Macromol. Symp. ***183,*** *173–178 (2002)*

Pattern Formation and Ordering in Thin Films of Crystallisable Block Copolymers

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Summary: We show that tapping-mode atomic force microscopy provides real-space and time-resolved observations of morphology and pattern formation resulting from crystallisation of annealed thin films of polyethyleneoxide or microphase-separated low-molecular-weight hydrogenated poly(butadiene-*b*-ethyleneoxide) diblock copolymers. Differences in viscoelastic properties allow distinguishing crystalline and molten (amorphous) areas with a nanometer resolution.

Introduction

For the understanding of polymer crystallisation, it is highly desirable to follow the ordering processes on a molecular scale. In this context, atomic force microscopy (AFM), in combination with complementary techniques like X-ray scattering, represents an extremely useful tool. In a more general context, we show that AFM allows us to investigate the behaviour of polymers close to interfaces and within submicrometer ultrathin films in order to understand the polymer morphology and ultimately predict the properties of polymer surfaces and thin films. AFM real-space observations provide information on the molecular pathways polymers take when forming a crystalline state, a question which has been already discussed for more than 40 years (see e.g. [1-7]). The geometry of a thin film of molecular thicknesses provides us with a high resolution and allows obtaining structural information on ordering, orientation and growth patterns. The crystallisation process can be used for the formation of regularly ordered, self-organised patterns on the nanometer-scale on surfaces. Here, we mainly focus on the morphologies resulting from crystallising diblock copolymers in the confined geometry of mesophases and of a thin film. First, however, we demonstrate analogies between crystallisation of polymers and crystallisation of other simpler systems like e.g. metals showing that the same mechanism of diffusion limited (DLA) growth is at work, resulting in typical DLA patterns. Based on these experimental findings a computer simulation model was developpped.

CCC 1022-1360/00/$ 17.50+.50/0

Experimental Section

Samples: The crystallising polymer is always polyethyleneoxide (PEO), either as a homopolymer or attached to an amorphous hydrogenated polybutadiene block (PB_h-PEO). Thin films (about 100 nm thick) were prepared by spincoating dilute toluene or methyl-cyclohexane solutions onto UV-ozone cleaned silicon wafers. To erase any non-equilibrium states induced by spincoating, all samples were annealed in the molten state at temperatures up to 150°C before further experiments were performed.

Table 1: Characteristics of the polymers used in this study.

SAMPLE	M_w(PEO)	M_w(PB_h)	M_w/M_n
PEO-2k	2000	--	1.1
PEO-7.6k	7600	--	< 1.1
PB_h-PEO (3.7-2.9)	3700	2900	1.1
PB_h-PEO (21.1-4.3)	21100	4300	1.15

Optical microscopy and AFM were used to determine the morphology, either in the melt state (optical microscopy) or after crystallisation (mostly AFM). All samples were crystallised at constant temperatures.

Atomic Force Microscopy (AFM): Measurements were performed with a Nanoscope IIIa/ Dimension 3000 (Digital Instruments) in the tapping mode at ambient conditions. Topographic (height mode) and viscoelastic (phase-mode) data were recorded simultaneously. It should be noted that semicrystalline polymers are well suited for the use of the "phase-mode" as the differences in viscoelastic properties between crystalline and amorphous regions are large. This allows an imaging mode based on a mechanical contrast, which is complementary to the topographic height imaging mode.

Results and Discussion

A. Crystallisation of adsorbed polymer monolayers

In a first approach, we determined the morphology of mono-lamellar crystals obtained from monolayers of PEO homopolymer [7-9]. The monolayers were prepared by annealing the films above the melting point. In the molten state, the polymer dewetted the substrate covered with a layer of adsorbed molecules. The origin of this autophobic behaviour is related to the difference in entropy (resulting from the different chain conformations) of adsorbed and free polymers.

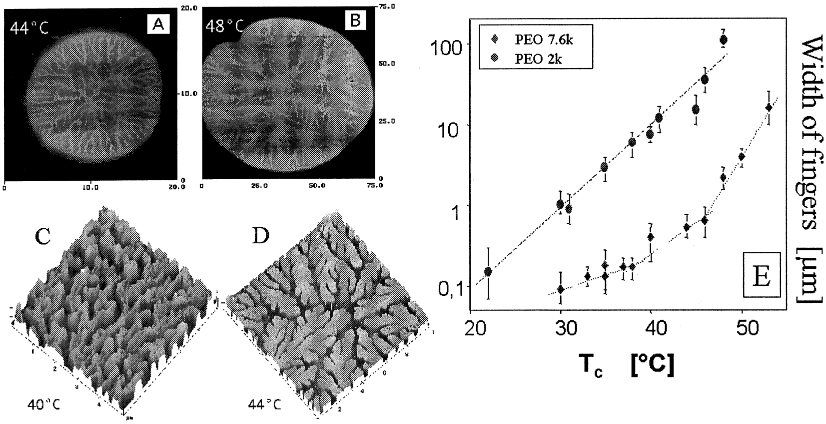

Fig. 1. AFM topography images showing the morphology of mono-lamellar PEO-7.6k crystals obtained at the temperatures indicated. The size of the images is: A: 20x20µm^2, B: 75x75µm^2, C: 5x5µm^2, and D: 10x10µm^2. Note that the patterns in A and B appear rather similar although the size of the image differed by almost a factor of 4.
E: Characteristic width of the fingers as a function of crystallisation temperature for the two homopolymers studied.

Due to a strongly reduced nucleation probability of polymers confined in the two-dimensional adsorbed monolayers, crystallisation started always in the thicker regions, e.g. at the rims collecting the material from the dewetted areas. In the case of circular holes, this lead to the formation of a finger-like pattern with all fingers started at the periphery of the hole and grew towards the centre. Typical examples are shown in Fig. 1. The resulting growth patterns are analogous to structures resulting from diffusion limited aggregation (DLA), frequently found in nature (e.g. snowflakes). Moreover, using the basic principles of DLA but adding polymer specific features like the possibility for chain folding, we succeeded in reproducing even fine details of the experimentally found features of the monolamellar crystals with a generic computer simulation model [10,11]. In particular, the increase of the characteristic width of the fingers (see Fig.1) with crystallisation temperature and the relaxation behaviour upon annealing of the non-equilibrium polymer crystals has been understood based on our simulations. Our results demonstrate clearly that many features of polymer crystallisation are analogous to growth processes like DLA which are found also in many other materials. The complex nature of polymers is introduded via the possibility of chain folding, leading to a sequence of quasi metastable states. These metastable states are responsible for the pronounced re-organisation phenomena found in polymer crystals [8,11], indicating the coupling between morphology and chain conformations.

B. Discrete variation of lamellar spacings with temperature in block copolymer

The crystallisation of polymers is a self-organisation process involving a hierarchy of ordered structures on several length scales starting from the crystal unit cell, over nano-sized crystallites up to hundreds of microns for spherulites. In block copolymer systems, these length-scales are superposed to, and sometimes in competition with, the mesoscopic structures due to the interaction (incompatability) of the blocks. Consequently, crystallisable block copolymers in thin films or at surfaces present interesting systems for the creation of patterned substrates exhibiting multiple lengthscales.

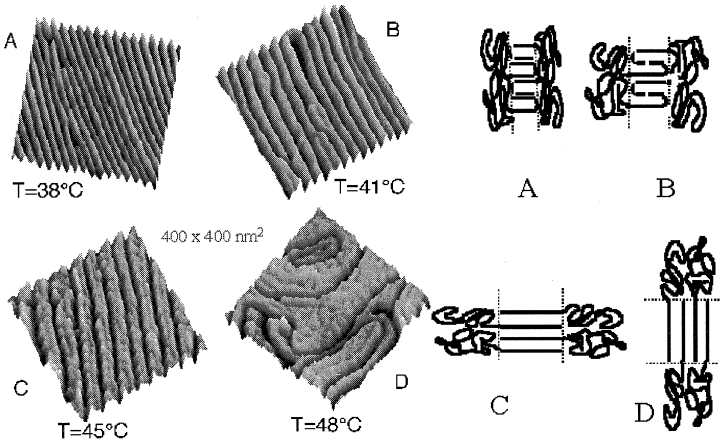

Fig. 2. Typical AFM phase contrast images obtained from PB_h-PEO (3.7-2.9) crystallised at the temperatures indicated. Note that the lateral spacing varied with temperature. The schematics on the right indicated a possible molecular explanation based on a variation in chain folding and orientation.

Here, we give an example for the almost symmetric PB_h-PEO (3.7-2.9) of how the characteristic lengthscale resulting from crystallisation can be varied by simply changing the temperature [12,13]. Due to the possibility of chain folding the average mean spacing can vary between 22 nm (1 fold) and 44 nm (NO fold) depending on the rate of crystallisation controlled by the crystallisation temperature T_c. The faster the polymer crystal grows the higher is the tendency for chain folds. In addition, we found that the orientation of the crystalline lamellae may be perpendicular (T_c <45°C) or parallel (T_c >45°C) to the surface.

B. Individual crystallisation and melting of polymer nanocrystals

In a third set of experiments we used the asymmetric block copolymer PB_h-PEO (21.1-4.3), where PEO presents the minority phase and forms spherical cells with a diameter of about 12 nm in the melt [14,15]. This sample did *not* crystallise at ambient conditions, even after storage at room temperature for many months. Only after cooling the samples to temperatures below about -20°C, crystallisation was observed. Melting, on the other hand, occurred at temperatures above about +40°C. Consequently, at room temperature the samples neither crystallised nor melted. This enabled AFM measurements of intermediate, partially crystallised states of these samples also at room temperature, preserving the structure obtained by crystallisation at low temperatures.

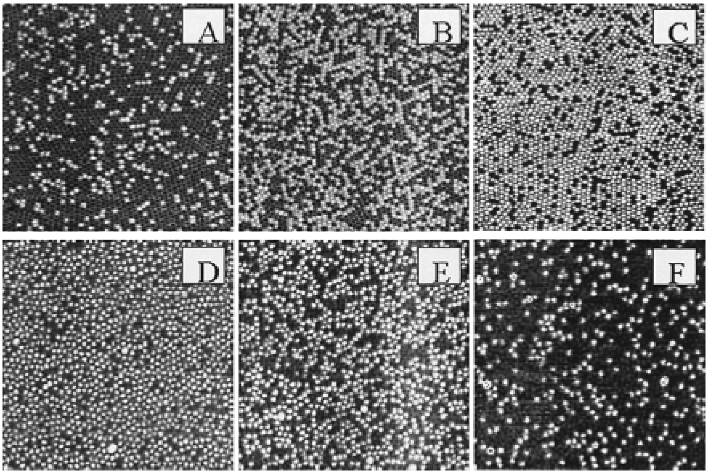

Fig. 3: AFM phase images showing the variation in the number and distribution of crystalline cells after crystallisation at -23°C for A: 5 min, B: 15 min and C: 120 min. The sample was then split into several pieces which were separately annealed for 2 min at D: 39°C, E: 42°C, and F: 44°C, respectively. The size of the images is $1 \times 1 \mu m^2$.

In Fig. 3 we give a few typical examples indicating that AFM allows also a time-resolved study of crystallisation and melting. The most fascinating aspect of this study is the finding that crystallisation was nucleated in each sphere independently, resulting in a random sphere-by-sphere crystallisation of the sample. Similarly, melting of these spheres was also a random process with respect to the melting temperature of the individual spheres.

Conclusions

We have demonstrated that AFM in combination with well-defined samples like thin films or even polymer monolayers allowed a direct relation between the morphology and the crystal growth processes. A key parameter in controlling the crystalline morphology is the number of chain folds (selected by the kinetics of crystallisation) which ultimately determines the lamellar spacing or thickness. Moreover, using block copolymer systems, we indicated possibilities for controlled patterning of polymer surfaces.

In polymers, the kinetics of the crystallisation process usually leads to different but well-defined metastable states, which in a second step after crystallisation can relax towards equilibrium, even at temperatures far below the melting point. The small thickness of our films and the low molecular weight of our polymers allowed us to observe such *secondary relaxations* in the crystalline state directly (via the change in morphology) and on accessible time-scales (see e.g. [8,11] .

Acknowledgements

We are indebted to G. Riess, P. Hoerner and R. Krikorian (Mulhouse/France) for providing us with the polymers. Fruitful discussions with T. Thurn-Albrecht and partial financial support by the EC under Contract No HPRN-1999-00151 are acknowledged.

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