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Determination of Mechanical Characteristics of Surface of Block Copolymers by Atomic Force Microscopy Techniques

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Abstract—An instrumental technique is proposed for the determination of two-dimensional maps of the local Young modulus and the adhesion force of a polymer surface using atomic force microscopy. Data on the surface characteristics of a nanostructured polymer, the styrene–butadiene–styrene triblock copolymer, are presented. Problems concerning the calibration of the method are discussed.

INTRODUCTION

Modern commercial scanning-probe microscopes are equipped with all the necessary means for studying surface characteristics of various materials. In particular, these instruments provide for high space resolution up to the atomic level for atomically smooth surfaces (mica, silicon, graphite), allow characterization of the samples in both air and liquid media, and make it possible to study the mechanical surface characteristics.

EXPERIMENTAL

Materials and Methods

Atomic force microscopy (AFM) studies were performed on a Nanoscope IIIa commercial scanning probe microscope (Digital Instruments, Santa Barbara, United States). Recording of force–distance curves and contact-mode measurements were carried out using Olympus OMCL-TR400PSA-1 triangular probes (curvature radius of a probe tip was less than 20 nm, cantilever length of 200 μm, spring constant of 0.08 N/m, and silicon nitride Si_3N_4 as a probe material) and Veeco silicon nitride probes with a spring constant of 0.06 N/m. In the case of a tapping mode, Nanoworld silicon probes with a resonance frequency of 300 kHz and silicon nitride-coated MikroMasch NSC11 probes (Tallinn, Estonia) with a resonance frequency of 330 kHz were used. Data were processed using the Digital Instruments software, the FemtoScan program ("Advanced Technologies Center") [1], and the Nanoscale Explorer program (product by the Institute of Theoretical and Experimental Physics) for the analysis of the mechanical properties of the test material. To construct the maps of elastic surface characteristics, we collected a data array of 64×64 force curves, where each curve contained 64 points.

In this work, we studied a styrene–butadiene–styrene triblock copolymer with $M_w = 1 \times 10^5$ and a polydispersity of 1.03–1.04; this polymer was prepared by living anionic polymerization. Test specimens for scanning probe microscopy were prepared by film casting of a 4% copolymer solution in toluene onto freshly cleaved mica surfaces. The solvent evaporated at room temperature, thus facilitating sharp microphase separation (Fig. 1).

AFM Force–Distance Curves

In AFM measurements, the sample surface is scanned by a sharp probe (curvature radius is below 20 nm) mounted at the end of a cantilever, which is a spring beam with a length of 100–200 μm. During scanning runs, the force acting on the probe from the sample is defined by Hooke's law, $F = kX$, where k is the spring constant of the cantilever and X is the beam deflection [2]. The AFM force curve depicts the dependence of deflection X on distance Z between the cantilever and the sample surface, which is obtained for a given surface point at a given maximum force load (Fig. 2a). Knowing this dependence, one may find the force that is necessary for attaining a desired deformation and determine the elastic surface characteristics. For the first time, force–distance curves were used to study the mechanical properties of lysozyme molecules [3]. Further, such curves were used to examine dextrans [4], poly(tetrafluoroethylene) [5], and some other polymers [6, 7].

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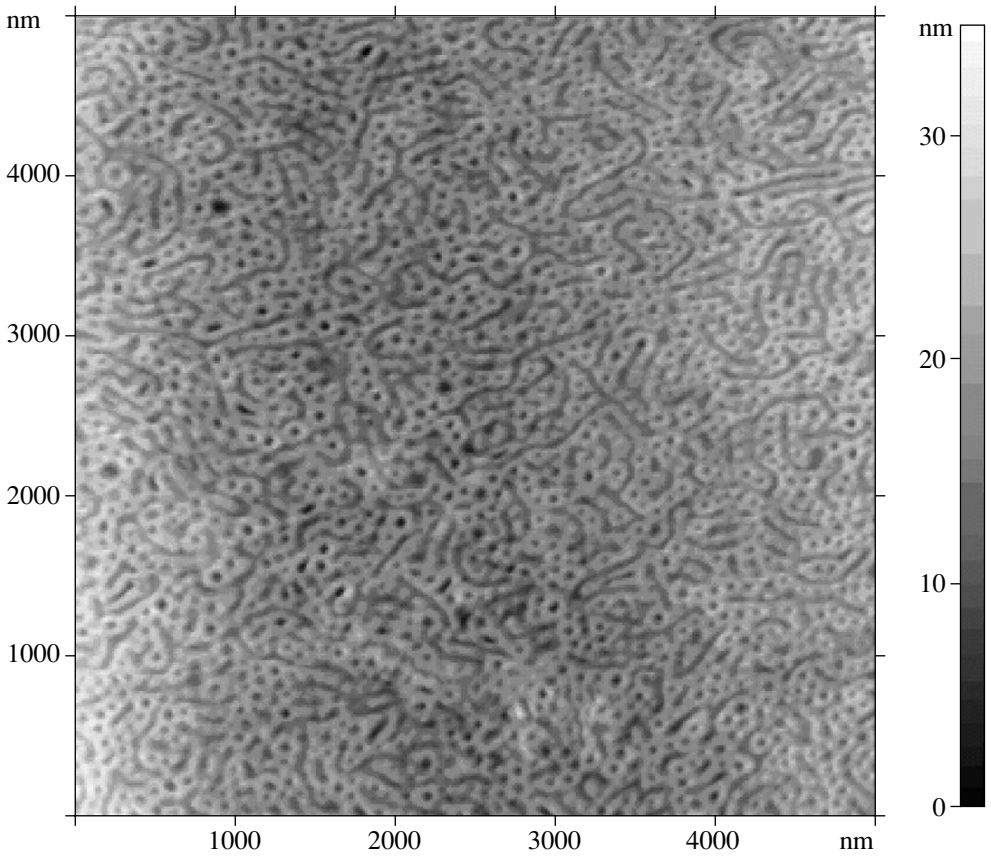

Fig. 1. Microphase separation in block copolymer (AFM image).

The force–distance measurement technique has certain limitations. In AFM studies, one cannot directly measure the distance between the sample and probe, and the estimation of zero distance presents a difficult task and leads to rather approximate values. Furthermore, for "soft" samples (samples with reduced mechanical rigidity), it is difficult to distinguish between the contribution of surface forces and sample deformation. When the elastic properties of thin films supported on a solid substrate are studied, overestimated values of the elastic modulus are obtained. This is due to the fact that the probe senses the underlying substrate surface [8].

By constructing force–distance curves for each surface point, it is possible to obtain a map of the distribution of mechanical characteristics over the sample surface. The construction of such maps is based on the initial data array, which involves the recording of force curves at various surface points. The NanoScale Explorer software allows relevant data arrays to be processed and the results to be displayed in a graphical form.

In constructing force curves, it is common practice to measure the value of cantilever deflection ΔZ_c on the sample position ΔZ_p with respect to the probe (Fig. 2a). For analyzing the mechanical characteristics, it is more convenient to pass to the dependence of ΔZ_c on $D = \Delta Z_p - \Delta Z_c$ (Fig. 2b). When a sample material is much softer than the probe material, D will describe the deformation of the sample by the action of the probe. The area under the $\Delta Z_c(D)$ curve represents the work A done by the sample under sample deformation.

On the assumption that sample deformation at a given pressure is elastic, the local Young modulus can be determined in terms of the Herz model [9, 10], which describes mechanical contact between two spherical objects. According to this model, the force acting on a sample is related to the sample deformation as follows:

$$F = B\sqrt{D^3}. \quad (1)$$

Here, $F = k\Delta Z_c$ and

$$B = \frac{1}{\left(\frac{3}{4}\frac{1-\sigma_p^2}{E}\right)\sqrt{\frac{1}{R_p}}},$$

where E is the local Young modulus, R_p is the probe curvature radius, and σ_p is the probe Poisson coefficient.

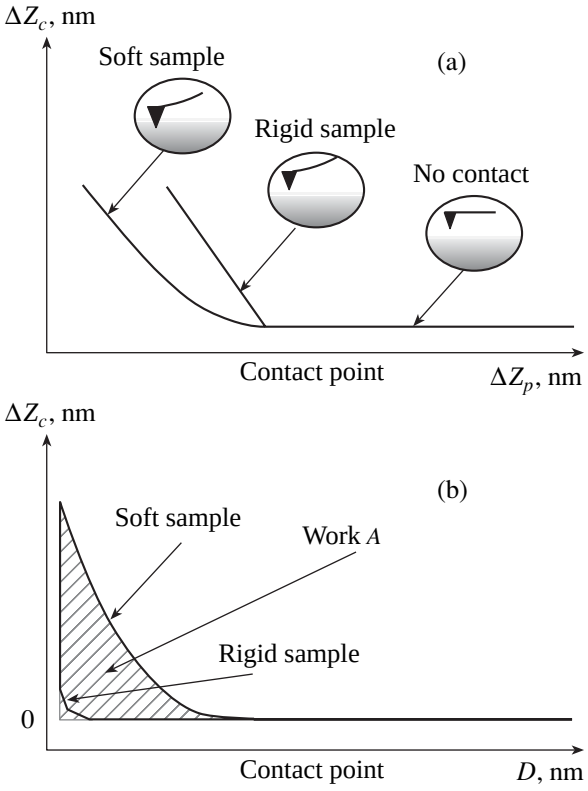

Fig. 2. AFM force–distance curves recorded during tip movement toward the surface for rigid and soft samples in the (a) $\Delta Z_c(\Delta Z_p)$ and (b) $\Delta Z_c(D)$, $D = \Delta Z_p - \Delta Z_c$ coordinates.

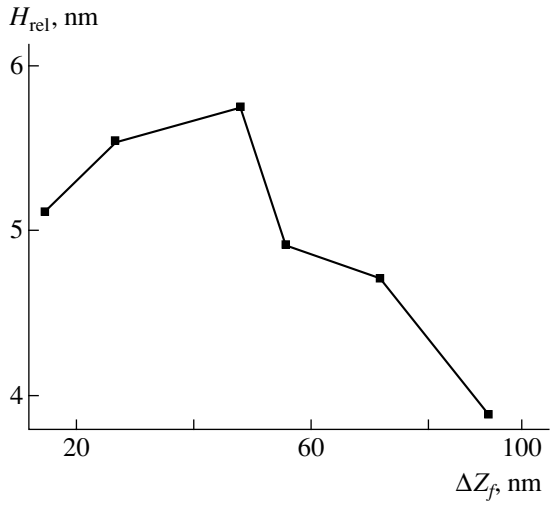

Fig. 3. Relative height of blocks in block copolymer H_{rel} vs. cantilever free oscillations ΔZ_f.

Approximation of a force curve recorded at a given point by relationship (1) using the least-squares method makes it possible to determine the ratio B/k and to find E. Therefore, the absolute Young modulus is calculated from the force curve according to the Herz model of elasticity. However, in most cases, the knowledge of the absolute values of elastic modulus is unnecessary and it is sufficient to have information on relative characteristics (for example, surface distribution of the modulus). This method is referred to as "force mapping" of the sample surface. The map of the surface distribution of A can be used for comparing the elastic characteristics of various surface regions. Indeed, the work done during the sample deformation by d is given by formula

$$A = \int_d^\infty F dD = \frac{2}{5} B \sqrt{d^5},$$

and the ratio between A at different arbitrary surface regions takes the following form:

$$\frac{A_1}{A_2} = \frac{\sqrt{d_1^5} E_1}{\sqrt{d_2^5} E_2} \quad (2)$$

(d_1, d_2, E_1, and E_2 stand for the deformation and the local Young moduli for two different surface regions, respectively). The $(d_1/d_2)^{5/2}$ value can be determined from the condition of equality of force loads at the above surface regions ($F_1 = F_2$) as

$$\frac{\sqrt{d_1^5}}{\sqrt{d_2^5}} = \frac{\sqrt[3]{E_2^5}}{\sqrt[3]{E_1^5}}.$$

Substituting this expression in Eq. (2), we arrive at the final form:

$$\frac{A_1}{A_2} = \frac{\sqrt[3]{E_2^2}}{\sqrt[3]{E_1^2}}. \quad (3)$$

Formula (3) can be used for comparing the elastic characteristics at different surface regions on the basis of the A values estimated from the AFM force curves in the $\Delta Z_c(D)$ coordinates. It should be noted that this approach (unlike the method for determining the absolute Young modulus) is free of drawbacks related to the uncertainty of the tip shape and contact point position (Fig. 2b).

RESULTS AND DISCUSSION

The AFM images of styrene–butadiene–styrene block copolymer films were obtained in both contact and tapping modes at various scanning parameters. Varied in the contact mode were the force load on the

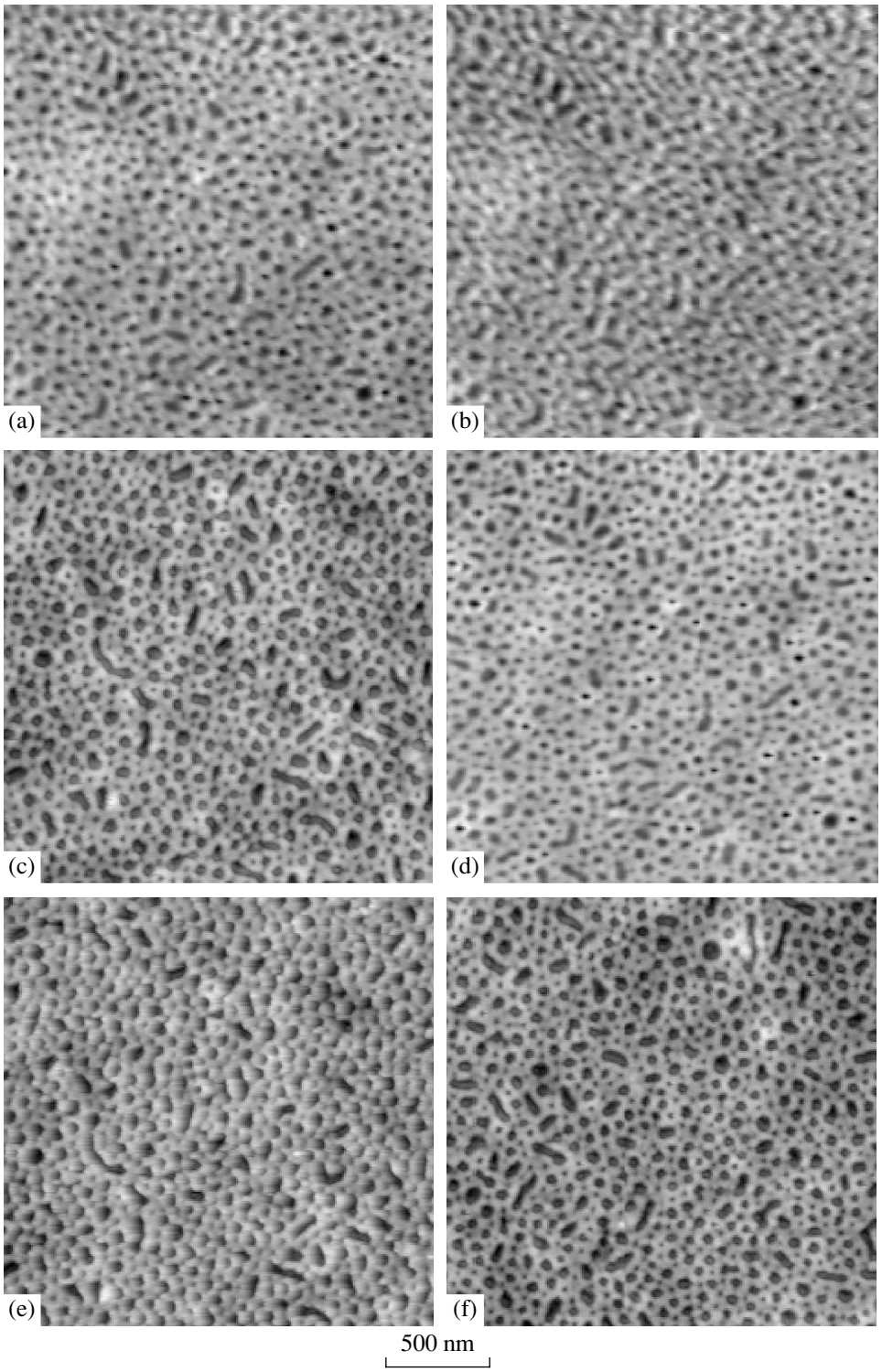

Fig. 4. AFM images of block copolymer in (a–c) resonance and (d–f) tapping modes at different applied forces. Amplitude of cantilever free oscillations is equal to (a) 15, (b) 48, and (c) 72 nm; applied force acting on the probe is (d) 4.5, (e) 16.9, and (f) 26.3 nN.

sample (from 4.2 to 29.4 nN) and, in the tapping mode, the amplitude of cantilever free oscillations (from 15 to 90 nm). As the load (or amplitude of free oscillations) is increased, the probe force acting on the sample surface increases. As the sample is composed of two different phases, its deformation should be different for the above two phases, and the difference between the heights of phases should increase with increasing the

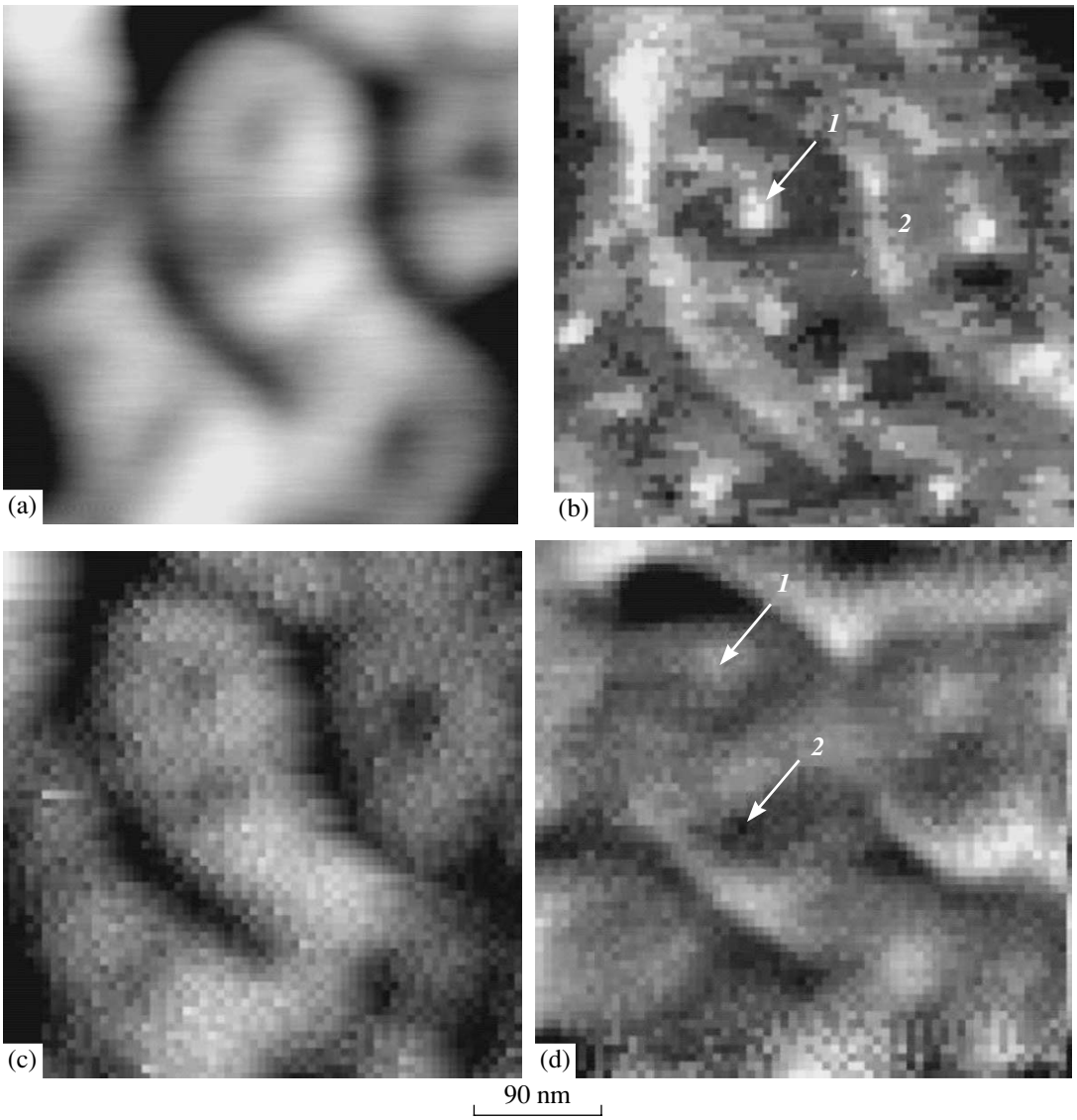

Fig. 5. Force mapping of styrene–butadiene–styrene copolymer film: (a) topography of film surface as measured in the contact mode; (b) distribution of adhesion forces in this surface region; (c) topography of film surface as obtained by force mapping; (d) work distribution during film surface deformation, the lighter regions corresponding to higher work values. Points *1* and *2* denote PB and PS phases, respectively.

force. In the resonance scanning regime, the expected dependence is observed only at low amplitudes of cantilever free oscillations (Fig. 3). At amplitudes below 20 nm (Fig. 4a) and above 70 nm (Fig. 4c), the quality of AFM images becomes poor. A free-oscillation amplitude of 48 nm turned out to be optimal for obtaining well-resolved and contrast images (Fig. 4b).

In the contact mode measurements, we could not reveal the expected dependence, which was due to the deterioration in image contrast at high applied forces (Figs. 4d–4f). To solve the problem of finding the local elastic characteristics of the block copolymer, we advanced another approach consisting in the force mapping of a film.

Using AFM force–distance curves, we studied the distribution of local elastic characteristics of the surface of styrene–butadiene–styrene copolymer films. In this case, the film surface was first scanned in the contact mode to record the corresponding topographic map. Then, the force curves were measured for a given surface region. Figure 5d shows the map of A distribution over a certain surface region of the film; Figs. 5a and 5c present the topographic images of the same regions recorded in the contact and tapping modes, respectively. Light and dark regions in the topographic map correspond to the inclusions of PS and PB phases, respectively. As is well seen, the image shown in Fig. 5d is inverted with respect to that in Fig. 5c (in Fig. 5d, the dark areas refer to more rigid regions).

Analyzing the force curves in the regions corresponding to PB inclusions (Fig. 6a) and averaging, we obtain the elastic modulus of the PB phase as $E = (2.1 \pm 0.4) \times 10^8$ Pa. For PS, $E = (1.0 \pm 0.3) \times 10^9$ Pa. In this case, the probe curvature radius is assumed to be equal to 10 nm, and the cantilever spring constant is 0.08 N/m.

While AFM force–distance curves measured during cantilever movement toward the surface allow the elastic characteristics of the test samples to be determined, those obtained during the retracting of the tip from the surface make it possible to measure the adhesion between the probe and the surface. This adhesion is complex in nature and is determined by the contributions of van-der-Waals interaction, electrostatic forces, surface tension, etc. [11, 12]. Its magnitude corresponds to the maximum negative cantilever deflection on the force curve (Fig. 6b). Figure 5b presents the map of the surface distribution of adhesion forces over the copolymer film surface. As is well seen, the adhesion is higher for PB (2.16 ± 0.05 nN) as compared with PS (1.71 ± 0.05 nN).

As regards the advanced procedure for determining the mechanical properties of polymer surfaces, the following essential remark should be made. The reported measurements and calculations of the absolute values of the Young modulus were performed with the allowance that the shape and radius of AFM probe are known. As is assumed in our calculations, the shape of the AFM tip is spherical, and its radius is equal to 10 nm. This assumption conforms to the parameters of various commercial cantilevers. It is for this type of cantilever that all the numerical data presented above (absolute values and errors) are valid. Evidently, different cantilevers have a certain scatter of their parameters (shape and dimensions), which may introduce a considerable error in measurement. We propose the following ways of solving this problem. Before an AFM experiment, cantilever parameters can be determined, for example, by means of an electron microscope. Many cantilevers are made of heavily doped silicon, and their examination does not require metal or carbon decoration of the probe tip. Therefore, one may observe the real, unperturbed probe geometry. However, this method is rather laborious and, hence, inconvenient.

The use of a reference sample with a given surface rigidity for the calibration measurements seems to be more expedient. In this case, an unknown probe radius will affect the attained spatial resolution, rather than the accuracy of measurements. When spatial resolution is not required, cantilevers with attached spherical particles made from various materials (quartz, PS, etc.), i.e., probes with known geometry, may be used.

There is another method for determining the probe geometry. This method consists in the reconstruction of probe geometry from the corresponding AFM images using deconvolution programs. A deconvolution algorithm is successfully implemented with the FemtoScan Online software [1]. However, this algorithm is not applicable to materials with reduced mechanical rigidity, including polymer materials.

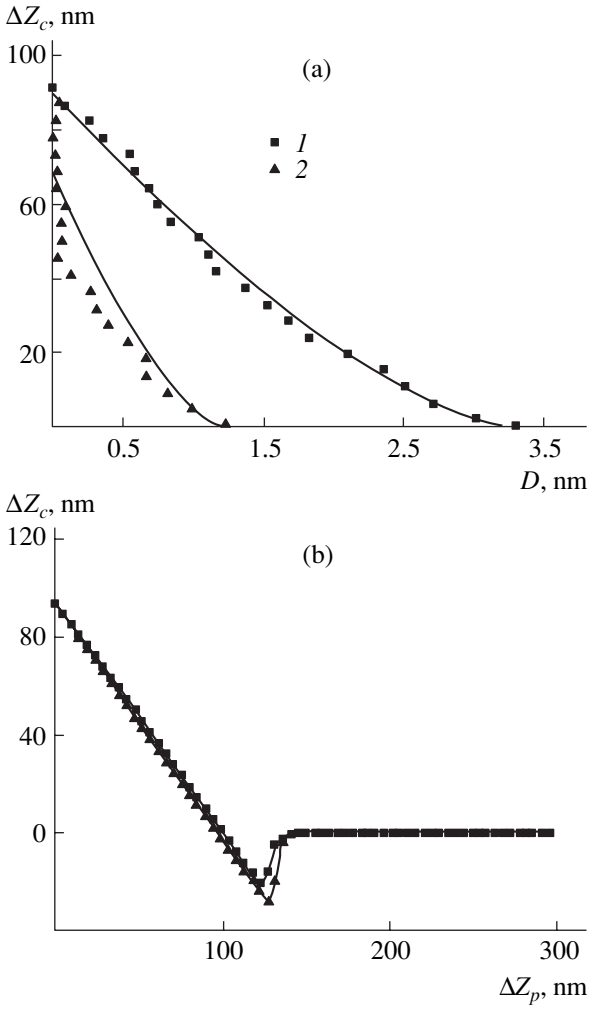

Fig. 6. Force–distance curves recorded at points *1* (PB) and (*2*) (PS) (shown in Fig. 5b) on the (a) forward and (b) back cantilever movement.

Another special feature of the presented method is that the calculation of the absolute Young modulus needs to employ model concepts (the Herz model or more accurate theories). Application of one or another theory can entail systematic errors. This difficulty can be eliminated by using a reference sample. The choice of the optimal reference sample remains an open question, and it needs to be solved in the future. What is important is that these problems can be solved with the use of the procedure developed in the present study.

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