (e-2) the corresponding height cross sections of (c-1) and (e-1), respectively; (d) phase image of the area marked with square in (c-1). The insets in (d) and (e-1) are the enlarged images of a $1.5 \mu\text{m}$ area in respective images. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 3. AFM height and phase images of a discontinuous monolayer structure, (a-1) and (b-1) as-prepared sample recorded at room temperature, (c-1) and (d-1) annealed at 75 °C for 20 h, washed with water at room temperature, then recorded at 75 °C, (a-2), (b-2), (c-2), and (d-2) corresponding line cross sections in the height and phase images, respectively. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

morphology. This is mainly attributed to an enhanced chain mobility at temperatures higher than the crystallization temperature at which the original crystalline structure formed. For example, lamellar thickening on a local scale upon annealing has been visualized directly by AFM on either polymer single crystals of micrometer size,^{13,14} or monolamellar polymer crystals.^{29,30} For the novel film structures studied here, annealing also gives insights regarding the role and fate of surfactant.

As described previously, by varying the polymer content of the spin-coated dispersion, discontinuous monolayer assemblies of PE crystals and continuous ultrathin films can be obtained. In both cases the primary crystals have preferred flat-on orientation with respect to the substrate surface, as indicated by, either the AFM height cross section profile on the crystal assemblies, or for the nascent continuous ultrathin films the observed variation of electron diffraction patterns from continuous (hk0) diffraction rings to arcs by

tilting the film surface with respect to the electron beam.⁹ To elucidate the effect of annealing on the orientation of crystallites in films of various thickness, annealing below the melting temperature was studied for both discontinuous monolayers of flat-on assembled primary crystals, and the ultrathin films composed of preoriented primary crystals.

Annealing of Discontinuous Monolayer Assemblies

For direct observation of the development of morphology, the annealing was carried out in situ on the hotstage of an AFM instrument. Annealing at 75 °C for up to 20 h did not induce significant changes of the crystal thickness, as illustrated by a comparison of the height in the images recorded at 75 °C and room temperature [Fig. 3(a,c) and corresponding height cross sections]. Interestingly, the surfactant aggregates could be removed by rinsing thoroughly with water without destroying the monolayer (as studied on a sample

Figure 4. AFM height images recorded during stepwise annealing of a discontinuous monolayer structure on a silicon wafer at different temperatures and time periods, (a) 75 °C, 20 h, (b) 90 °C, 37 min, (c) 110 °C, 125 min, (d) 32 °C, 30 min. (e,f) enlarged inverted height images of the areas ($0.5 \times 0.5 \mu\text{m}^2$) indicated in (a) and (c), respectively, (g) corresponding line cross sections in (a), (b), and (c); (d-2) corresponding line cross section in (d-1). As a guide to the eye, the square marked area in (d-1) indicates the area scanned in (a–c). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

annealed at 75 °C). This is confirmed by the disappearance of about 2 nm “islands” between assembled particles in both height and phase

images [Fig. 3(a–d)]. AFM images were taken at several positions to ensure that they are representative for the sample surface.

To follow the evolution of morphology with temperature and time, AFM images were recorded at the same position during further annealing [Fig. 4(a–c)]. With increasing of the annealing temperature to 90 °C, no pronounced reorganization occurred, besides a smoothening of the monolayer surface on a local scale [Fig. 4(b)]. The average thickness did not increase significantly as indicated by the line cross section.

After further annealing at 110 °C for 125 min, significant thickening was observed in some areas [for better illustration, compare inverted height images of two representative thickened areas, Fig. 4(e,f)]. The “cheese-hole” structure of the covered areas in the original sample, reflecting the boundaries between the primary crystalline domains, has disappeared nearly completely, probably due to enhanced diffusion of the chains on the substrate at higher temperature. Corresponding line cross sections show that the maximum thickening amounts to about 13 nm, by comparison to the average thickness of about 7 nm at 75 °C [Fig. 4(g)]. Notably, a partial melting was observed in the nearby regions marked with arrows, as indicated by a drastic decrease of height at the corresponding positions. The height cross section profiles of Figure 4(a–c) show that the lateral extension of the assembled particles decreases slightly with increasing height at higher temperature, as expected [Fig. 4(g)]. However, with consideration of the amorphous layers which are unlikely to be completely penetrated by the AFM tip under the applied moderate tapping force, the thickening effect we observed here just slightly exceeds the initial folding length of 12 nm for linear PE at a crystallization temperature of 110 °C as reported by Barham et al.³¹ Annealing for a longer time at 110 °C did not result in a further increase of lamella thickness. Note that the applied moderate imaging force has no additional effect on the observed lamellar thickening, as confirmed by a height cross section on a larger scanning area which includes the continuously scanned region in the images described earlier, and previously unscanned neighboring areas. A similar extent of lamellar thickening was observed over the whole length of the line scan [Fig. 4(d–1,2)]. The thickened lamellae maintained their thickness after cooling to room temperature, as expected.

Note that by comparison to a typical lateral extension of several microns of the polymer single crystals subjected to the previous literature studies, the lateral dimension of the crystal assemblies

studied here is in the range of hundreds of nanometres, thus the neighbouring chains of each crystallite available for its reorganization are highly limited. Based on the aforementioned observations, we assume that the lamellar thickening in the discontinuous monolayer occurs via local disentanglement and reorganization of chains in the amorphous phase due to enhanced mobility at elevated temperatures, rather than chain unfolding as reported for ultralong alkane and PE single crystals.^{14,32} The persistence of flat-on lamella orientation is in agreement with previous AFM observations on annealing of isolated solution-grown PE single crystals in the absence of traces of organic solvent.¹⁴

To investigate whether surfactant molecules have any effect on the lamella thickening, annealing of the discontinuous monolayer was also carried out without any intermediate washing procedure, which was usually employed in film sample preparation to remove SDS desorbed from the particle surface in deposition via spin-coating. The results show a similar trend of lamella thickening versus the annealing temperature (Supporting Information Fig. S4). A significant thickening effect was observed at a high temperature of 110 °C, with simultaneous partial melting adjacent to the thickened regions (indicated by the formation of holes), as expected from the observations described earlier during annealing of the washed sample. A maximum thickening was observed to a similar extent of up to 14 nm (from an original height of 8 nm) at 110–115 °C [Supporting Information Fig. S4(e)]. In contrast, the thickness of the areas covered only by SDS aggregates [marked with arrows in Supporting Information Fig. S4(a,e)] remained nearly constant up to 115 °C. Therefore, a significant contribution to the observed height increase of PE monolayers by aggregation of surfactant residues can be excluded.

Annealing of Continuous Ultrathin Crystalline Films

A nascent continuous film of about 50 nm was annealed in a Linkam hotstage, and studied by AFM after rapid cooling (with a cooling rate of 50 K min^{−1}) to ambient temperature (Fig. 5). AFM images were recorded at the same position for direct comparison. After annealing at 95 °C for 24 h, new structures of about 30 nm in height and several hundred nm in diameter appeared in height images [marked with arrows in Fig. 5(b)].

Figure 5. AFM images recorded during annealing of an ultrathin film (ca. 50 nm) below the melting temperature. (a) nascent film, (b) annealed at 95 °C for 24 h, (c-1) and (c-2) enlarged images of area marked with square in (b), (d-1) and (d-2) after rinsing the sample with water, (e) annealed at 120 °C for 13 h, (f) annealed at 130 °C for 20 h. (a), (b), (c-1), (d-1), (f) are height images; (c-2), (d-2), (e) are phase images. (c-3) and (c-4) are the corresponding cross sections in (c-1) and (c-2), respectively. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

For better illustration, height and phase images of the square marked area in Figure 5(b) are enlarged in Figure 5(c-1), which show that these newly appeared structures consist of several layers, with a thickness of about 5 nm for each layer as given by the height cross section profile. The phase image [Fig. 5(c-2)] reveals that the

stacking of multilayers is often surrounded by some "island" like structures, which also show different phase variation from the surrounding area. However, by rinsing the film-air interface with water, the previously observed dots and "islands" were removed in both height and phase images [Fig. 5(d-1,2)]. This indicates their composition of

Table 1. Static Contact Angles of the Films

		Annealed < T_m (°)	Recrystallized from the Melt (°)		
Nascent Film (°)		Washed		Washed (°)	
Discontinuous monolayer	30	60 ^a	75	80 ^c	80
15 nm film	20	90 ^a	105	60 ^c	60
50 nm film	<20	90 ^b	90	90 ^d	90
220 nm film	<20	90 ^b	95	95 ^d	105

^a Annealed at 75 °C.^b Annealed at 95 °C.^c Annealed at 130 °C.^d Annealed at 160 °C.

The experimental accuracy of contact angle determination is estimated to be about $\pm 10^\circ$. The static contact angle on a freshly cleaned silicon wafer substrate was determined to be $< 20^\circ$.

aggregated surfactant, probably formed by migration of SDS extruded towards the film-air interface upon annealing. A similar extrusion effect of surfactant during annealing of latex films has been observed previously.³³ Further annealing at higher temperatures up to 120 °C shows no additional formation of SDS aggregates, or any changes of surface morphology. Moreover, the boundaries between crystalline domains can still be clearly recognized in the phase image after annealing at a such high temperature, which indicates no occurrence of surface melting even at 120 °C [Fig. 5(e)]. After annealing at a temperature up to 130 °C, a dendrite like morphology formed after rapid cooling to room temperature [Fig. 5(f)], which is characteristic of melt-crystallization in ultrathin films.

These findings show lamellar thickening on a local scale to occur in the discontinuous monolayers upon annealing at a sufficiently high temperature of about 110 °C. Annealing of the continuous ultrathin crystalline films at temperatures up to 120 °C did not induce observable changes of film morphology, which would, however, be more difficult to detect by comparison to the discontinuous monolayer, as the extent of expected lamellar thickening is in the range of the surface roughness of the nascent ultrathin continuous films.

Distribution of Surfactant in the Films

Taking into account the composition of the as-prepared PE dispersions (ca. 2 wt % polymer content and 0.7 wt % surfactant content), and as a simplification assuming spherical PE particles with a diameter of 10 nm, the specific particle surface coverage per SDS molecule is estimated to be about

0.8 nm², which agrees well with a reported value of an effective head group area of 0.62 nm² for SDS in neat water.³⁴ The SDS surfactant added into the polymerization medium can be assumed to adsorb onto the surface of the PE particles formed completely, affording their colloidal stability. The high surface tension of 60 mN m⁻¹ also confirms the absence of SDS micelles in the as-prepared PE dispersions. During film formation from surfactant-stabilized polymer dispersions, the surfactant molecules desorb from the particles and form aggregates, which, depending on the compatibility of the surfactant with the polymer, may be uniformly distributed within the film, or enriched at the film interfaces.²² Enrichment of surfactant molecules at both the polymer-substrate interface and the film-air interface has been directly observed by various spectroscopic methods.³⁵ However, these observations have only been realized in μm thick films, due to a depth resolution limit. To estimate the distribution of surfactant in our nascent and annealed films at different film thicknesses, static contact angles were determined (Table 1).

For the nascent continuous films, low contact angles of $\leq 20^\circ$ were observed for the whole range of film thicknesses studied, which indicates the enrichment of surfactant at the film-air interface. Annealing below melting temperature, at 75 and 95 °C for ultrathin and thin films, respectively, already resulted in significantly increased contact angles, despite that formation of SDS aggregates on the film-air interface was observed after this low temperature annealing step (Fig. 5). In addition, the annealed film could not be floated off the substrate as in the case of nascent films, which renders it feasible to rinse the film-air interface of

the annealed films with water intensely. However, no significant changes of contact angles were observed before and after the rinsing procedure. The earlier observations suggest that the film-air interface of the nascent films was covered by desorbed SDS, although the SDS layer can not be directly observed by AFM. Upon heating, the continuous SDS layer, probably also surfactant migrated from the film-substrate interface, form large aggregates at the film-air interface. However, since the lateral dimension of these aggregates (several hundreds of nm) is very small as compared to the size of a water droplet (~ 2 mm in diameter) applied in the contact angle measurements, the wettability of the film-air interface is rather dominated by the hydrophobic PE film, which is in agreement with theoretical predictions of the contact angle on a smooth but chemically heterogeneous surface according to the Cassie equation.³⁶ For films thicker than 50 nm, higher annealing temperatures or longer annealing time were required to increase the contact angle to a similar extent (Table 1), which is probably due to hindered diffusion of the surfactant molecules in the thicker films. For the as-prepared discontinuous monolayer, an intermediate contact angle of 30° between a freshly cleaned silicon wafer substrate and PE film was observed, which increased to a smaller extent after annealing. This is probably due to too low amount of SDS in such thin material to form a continuous surfactant layer [Fig. 3(a,b)]. In the films recrystallized from the melt, the contact angle was observed to increase to a similar extent as in annealed films, except for the slight decrease in a 15 nm ultrathin film, which may be attributed to a discontinuous coverage of the substrate after melting [Fig. 2(e-1,2)].

SUMMARY AND CONCLUSIONS

Thin and ultrathin semicrystalline PE films of variable thickness can be prepared from aqueous dispersions of prefabricated nanocrystals. This approach differs fundamentally from more traditional routes to submicron semicrystalline films, in which the polymer is initially in an entirely disordered state (usually in organic solvents), and the crystalline order is only formed on the substrate upon solvent evaporation and/or cooling.

Spin-coating afforded continuous films composed of nanocrystals of linear PE, interacting via their amorphous surfaces, with a thickness from as low as 15 nm up to several hundred nm. These

nascent films possess a homogeneous topography over hundreds of micrometers, as revealed by both AFM and TEM. For a 40 nm film and thicker films studied, recrystallization from the molten state upon cooling did not result in dewetting and afforded again continuous films despite the presence of surfactant. The morphology of the recrystallized films depends on their thickness. While thicker films are composed of polygonal spherulites, randomly grown edge-on oriented lamella predominate thin films due to one dimensional confinement. Dominant formation of flat-on lamella was observed only in a film of 15 nm thickness. Overall, the morphology of these melt-recrystallized films is similar to the films originally cast from solution, and not influenced by the surfactant introduced with the original primary nanocrystals.

Thermal annealing of discontinuous assembled monolayers of PE nanocrystals below the melting temperature resulted in lamella thickening without changes of crystal orientation, or structure of the particle assemblies, likely via local disentanglement and reorganization of polymer chains.

Surfactant adsorbed to the nanocrystal surface in the aqueous dispersion desorbed at least partially during formation of the nascent films. Upon annealing below the melting point, the surfactant molecules migrate toward the film-air interface to form aggregates, which can be removed by rinsing with water, without any other observable undesired effect on film structure, and stability.

The approach reported can also be of practical interest for the preparation of semicrystalline polymer film under conditions where organic solvents and elevated temperatures are undesired, for example, due to substrate sensitivity.

METHODS

Materials and General Considerations

PE nanoparticle dispersions were prepared according to ref. 37. In brief, an aqueous surfactant-containing solution (SDS concentration of ca. 7.5 g L^{-1}) of the water soluble catalyst precursor [$(\kappa^2\text{-}N,O\text{-}6\text{-C(H)=N(2,6\text{-}\{3,5\text{-}(\text{F}_3\text{C})_2\text{C}_6\text{H}_3\}_2\text{C}_6\text{H}_3)\text{-}2,4\text{-I}_2\text{C}_6\text{H}_2\text{O})\text{NiMe(L)})$ (L = di- or trisulfonated triphenylphosphine)] was exposed to 40 atm ethylene pressure at 15°C for 30 min. The polymer dispersions were used as obtained for further film preparations. The polymer content of the dispersions was determined by precipitating an aliquot of the dispersion with excess of methanol.

The obtained bulk polymer was filtrated and dried under vacuum overnight. The molecular weight was determined by size exclusion chromatography at 160 °C (vs. linear PE standards). Thermal properties of the bulk polymers and dispersions were determined by DSC on a Netzsch Phoenix 204 F1. The degree of branching was determined from ^{13}C NMR spectra of isolated bulk polymers in 1,1,2,2-tetra-chloroethane- d_2 recorded at 120 °C. Particle size of the dispersions was determined by DLS on a Malvern Nano Zeta Sizer ZEN 3600 (173° back scattering) on diluted dispersions obtained by adding a few drops of as-prepared dispersion to about 1 mL of distilled water.

Preparation of Films

Polished glass slides or silicon wafers were cleaned by immersing in a 7:3 vol. mixture of 96% H_2SO_4 and 30% H_2O_2 at 80 °C for about 30 min, rinsed thoroughly with distilled water in an ultrasonic bath, and dried in air. Freshly cleaved mica was used as such. The films were prepared by placing 30–40 μL of PE dispersions of variable polymer solids content onto a clean substrate, then spin-coating with a rotation speed ranging from 2000 to 4000 rpm at room temperature on a custom-made spin-coating device. Thicknesses of thus obtained films was determined by AFM measurements on purposely introduced scratches at several different positions on the film surface. The nascent films appear transparent. For TEM analysis, the as-prepared film on a substrate was inserted into distilled water at an angle of about 45°. The floated-off film was then transferred onto a copper grid and dried at room temperature overnight before TEM analysis. For annealing experiments the film was annealed with an appropriate temperature program in a Linkam hotstage (THMS 600) equipped with liquid nitrogen cooling.

AFM Imaging

The topography of the films was measured with a JPK NanoWizard instrument in the intermittent contact mode using a Silicon tip with force constant of 40 N m^{-1} and resonant frequency of about 300 kHz. The set point amplitude A_{sp} was set just sufficient to follow the topography of the film, and minimize any possible deformation of the film surface by the scanning probe. Height, phase and amplitude images were recorded simultaneously. For measurements at elevated temper-

atures, the sample was heated to the desired temperatures on a heating stage incorporated in the scanning system. The temperature variation of the heating stage was determined separately to be ± 2 °C with a PT100 thermocouple. The thermal drift of the cantilever resonance curve was tuned at each measurement temperature.

AC Calorimetry

Differential AC calorimetry measurements were carried out according to ref. 38 in the group of Prof. Christoph Schick at the University of Rostock, Germany. PE dispersions were directly spincoated onto the SiN_4 membrane of a chip sensor. The film thickness of the film obtained was estimated by AFM measurements of films prepared on a silicon wafer under identical conditions. Temperature scanning was applied from 60 to 140 °C with a linear heating rate of 2 K min^{-1} at a fixed temperature oscillation frequency of 20 Hz and oscillation amplitude of 1 V. First heating traces were used to evaluate the melting temperature of nascent films.

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REFERENCES AND NOTES

1. Frank, C. W.; Rao, V.; Despotopoulou, M. M.; Pease, R. F. W.; Hinsberg, W. D.; Miller, R. D.; Rabolt, J. F. *Science* 1996, 273, 912–915.
2. Mareau, V. H.; Prud'homme, R. E. *Soft Materials*, Dutcher, J. R.; Marangoni, A. G., Eds.; Marcel Dekker: New York, 2005; pp 39–71.
3. Tong, Q.; Krumova, M.; Mecking, S. *Angew Chem Int Ed* 2008, 47, 4509–4511.
4. Weber, C. H. M.; Chiche, A.; Krausch, G.; Rosenfeldt, S.; Ballauff, M.; Göttker-Schnetmann, I.; Tong, Q.; Mecking, S. *Nano Lett* 2007, 7, 2024–2029.
5. Wang, Y.; Ge, S.; Rafailovich, M.; Sokolov, J.; Zhou, Y.; Ade, H.; Lüning, J.; Lustiger, A.; Marom, G. *Macromolecules* 2004, 37, 3319–3327.
6. Kim, J. H.; Jang, J.; Zin, W. *Macromol Rapid Commun* 2001, 22, 386–389.

7. Yakabe, H.; Sasaki, S.; Sakata, O.; Takahara, A.; Kajiyama, T. *Macromolecules* 2003, 36, 5905–5907.
8. De Rosa, C.; Auriemma, F. *Lecture Notes Phys* 2007, 714, 345–372.
9. Strobl, G. R. *The Physics of Polymers*, 3rd ed.; Springer: Berlin, 2007.
10. Keller, G. R. *Phil Mag* 1957, 2, 1171–1175.
11. Fischer, E. W. *Z Naturforsch* 1957, 12, 753–754.
12. Rastogi, S.; Spoelstra, A. B.; Goossens, J. G. P.; Lemstra, P. J. *Macromolecules* 1997, 30, 7880–7889.
13. Loos, J.; Tian, M. *J Polym Sci B* 2001, 39, 763–770.
14. Magonov, S. N.; Yerina, N. A.; Ungar, G.; Reneker, D. H.; Ivanov, D. A. *Macromolecules* 2003, 36, 5637–5649.
15. Sirota, E. B. *Macromolecules* 2007, 40, 1043–1048.
16. Strobl, G. R. *Progr Polym Sci* 2006, 31, 398–442.
17. Mellbring, O.; Kihlman Øiseth, S.; Krozer, A.; Lausmaa, J.; Hjertberg, T. *Macromolecules* 2001, 34, 7496–7503.
18. Jeon, K.; Krishnamoorti, R. *Macromolecules* 2008, 41, 7131–7140.
19. Sommer, J.; Reiter, G. *Adv Polym Sci* 2006, 200, 1–36.
20. Wang, Y.; Rafailovich, M.; Sokolov, J.; Gersappe, D.; Araki, T.; Zou, Y.; Kilcoyne, A. D. L.; Ade, H.; Marom, G.; Lustiger, A. *Phys Rev Lett* 2006, 96, 28303.
21. Hugger, S.; Thomann, R.; Heinzl, T.; Thurn-Albrecht, T. *Colloid Polym Sci* 2004, 282, 932–938.
22. Steward, P. A.; Hearn, J.; Wilkinson, M. C. *Adv Colloid Interface Sci* 2000, 86, 195–267.
23. Schantz, S.; Carlsson, H. T.; Andersson, T.; Erkselius, S.; Larsson, A.; Karlsson, O. J. *Langmuir* 2007, 23, 3590–3602.
24. Bartczak, Z.; Argon, A. S.; Cohen, R. E.; Kowalewski, T. *Polymer* 1999, 40, 2367–2380.
25. Mareau, V. H.; Prud'homme, R. E. *Macromolecules* 2005, 38, 398–408.
26. Ma, Y.; Hu, W.-B.; Reiter, G. *Macromolecules* 2006, 39, 5159–5164.
27. Schönherr, H.; Frank, C. W. *Macromolecules* 2003, 36, 1188–1198.
28. Wang, Y.; Chan, C.-M.; Ng, K.-M.; Li, L. *Macromolecules* 2008, 41, 2548–2553.
29. Reiter, G.; Castelein, G.; Sommer, J.-U. *Phys Rev Lett* 2001, 86, 5918–5921.
30. Also Cf. Petermann, J.; Gleiter, H. *Phil Mag* 1973, 28, 1279–1286.
31. Barham, P. J.; Chivers, R. A.; Keller, A.; Martinez-Salazar, J.; Organ, S. J. *J Mater Sci* 1985, 20, 1625–1630.
32. Yao, Y.-F.; Graf, R.; Spiess, H. W.; Rastogi, S. *Macromolecules* 2008, 41, 2514–2519.
33. Aramendia, E.; Mallécol, J.; Jeynes, C.; Barandiaran, M. J.; Keddie, J. L.; Asua, J. M. *Langmuir* 2003, 19, 3212–3221.
34. Butt, H.-J.; Graf, K.; Kappl, M. *Physics and Chemistry of Interfaces*, 2nd ed.; Wiley: Weinheim, 2006.
35. Belaroui, F.; Grohens, Y.; Boyer, H.; Holl, Y. *Polymer* 2000, 41, 7641–7645.
36. Woodward, J. T.; Gwin, H.; Schwartz, D. K. *Langmuir* 2000, 16, 2957–2961.
37. Göttker-Schnetmann, I.; Korthals, B.; Mecking, S. *J Am Chem Soc* 2006, 128, 7708–7709.
38. Huth, H.; Minakov, A. A.; Schick, C. *J Polym Sci B* 2006, 44, 2996–3005.