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Short Communication

Morphological studies of spin-coated films of poly(styrene-block-methyl methacrylate) copolymers by atomic force microscopy

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Abstract: The surface structure of very thin (15–20 nm) spin-coated films of a symmetrical poly(styrene-*b*-methyl-methacrylate) block copolymer on silicon and mica is analyzed by atomic force microscopy (AFM). The films show a surface corrugation of a very regular ~ 100 nm lateral periodicity and ~ 6–8 nm amplitude. Film thickness is measured by AFM at induced film defects and checked by ellipsometry. XPS shows that both blocks are at the film surface. Selective degradation of the methyl methacrylate block is used for contrast enhancement and allows to assign poly(styrene) to the elevated surface regions and poly(methyl methacrylate) to the substrate/film interface.

Friction interactions of the AFM tip with the film surface may be used to induce high orientational ordering of the morphological pattern perpendicular to the fast scan direction.

Key words: Thin block copolymer films – morphology – atomic force microscopy – contrast enhancement – orientational ordering – poly(styrene-*b*-methyl methacrylate)

Introduction

Block copolymers, especially those with immiscible blocks as constituents, were immediately subjected to intense investigation since they became available in the mid-1950s [1]. Depending on the volume fraction of the block components, they show a rich variety of phase separated equilibrium bulk morphologies (micellar, cylindrical, lamellar, double diamond). The development of these morphologies is theoretically quite well understood by meanfield theories (e.g., [2]) or Monte Carlo studies (e.g., [3]).

Broad interest exists on using block copolymers as surfactants to improve the properties of polymer blends in which the copolymer blocks may be identical or different to the homopolymers in the blend (A/a – b/B type [4], C/a – b/D type [5]). The block copolymer may be considered as a thin interfacial film, with the blocks extending into the respective homopolymer phase of the blend.

Diffraction methods [6], electron microscopy [7] and SIMS [8] are commonly used techniques to investigate thin block copolymer films, still several units of phase correlation lengths thick (e.g., measured in units of the long period of diffraction experiments) and close to thermodynamical equilibrium. The morphological sequences are usually studied either only one-dimensional in direction normal to the film surface (diffraction, SIMS, for higher dimensionality in diffraction experiments on thin films cf. [9]) or in a cutting plane with the plane normal in the film surface (electron microscopy), i.e., two-dimensional. Symmetrical styrene methyl methacrylate block copolymers have been widely studied by these methods by T. P. Russel et al. [6, 8–10]. Due to thickness or interface constraints three-dimensional structuring has been observed by G. Coulon [11] at the surface of these films by interference microscopy, which provides three-dimensional structures, but shows sufficient resolution

($\sim 10^0$–10^2 nm) only in normal direction of the film surface.

Atomic force microscopy (AFM) is able to analyze the three-dimensional surface structure with high resolution in each dimension and has been applied to study the structure formation process [12] and morphological surface structures of relatively thick films [13].

When the film thickness decreases to values in the order of or below the bulk phase correlation length, due to the enhanced influence of surface (interface) energies and spatial restrictions new three-dimensional morphological patterns are to be expected. This holds even more, if the films are not very close to the thermodynamical equilibrium, but are studied in their kinetically defined morphology that develops upon spin-coating or similar film forming procedures, which are important for hypothetical applications.

Henkee et al. [14] examined the phase morphology of very thin films of poly(styrene-*b*-butadiene) by electron microscopy. The films were generated by evaporating the solvent of a drop of a dilute solution on carbon. The symmetrical block copolymer showed a lamellar-like phase structure with the normal direction of the lamellae lying in the surface plane.

In this communication we want to report on first investigations of the phase structure of very thin, spin-coated films of a symmetrical poly(styrene-*b*-methyl methacrylate) block copolymer by atomic force microscopy in terms of morphological structure, film thickness, attributing chemical (block) components to the surface topography via contrast enhancement (analogous to staining in electron microscopy). In addition to this, we report on the possibility to orient morphologies via tip interaction.

Experimental

The poly(styrene-*b*-methyl methacrylate) block copolymer {P(S-*b*-MMA)} SM120 was supplied by R. Stadler, Univ. Mainz, and is described elsewhere [5, 15]. The molecular weights of the styrene and the MMA blocks are 128 and 147 kg/mol, respectively; $M_W/M_n = 1.11$; the styrene block has a weight fraction of 40% in the copolymer.

We prepared thin block copolymer films by spin-coating from a toluene solution (2.5 g/l), which is a non-preferential solvent at room temperature. Three drops of polymer solution were spin-coated at room temperature onto the substrate at 8000 rpm for 1 min. The samples were dried in vacuum for 10 min at room temperature and heated to 70 °C for 2 days for further drying.

The substrate was either freshly cleaved mica or polished silicon wafers (ca. 5 × 5 mm). The silicon wafers have a thin surface layer of natural dioxide and were cleaned by rinsing with toluene and subsequent plasma cleaning (100 W for 10 min). The uncoated silicon wafers show a structureless surface roughness of less than 4 nm on 100 × 100 μm, as measured by AFM.

The atomic force microscope used is a Nanoscope III of Digital Instruments. We used micro-fabricated, triangular Si_3N_4-springs (length 200 μm, force constant 0.12 N/m) with integrated pyramidal tips.

Results

Surface topography

Figure 1 shows the typical surface topography of a thin SM120 film on silicon. The height is indicated as gray-scale. The film surface shows a corrugation of 6–8 nm depth and a very regular period of ~ 100 nm (maximum of the FFT power spectrum of the topographical presentation in Fig. 1), which is in the range of the bulk phase correlation lengths to be expected for this material (cf. e.g. [4]). The structure is the same for films spin-coated onto mica. No preferential orientation of the corrugational pattern, which might have been induced by the spin-coating process or by "epitaxial" influence of the mica surface, has been observed.

The characteristics of the lateral corrugation pattern in Fig. 1 are similar to phase structure characteristics of lamellar block copolymers in their bulk equilibrium state as observable by electron microscopy of cutting planes and similar thin film features have been called "lamellae" [14] in electron microscopical investigations. But one has to be aware that

i) lamellae are three-dimensional and the very thin film has constraints in the third (thickness) dimension below the characteristic (ca. 80 nm) value of the bulk microdomain stacking and

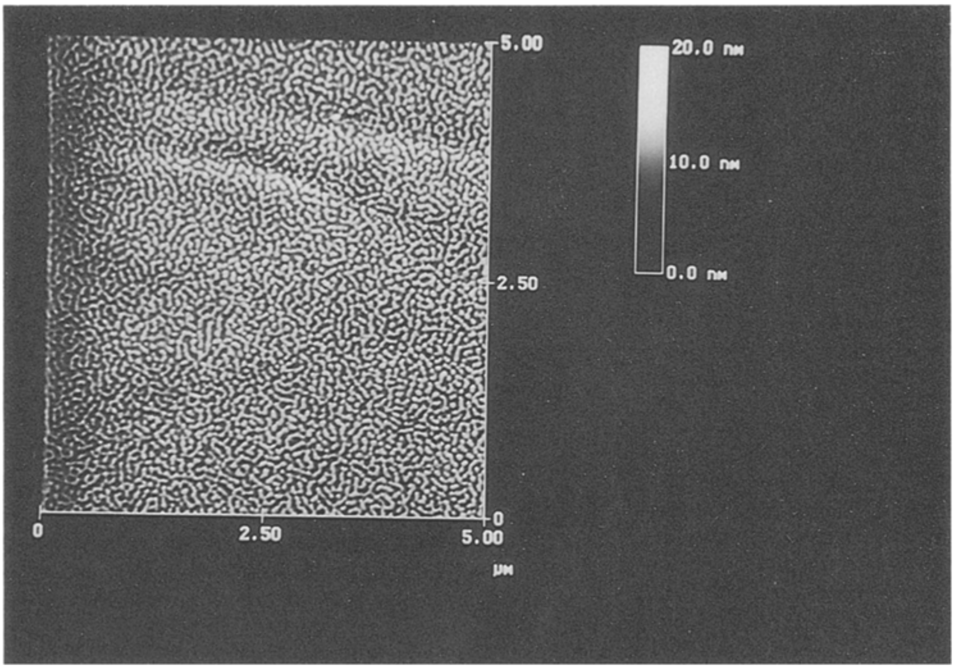


Fig. 1. Surface topography of a spin-coated film of SM120 on mica. The height is indicated by the gray-scale bar

ii) contrast in atomic force microscopy is (at least in the basic constant force experiment) essentially topographic.

Phase structure

Due to the high surface energy of silicon dioxide and the slightly higher surface energy of PMMA relative to PS (41.1 mN/m vs. 40.7 mN/m [10]) a preferential segregation of the MMA block to the wafer (or mica) surface, and a preferential segregation of the styrene block to the air interface might be anticipated. Preferential segregation of this type is found with more than 100-nm-thick, thermodynamically equilibrated films (e.g., [10]).

To derive a morphological model from the topographical surface structure further information is needed. First the film thickness has to be determined and second the topographical features have to be assigned to the block structure.

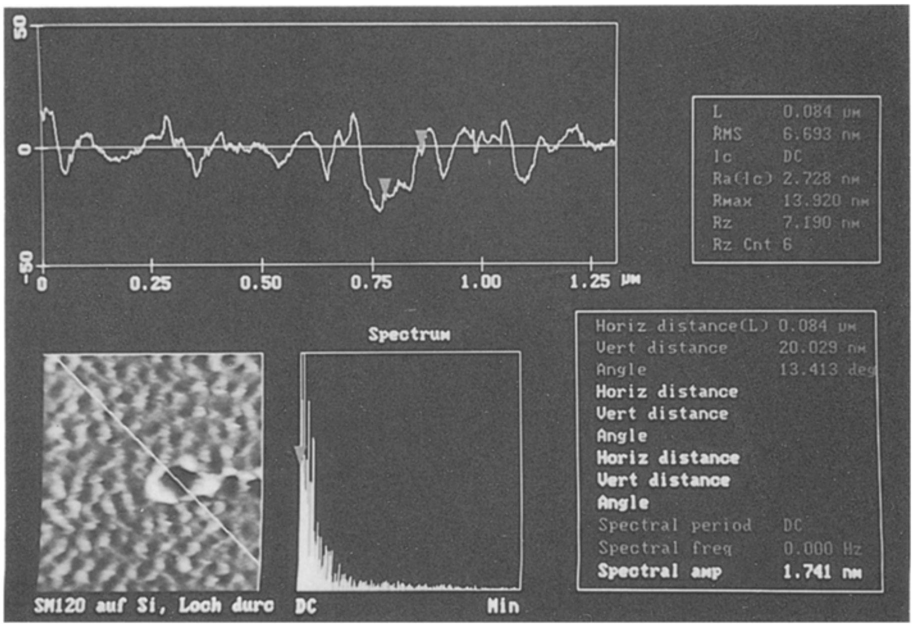
To measure the thickness with an atomic force microscope, a structural defect has to extend over the whole film thickness. The nature of the defect may be intrinsic to the film structure or may be induced by deliberately damaging the film. We performed two types of experiments: In the first, we scanned a small region (~ 100 nm) at high frequency and used the feedback loop of the instrument to set the tip to resonant vibrations, i.e., we tried to use the tip to dig a hole into the film. In these experiments we omitted the drying step at 70 °C, to have the film plasticised by residual solvent. The holes were 18–25 nm deep (Fig. 2).

The second experiment to measure the film thickness consists of slightly scratching a thoroughly dried polymer-coated silicon wafer with a sharp metal pencil. The heights of the film edge at the scratching trace are ca. 15 nm.

These results were cross-checked by ellipsometry, which – besides finding 3.2 ± 0.2 nm for the silicon dioxide layer at the wafer surface – gives a thickness of 15 ± 3 nm by applying a very simple model of an optically homogeneous film.

The integral concentrations of the monomeric units at the film surface were determined by x-ray photon spectroscopy (XPS), according to [10], but using different fitting functions [16, 17]. The spectral fitting was best with 40 monomer-% styrene and 60 monomer-% MMA in the accessible surface (ca. 3–5 nm), i.e., about equal to the block monomer fractions in the copolymer. This indicates that both blocks are present at the polymer surface.

The assignation of topographical features to the respective blocks by AFM methods is possible by contrast enhancement via selective degradation of



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L         0.084 μm
RMS       6.693 nm
lc        DC
Ra(lc)    2.728 nm
Rmax      13.920 nm
Rz        7.190 nm
Rz Cnt    6
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Horiz distance(L) 0.084 μm
Vert distance     20.029 nm
Angle             13.413 deg
Horiz distance
Vert distance
Angle
Horiz distance
Vert distance
Angle
Spectral period    DC
Spectral freq      0.000 Hz
Spectral amp       1.741 nm
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Fig. 2. a) Surface topography of a spin-coated film of SM120 on a silicon wafer. The residual solvent has not been removed. The height is indicated by gray-scale. The hole in the center was created by scanning a 100-nm region at high frequency, while the feed back loop was used to set the tip into resonant vibrations. b) Height profile along the line indicated in a). The depth of the hole, relative to the mean height of the film surface is ca. 20 nm

the MMA block. Upon electron beam radiation poly(methyl methacrylate) is rapidly degraded via a monomer unzipping mechanism. This effect is used in electron microscopical contrasting [4]. We used a plasma cleaner with air of high humidity to degrade the MMA block. A polymer film was characterized by AFM, plasma treated for some seconds and then characterized again. We repeated this cycle several times. In the first cycles the topographically low lying areas of the topography got deeper, i.e., the top-to-bottom distance of the surface corrugation increased form ~ 6 nm until – after some cycles – at the distance of 16 nm a limit was reached, according to the film thickness. This result allows to assign the styrene block to the prominent topographical features, whereas the MMA block forms a contact layer at the silicon dioxide (or mica) surface.

Orientation induced by surface-tip interactions

Upon scanning the sample surface with the AFM-tip in the topographic mode, it is usually assumed that only forces perpendicular to the surface are effective. This is a good approximation with hard surfaces and low forces. With soft, ductile surfaces or at high perpendicular forces, lateral forces due to friction between the moving tip and the sample become prominent. (In the actual experiments not the tip but the sample is moved, which is not relevant for the argumentation). Lateral force microscopes (LFM), which are commercially available, are designed to measure these friction forces.

Induction of structures perpendicular to the fast scan direction of the AFM tip has been reported by Leung and Goh [18] at previously unstructured polystyrene homopolymer surfaces with forces of 10^{-7} N. Lower forces in the range of $1–10 \cdot 10^{-9}$ N showed no effect on the polystyrene homopolymer surface.

Therefore, we did not expect, and actually did not observe, tip-induced changes in the surface morphology. But if the sample preparation of the block copolymers films is altered by omitting the solvent removal steps, the polymer film stays in a soft, plasticised state, due to residual solvent. Scanning this type of films showed friction effects and upon scanning for 30 to 60 min the corrugation pattern was oriented perpendicular to the fast scan direction (Fig. 3). While the corrugation depth increases in this process, the lateral period of ~ 100 nm is conserved, i.e., considering the phase assignment, the styrene phase is oriented to reduce the curvature of the phase boundaries. The softness of the samples also reduces the resolution of the micrograph in Fig. 3. If the scanning direction is rotated the corrugational orientation

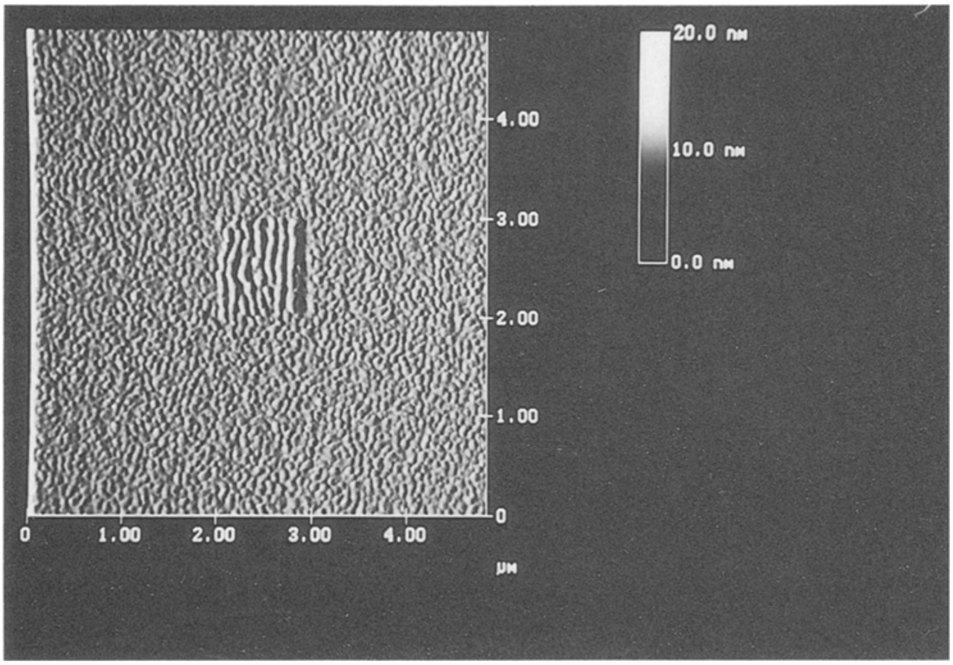

Fig. 3. Surface topography of a spin-coated film of SM120 on mica. The residual solvent has not been removed. The height is indicated by gray-scale. Before registrating this surface structure a square of 1 μm in the center has been scanned for 1 h. The fast scan direction was from left to right

is observed to follow the rotation until perpendicular orientation is reached again.

Independent from our investigations, Magonov recently reported on similar observations of tip-induced orientation at films of a comparable poly(styrene-*b*-methyl methacrylate) [19].

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