

Analysis of the Structure of Block Copolymer Films by Atomic Force Microscopy

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Abstract—The structure of thin films of the polystyrene–polymethylacrylate–polystyrene triblock copolymer was studied. Universal algorithms to analyze atomic-force-microscopy images of thin block-copolymer films were developed.

Key words: block-copolymer, thin films, atomic-force microscopy.

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INTRODUCTION

At present the studies of microphase segregation in thin block-copolymer films are of great interest because the usage of block-copolymer films is very promising for the creation of nanomaterials. Block copolymers consist of two or more polymer chains (blocks) of different chemical compositions coupled by a covalent bond. The cases when the constituent blocks are strongly incompatible, i.e., the interaction between the parts of different blocks is not favorable if compared with the interaction of the same parts, are of special interest. The incompatibility results in microphase segregation in a system: blocks segregate, forming individual phases with a definite order in their location.

Microphase segregation in films provides possibilities for producing nanomembranes. By treating the copolymer films physically or chemically one of the phases can be eliminated, forming membranes with spherical or cylindrical pores [1, 2]. Filling cylindrical pores with the ferromagnetic material allows one to obtain magnetic ultra-highly dense information carriers and nanowires [3, 4]. Filling membranes on the basis of block copolymers with conducting polymers, such as polyaniline [5, 6], polypyrrole [7] or polythiophene [8] allows one to produce electroconductive composite materials. Introducing specific antibodies into membranes provides an option to use them as biosensors [9]. Nanoparticles may be synthesized in the pores inside block-copolymer films [10].

To obtain nanomaterials with desired properties one should know the statistical values of the parameters of these films: width, lamellar structure period, and domain size. Current methods of treating atomic-force-microscopy (AFM) images [11, 12] do not allow one to treat a large number of measurements to obtain the sta-

tistical characteristics of the studied materials. Moreover, the values of the parameters of microphase segregation obtained with different calculation methods differ a lot. Therefore, the necessity arises to develop universal algorithms to analyze the structure of block-copolymer films.

EXPERIMENTAL

Films of the polystyrene (PS)-polymethylacrylate (PMA)-polystyrene triblock copolymer were studied. To obtain macromolecules pseudoliving radical polymerization was used. Two series of samples were used: $M_n = 75\,000$, [PS] : [PMA] = 1 : 2 and $M_n = 30\,000$, [PS] : [PMA] = 1 : 1. Polydispersity was 1.4–1.5.

Thin films were prepared from a 1% solution of a polymer in chloroform by direct adsorption on freshly cleaved mica. The solvent was evaporated in saturated chloroform vapor to obtain equilibrium conformations of microphase segregation.

Atomic force microscopy (AFM) was carried out on a Nanoscope-3a (Digital Instruments, Santa Barbara, US). AFM data were treated with Femtoskan Online software (Center of Promising Technologies, Moscow) [13].

Atomic force microscopes may function in various scanning regimes. Contact and semi-contact (dynamic) regimes are the most widespread. In the contact regime, “soft materials” may be carried along by the scanning tip and the surface of such materials may be modified by the tip during scanning. As a result, it is not possible to obtain their image. In the semi-contact regime the force impact of the tip on the sample is much less than that in the contact regime. This allows one to obtain stable images.

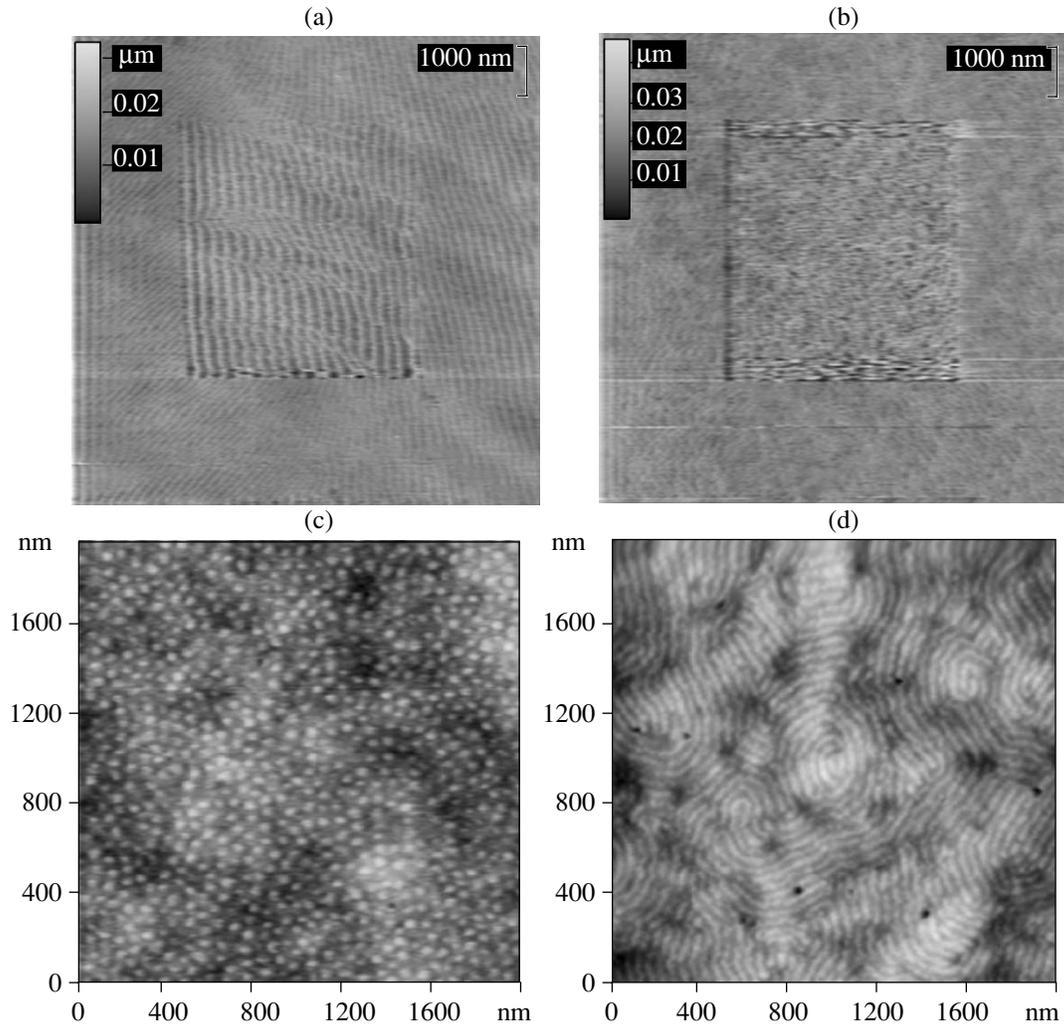


Fig. 1. AFM-images of the polystyrene–polymethylacrylate–polystyrene films at [PS] : [PMA] = 1 : 2 (left) and 1:1 (right). a, b morphology change at the contact scanning regime; c, d images of the domain and lamellar structures of the microphase segregation in the polystyrene–polymethylacrylate–polystyrene films obtained in the semi-contact scanning regime.

To determine the optimal experimental regime it was determined whether the film morphology changed in the contact and dynamic scanning regimes. To this end, at first a sample area with dimensions of 5 by 5 μm and then a larger area, including the area studied previously, were scanned. In the contact scanning regime the film morphology changed. Figure 1 (a, b) shows the characteristic “smearing” on the primary scanning area. In the semi-contact regime the changes in the morphology were not observed (Fig. 1 (c, d)). Therefore this regime was used in further studies.

In the dynamic scanning regime the AFM tip oscillates at the resonance frequency with a given amplitude A_0 (initial amplitude) under an external force. As the tip approaches the studied surface the oscillation amplitude decreases. When the tip is moved along the surface during scanning the tip oscillation amplitude is kept to the given value A (working amplitude) by the feedback,

i.e., the tip trajectory repeats the relief of the surface under investigation. The lower the ratio $S = A/A_0$, the larger the force of the impact of the tip on the sample. In [14] it was shown that the relief of the block copolymer films obtained on the AFM images is due to different phase deformations at the same force impact of the tip on the films during scanning. In this connection the phase contrast ΔH , being the deformation difference for different phases at the same force impact of the tip, was introduced. To determine the scanning parameters enabling the maximal contrast, the sample surface was scanned in the dynamic AFM regime with different values of the scanning parameter S . Figure 2 shows the contrast dependences on the force impact. As the force impact increases, the contrast increases as well, reaching its maximal value in the region of $S = 0.70 \pm 0.05$. A further increase of the force impact results in a decrease of the contrast. For samples with the relative

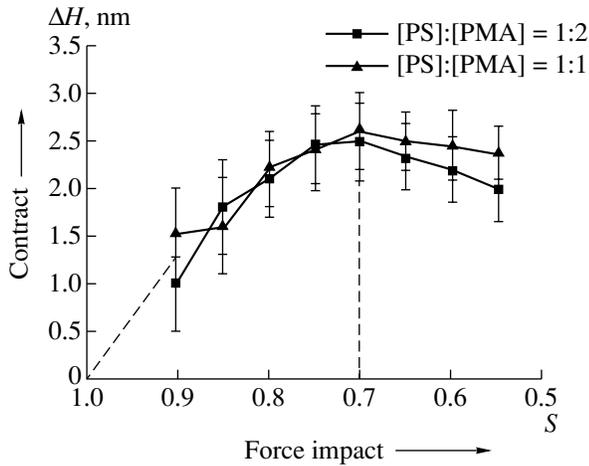


Fig. 2. Dependence of the phase contrast ΔH on the force impact of a cantilever on the surface of the polystyrene–polymethylacrylate–polystyrene films during scanning at $[\text{PS}] : [\text{PMA}] = 1 : 2$ and $1 : 1$.

chain concentrations $[\text{PS}] : [\text{PMA}] = 1 : 2$ the microphase segregation structure is smeared out during prolonged scanning in the dynamic regime with $S = 0.65 \pm 0.05$. At $S = 0.65 \pm 0.05$ the structure was not smeared out for scanning the films with the relative chain concentrations $[\text{PS}] : [\text{PMA}] = 1 : 1$. Thus, the optimal scanning parameter was chosen as $S = 0.70 \pm 0.05$.

RESULTS AND DISCUSSION

AFM images of the morphology of thin films of the polystyrene–polymethylacrylate–polystyrene triblock

copolymer were obtained. In films with $[\text{PS}] : [\text{PMA}] = 1 : 2$ the domain structure of the microphase segregation was observed (Fig. 1c). In films with $[\text{PS}] : [\text{PMA}] = 1 : 1$ a lamellar structure was observed (Fig. 1 (d)).

To obtain the statistical characteristics of these films it was necessary to create universal algorithms for the analysis of the domain and lamellar structures of the block copolymer films on the basis of treating a large number of measurements. Let us consider the analysis of each of the structures of the microphase segregation separately.

Analysis of the Domain Structure

The mean statistical size of domains is an important characteristic in the analysis of the domain structure. The contrast is due to the different deformations of phases and therefore it was proposed to use the height segregation of phases. All regions below a chosen level were considered to be the “soft” phase of polymethylacrylate and were substituted with the zero height. All regions above this chosen level were considered to be the “hard” phase of polystyrene and were substituted by the maximal height (Fig. 3). However, the roughness of the film surface (macrorelief) along with the microphase segregation does not allow one to choose a unique level for the phase segregation. To eliminate the effect of the macrorelief the Fourier spectrum of AFM images was treated as follows. Low-frequency harmonics corresponding to the macrorelief were taken as zero and high-frequency harmonics forming the pattern of the microphase segregation were kept unchanged.

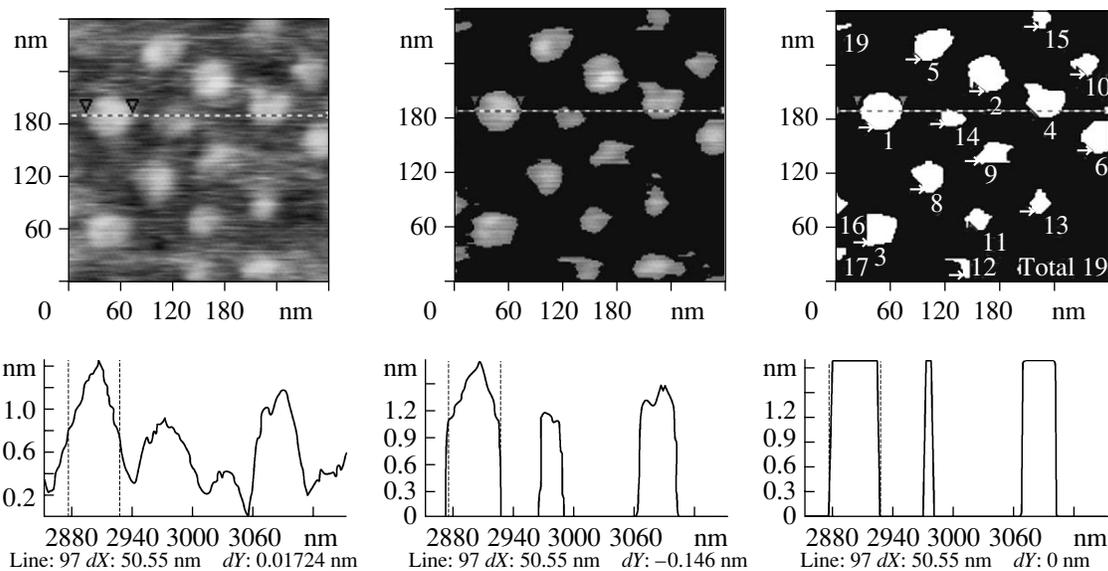


Fig. 3. Segregation stages of the AFM-image of the domain structure of the polystyrene–polymethylacrylate–polystyrene films at $[\text{PS}] : [\text{PMA}] = 1 : 2$ in the region of different phases. The change of the topography map (top) and cross-section (bottom) at the interchange of the regions higher and lower that the chosen level of the phase segregation for the minimal and maximal height, respectively.

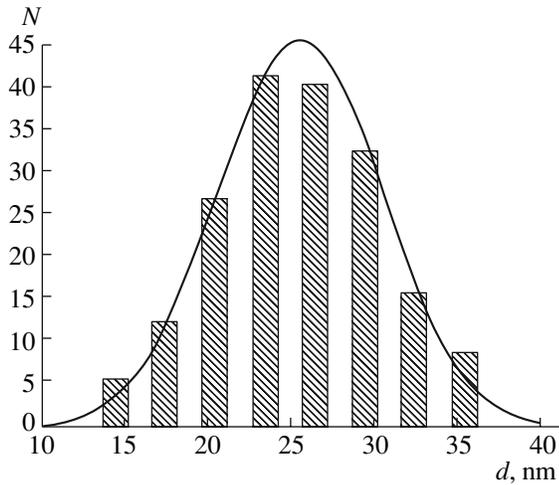


Fig. 4. Size histogram of the polystyrene-polymethylacrylate-polystyrene domains at [PS] : [PMA] = 1 : 2. The mean domain size $d = 25 \pm 10$ nm.

Then an array of the domain areas was obtained using Femtoskan Online software. The domain diameters were calculated under the assumption of the domain spherical symmetry. The mean domain size and its dispersion were calculated from the relevant histogram of domain sizes and the statistical curve of the normal distribution (Fig. 4). The mean domain size for polystyrene-polymethylacrylate-polystyrene ([PS] : [PMA] = 1 : 2) was $d = 25 \pm 10$ nm.

Analysis of the Lamellar Structure

Important parameters of the lamellar structure are its period, the direction of the orientations of lamellas and the degree of their ordering.

The cross-section of an AFM image of a lamellar structure is a periodic curve. The Fourier transform consideration allows one to separate low-frequency harmonics forming a microrelief, and a harmonic forming a lamellar structure. By measuring the frequency of the latter, it is possible to obtain the period of the lamellar structure. The lamellar structure of block copolymer films often does not keep its orientation at the scale exceeding several periods of the lamellar structure, hampering creation of a cross-section of a large number of lamellas.

The study of the two-dimensional Fourier transform of AFM images allows one to avoid difficulties in choosing the direction of the cross-section of lamellas and to obtain information, both about the period of the lamellar structure and its orientation.

In the case of the ideal orientation of the direction of lamellas along the preferential direction, the harmonics forming the pattern of the microphase segregation will produce two points on the Fourier image. The displacement of lamellas from the preferential direction results in the arcs on the Fourier images (Fig. 5).

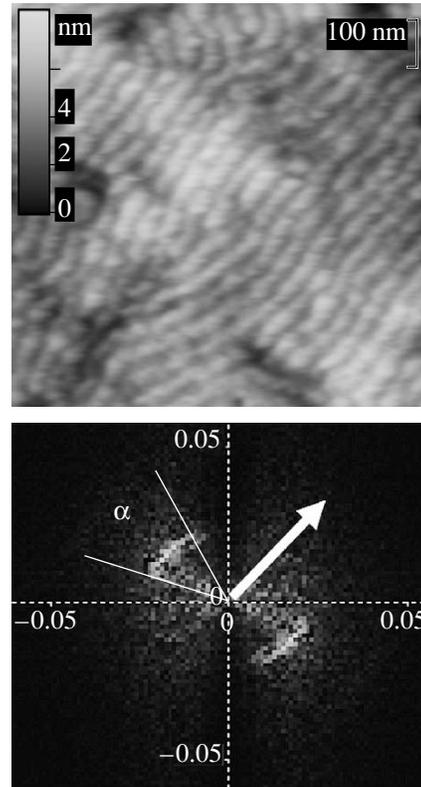


Fig. 5. AFM-image of the lamellar polystyrene-polymethylacrylate-polystyrene structure at [PS] : [PMA] = 1 : 1 and its Fourier image (bottom). The white arrow in the Fourier image shows the main direction of lamellas, α is the angle limiting arcs formed by the harmonics of the lamellar structure.

The analysis of the two-dimensional Fourier transform of the experimental images allows one to numerically characterize the lamellar structure of the microphase segregation to the greatest extent. The arc radius determines the period of the lamellar structure $D = 45 \pm 5$ nm. The symmetry axis of the arc positions determines the principal direction of the orientation of lamellas (Fig. 5). To numerically characterize the degree of the orientation of lamellas one can also introduce the ordering $L = D\pi/\alpha$ with α being the angle limiting the arcs in the Fourier image. In the ideal case of the strict orientation of lamellas, $\alpha \rightarrow 0$ and $L \rightarrow \infty$. At the large scale in real films the lamellar structure loses the preferential direction and arcs on the Fourier transform of the image transform into circumferences (Fig. 6a). In this case, the ordering L is the period of the lamellar structure D ($\alpha \rightarrow \pi$, $L \rightarrow D$).

Features of the Dynamic Scanning Regime

The AFM study of a surface in the dynamic scanning regime provides the surface topography $Z(X, Y)$, and phase-shift map $\Phi_{\Delta\phi}(X, Y)$ and amplitude deflection map $A_{\Delta A}(X, Y)$ of the tip oscillations.

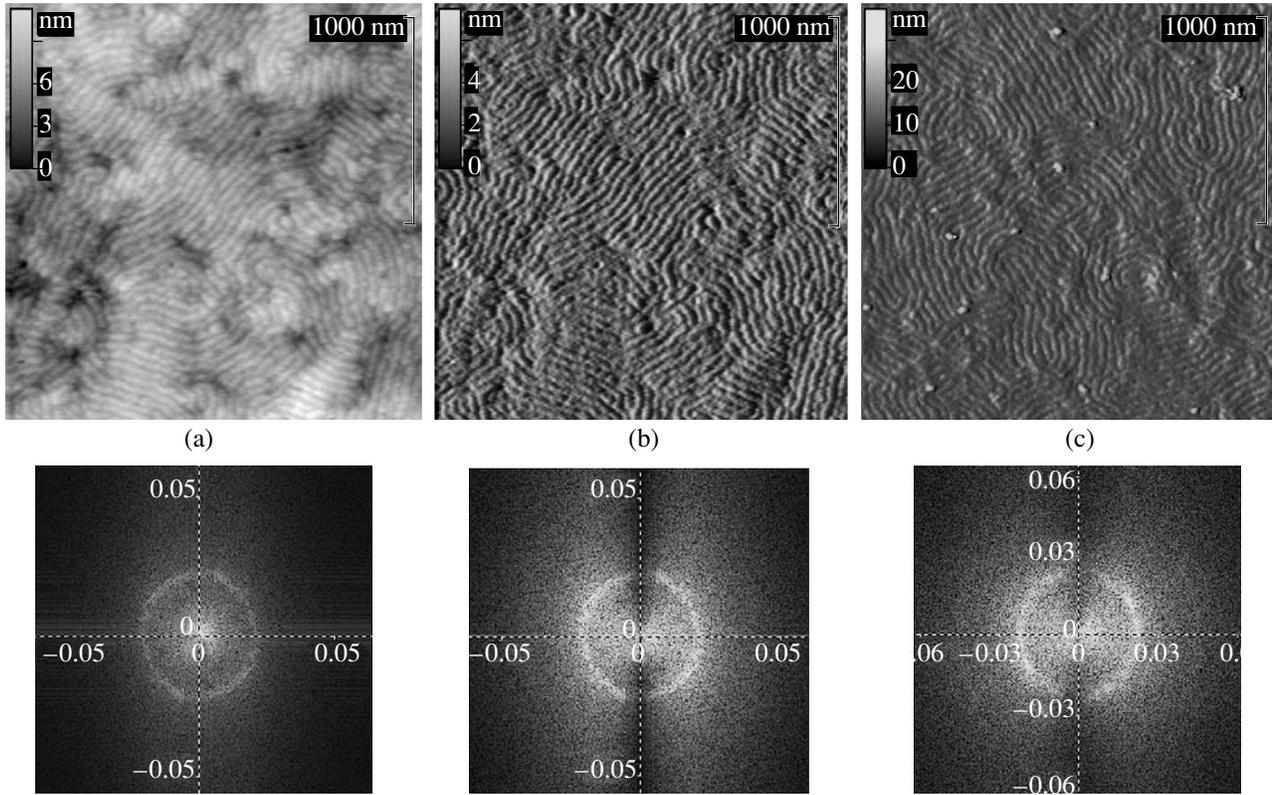


Fig. 6. AFM-image of the topography (a), amplitude deflection map (b) and phase shift map (c) of the lamellar polystyrene–poly-methylacrylate–polystyrene structure at [PS] : [PMA] = 1 : 1 and their Fourier images (bottom).

The $\Phi_{\Delta\varphi}(X, Y)$ map reflects the phase shift between the forced oscillations of a tip and the force causing the tip oscillations. In the absence of contact with a sample the tip oscillates in resonance and the phase shift is $\pi/2$. Upon tip contact with a sample the system shifts from the resonance, the additional elastic forces (the repulsion between the tip and the sample) reduce the oscillation amplitude and contribute to the phase shift. Thus, the $\Phi_{\Delta\varphi}(X, Y)$ reflects the balance of visco-elastic surface properties. The amplitude deflections $A_{\Delta A}(X, Y)$ reflect the changes of the actual amplitude of the tip oscillations from the working oscillation frequency kept by the feedback. One of the factors leading to these deflections is the sample deformation under the force impact of the tip during scanning. The larger the sample deformation, the larger the deflections from the working amplitude. Thus, the phase shift map $\Phi_{\Delta\varphi}(X, Y)$ and amplitude deflection map $A_{\Delta A}(X, Y)$ of the tip oscillations may reflect the structure of the microphase segregation due to different visco-elastic properties of phases.

The analysis of $\Phi_{\Delta\varphi}(X, Y)$ may be useful in the case where both phases have large moduli of elasticity, their deformations are small and the height segregation of the image topography region is problematic. The analysis of $A_{\Delta A}(X, Y)$ may be useful when the moduli of

elasticity of the phases are small and their values differ much.

The problem of choosing the level of phase segregation when analyzing the domain structure on the phase shift map $\Phi_{\Delta\varphi}(X, Y)$ and amplitude deflection map $A_{\Delta A}(X, Y)$ of the tip oscillations is simplified due to the absence of the influence of the microrelief of the sample under investigation on these images. Due to there being no influence of the microrelief, Fourier images $\Phi_{\Delta\varphi}(X, Y)$ and $A_{\Delta A}(X, Y)$ are highly contrasting, simplifying the lamellar structure analysis (Fig. 6c, d).

These algorithms were used to analyze the phase shift map $\Phi_{\Delta\varphi}(X, Y)$ and amplitude deflection map $A_{\Delta A}(X, Y)$ of the tip oscillations of the samples under investigation. The relevant results coincided with those obtained by treating topographical images.

Determination of the Film Thickness

To determine the film thickness, combined AFM studies in the contact and dynamic scanning regimes were used. The contact scanning regime with strong attractive forces was used to eliminate block-copolymer films from the scanning region. The elimination area was 1 by 1 μm . Then the sample area of 5 by 5 μm , including the area of the previous scanning in the contact regime was scanned. The height drop between the

film surface and the cleaned mica surface enabled the estimate of the film thickness. For films with different relative PS concentrations the thickness was $H = 50 \pm 20$ nm.

CONCLUSIONS

The present algorithms allow one to obtain the statistical characteristics of materials under investigation by treating large samplings providing the description of the general properties of these materials. Moreover, these algorithms for the analysis of the AFM images of block-copolymer films are universal and may be used in the software treatment of images in the automated regime. As a result, the time for obtaining statistical characteristics of materials under investigation is strongly reduced. The average size of PS domains ([PS] : [PMA] = 1 : 2) and the lamellar structure period ([PS] : [PMA] = 1 : 1) in the films of the polystyrene–polymethylacrylate–polystyrene triblock copolymer were determined by using these algorithms.

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