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ANNEALING OF ULTRATHIN POLYETHYLENE FILMS FROM AQUEOUS DISPERSIONS

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Introduction

Thin and ultrathin crystalline polymer films are of fundamental scientific and practical interest, e.g. in terms of their mechanical properties or of crystallization in a confined environment. A common route to ultrathin crystalline polymer films is spin-coating from solution, often at high temperature, which involves formation of crystalline structures during solvent evaporation. Recently, we have found that ultrathin crystalline polyethylene films can be prepared at room temperature by evaporation of aqueous dispersions (**I**) of polyethylene nanocrystals.[1] The latter possess a lamella thickness of 6 nm with a thin amorphous layer of 1 nm on the lamella surface, and a lateral pseudo-diameter of ca. 12 nm.[2] That is, although the particles are semicrystalline, the minor amorphous portion is located entirely at the surface, due to their single lamella nature. This enhances interactions between the original particles in (ultrathin) films.

By variation of the catalyst utilized in the preparation of the dispersions,[3] nanoparticles of similar overall size can also be prepared which are composed not of linear but of branched polyethylene (ca. 50 methyl branches / 1000 carbon atoms), and are much less crystalline.[1] These dispersions (**II**) are of interest here for comparative purposes.

Orientation of crystals in semicrystalline polymer films and the effect of annealing has been studies intensely. Surface-induced reorientation has been reported for drawn polyethylene films, at temperatures below the bulk melting point.[4] Annealing at 124°C induced orientation with the (110) face parallel to the free film surface, in addition to the fibre texture along the drawing direction in the as-drawn film. Melting of crystals with lattice defects below the bulk T_m, and migration of amorphous phases during annealing were suggested as possible mechanisms of this process.[5] It has also been reported that annealing on single crystalline polyethylene results in thickening of the crystals and reorientation of the lamellae.[6]

We report preliminary studies of the annealing of the aforementioned ultrathin films formed from nanocrystal dispersions.

Experimental

Polyethylene nanoparticle dispersions were prepared and characterized as described elsewhere.[3] In brief, an aqueous surfactant-containing solution of the water soluble catalyst precursor $[\{\kappa^2\text{-}N,O\text{-}6\text{-}C(H){=}N(2,6\text{-}\{3,5\text{-}R_2C_6H_3\}_2C_6H_3)\text{-}2,4\text{-}R'_2C_6H_2O\}NiMe(L)]$ (R = CF_3 for preparation of dispersion **I**, R = CH_3 for preparation of dispersion **II**; L = di- or trisulfonated triphenylphosphine) was exposed to 40 atm ethylene pressure at 15 °C for 30 min, which affords polyethylene dispersions with particle sizes of ca. 10 nm as determined by dynamic light scattering. The bulk crystallinity of the polymers from dispersion **I** and **II** are 60% and <20%, respectively, as determined by differential scanning calorimetry (DSC).

Ca. 2 wt.-% polyethylene dispersions were spincoated onto a freshly cleaved mica or pre-cleaned glass substrate to afford the nascent films (film **I** and **II** designate the film formed from dispersion **I** and **II**, respectively). Annealing of the nascent films was carried out in a Linkam hotstage. Before AFM measurements, the samples were brought to room temperature with a cooling rate of 50 K min^{-1} or 20 K min^{-1} after annealing below or above $T_{m,}$ respectively. Height and phase images of the film before and after annealing were recorded simultaneously with a JPK NanoWizard AFM operated at intermittent contact mode using a Silicon cantilever with force constant of 40 N m^{-1} and a resonant frequency of about 300 kHz.

Results and Discussion

Continuous ultrathin polyethylene films of ca. 50 nm thickness (determined independently from AFM, energy loss in TEM, and ellipsometry) were obtained via spincoating the aqueous dispersions onto glass or mica. Nascent films from dispersion **I** and **II** are continuous and macroscopically homogenous as observed by AFM and TEM, with detailed variation of surface roughness and electron density on a local scale.[1] Electron diffraction on the nascent film **I** with the incident beam perpendicular to the film surface shows sharp (*hk0*) diffraction rings. After annealing of the nascent film **I** above the melt transition temperature of the bulk polymer (T_m 132°C), edge-on lamella formed as observed from AFM height and phase images, which is the thermodynamically favoured crystalline form for melt-crystallization in films above a critical thickness of ca. 20 nm.[7]

The nascent films **I** were annealed at temperatures considerably below the bulk T_m. A continuous coverage of the substrate was retained, without any undesired dewetting. After annealing at 95 °C for 72 h, large multilayer structures were observed by AFM (Figure 1). The lateral dimension of these structures varies between several hundreds of nanometers and a micron. The height is mostly in the range of tens of nanometers. Line scans of the AFM height image show that the layers of these multilayer structures have a rather flat surface, and a thickness of about 5 to 10 nm, which is consistent within experimental error with both the lamella thickness of the original polyethylene nanocrystals, i.e. the original building blocks of the film, and also the initial chain folding length observed by Barham et al. in crystallization from the melt at 95 °C.[8] Line scans on the phase images also show the interactions between the AFM tip and the surfaces of these structures to be more repulsive and much less variable by comparison to the rest of the annealed film, which implies that the materials in such areas is crystalline.

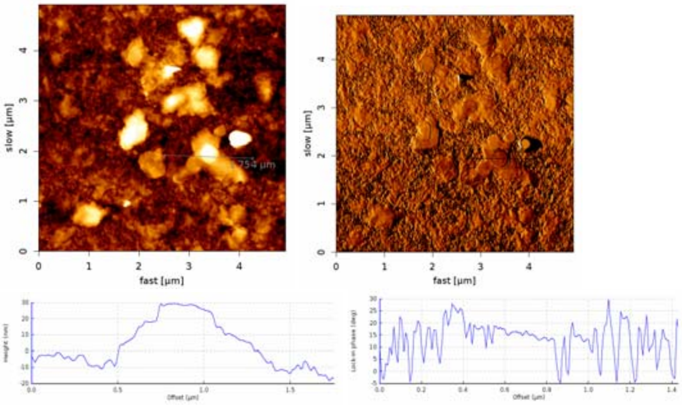

Figure 1. Height (left) and phase (right) AFM images and respective line scans of film **I** after annealing at 95 °C for 72 h.

Although the original dispersions contain no free surfactant, they do contain surfactant which colloidally stabilizes the particles.[3] Thus, the presence of surfactant in the films must be considered. Water contact angle measurements can give a rough indication of the composition of the film surface. A static contact angle on the nascent film **I** of only 15° was observed. After annealing below and above T_m, the contact angle on the annealed film surface increased to 30° and 65°, respectively (the contact angle of neat HDPE film is reported to be 82° [9]). This indicates that by annealing the amount of surfactant on the film surface is reduced, possibly surfactant migrates to the film-substrate interface.

In comparative studies, low-crystalline films **II** were annealed. After annealing at 120°C for 20 min (T_m of bulk polymer 70°C), partial dewetting was observed by AFM. Annealing at 40°C for 48 h did not result in any significant change of the observed film morphology, as expected.

The above observations in summary suggest that the larger structures (Figure 1) observed upon annealing of the crystalline ultrathin films, prepared from aqueous nanocrystal dispersions, are likely composed of polyethylene, in the form of crystalline sheets of several 100 nm extension. Ongoing studies are directed at confirming this interpretation and further elucidating the structure of the annealed films by diffraction techniques, and at following the annealing process over time.

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