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ORIGINAL CONTRIBUTION

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On the nanostructure of polymer layers formed by adsorption from binary and ternary solutions on a solid SiO_2: a combined adsorption and atomic force microscopy (AFM) study

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Abstract The thickness of nanolayers formed by adsorption from dilute and semi-dilute solutions on a solid SiO_2 surface has been estimated from adsorption isotherms and atomic force microscopy (AFM) measurements for polystyrene, poly(butyl methacrylate), and their mixtures. The thickness of the adsorption layers depends strongly on the adsorption conditions and is controlled by several features of the adsorbing entities. In a low-concentration regime of adsorption, the length of polymer chains and the nature of their interaction with the substrate are the most important factors controlling the adsorption process. Above the critical concentration C^*, macromolecular clusters (aggregates of several overlapping chains) are formed in a solution as a result of polymer chains self-assembly. Therefore, the final adsorption layer thickness is determined mainly by the size of the clusters in this concentrated regime of adsorption. We also demonstrate that in the case of polymer mixtures, the adsorption leads to formation of mosaic structures with alternation of the polymeric components in plane of the substrate and a characteristic domain size of approximately 200 nm for each of the components. AFM study reveals that the adsorbed layers are fractal structures whose fractal dimensions depend on the type of the polymer and the adsorption process. We demonstrate therefore that the structure of nanolayers of polymers and their mixtures on the solid surface can be regulated by variation of the adsorption conditions.

Keywords Nanolayers · Polymer adsorption from solutions · Fractal structures · Polymer mixtures · Self-assembling

Introduction

The process of static self-assembly can be defined as a process of spontaneous ordering in a closed thermodynamic system, which proceeds in the direction of minimization of its Gibbs free energy [1]. Such processes have been studied for many polymeric systems [2–5]. Those of particular interest are such self-assembly processes occurring in monolayers. Self-assembled monolayers are molecular assemblies that are formed by immersion of an appropriate substrate into a solution of a surfactant in an organic solvent [6].

While formation of self-assembled monolayers of small molecules was studied for several decades [6, 7], the processes of self-assembly of polymeric molecules that take place at the interface with solid by adsorption have attracted considerable attention only recently. Meanwhile, such processes are important both for basic research and practical applications as they lead to the formation of nanoscaled adsorption layers of a complicated structure.

Of a special interest are also fractal characteristics of adsorption layers, which depend on their structure. It is presently recognized that macromolecular coils are fractal objects. The fractal dimension D of macromolecular coils

in solution depends on the length of the Kuhn segment and on the nature of solvent being used [8, 9]. It is evident that the fractal properties of adsorption layers should be determined by the fractal dimensions of coils or macromolecular clusters formed in solution as a result of self-assembly process [10]. The formation of thin polymer layers at the interface with solid also plays an important role when producing layered nanocomposites using the exfoliation–adsorption method [11]. Formation of adsorption layers at the interface with solids is a unique technique of producing nanoscale films with a fine control of their thickness and structure [12]. These features of the adsorption process are related to one special characteristic of the polymer adsorption process that is the dependence of the properties and thickness of the adsorbed layer on the conformational state of polymer chains [13]. Depending on a solution regime (dilute, semi-dilute, concentrated one), the structure of the adsorption layer can be varied in a wide range. In a route of adsorption from a very dilute solution, macromolecules possess various conformational states at the adsorbent surface (so-called trains, loops, and tails). At higher concentration, the adsorption of macromolecular coils as a whole takes place. In the concentration region near the critical solution concentration C^*, the macromolecular clusters of fluctuation nature are formed as a result of self-assembly. These clusters can pass to the adsorbent surface and determine the structure of adsorption layers. Therefore, the adsorption from polymer solutions is a universal process of giving a great variety of the structures, formed by one and the same polymer. The dimensions of molecular coils are in the range of several tens of nanometers [14], whereas the cluster dimensions are in the order of 40–300 nm [15]. That is to say, these dimensions predetermine the formation of nanoscale adsorption layers.

Another interesting type of nanoscale adsorption layers may be produced by adsorption in mixed polymer systems, i.e., from a solution of two different polymeric components. In the latter case, the thermodynamic compatibility of two species in the solution exerts the essential influence both on the adsorption process and the structure of the final adsorption layer. The latter will be determined both by the ratio of polymer components in the layer and by their thermodynamic compatibility [13].

The aim of the present investigation is to establish the effect of the adsorption regime on the conditions of self-assembly of polymer molecules on the solid surface by adsorption from binary (polymer–solvent) and ternary (polymer–polymer–solvent) systems and to find out the features and fractal characteristics of the adsorption nanolayers.

Experimental

Two polymers, polystyrene (PS) and poly(butyl methacrylate) (PBMA), and their blends at the component ratio of 1:1 (*w*/*w*), were chosen for investigation. Their characteristics are the following: PBMA: $M_w=2.7\times10^5$, $M_w/M_n=1.9$ and PS: $M_w=2.2\times10^5$, $M_w/M_n=1.95$.

The experimental methods of the adsorption measurements were described elsewhere [16]. For the polymers and their mixtures, the critical concentration of overlapping C^* was determined from the data on intrinsic viscosity ($C^*_{PBMA}=0.95$ g/100 ml; $C^*_{PS}=1.1$ g/100 ml) [13]. The thickness of the adsorption layers was calculated from the experimental adsorption isotherms. To calculate the thickness of adsorption layers for the case of adsorption of the mixtures, the following equation was used:

$$\delta_{mix} = \left(A_1/\rho_1 + A_2/\rho_2\right)/S_{ads},$$

where ρ is the polymer density in the adsorption layer, A is adsorption of component 1 or 2, and S_{ads} is a square of adsorbent surface. It was accepted that the difference in the densities of a polymer in the adsorption layer and in the bulk is not essential.

Another method of estimation of the thickness and the structural features of the adsorption layer was based on the method of atomic force microscopy (AFM). The specimens for AFM measurements were prepared as follows: Thin plates of the adsorbent (glass or silicon substrates) were cleaned according to a standard procedure [17]. These substrates were immersed into polymer solution of a particular concentration below and above C^* for 6–8 h to achieve establishment of the adsorption equilibrium. Then, substrates were quickly removed from the solution, cleansed with pure solvent to remove the wetting layer of the polymer solution, and then dried in air. The basis for this procedure consists of the fact that desorption of polymers from the adsorbent surface is known to proceed extremely slow, if any. The special experiments have shown that after such procedure, the wetting layer of non-adsorbed polymer can be easily removed (as follows from the thickness measurements by AFM before and after cleansing).

The surface structure study and thickness determination of the adsorbed layers were done with the AFM. An Autoprobe CP (Thermomicroscopes, USA) machine was employed in two different modes of operation: in non-contact mode to study the structure and surface roughness and in force modulation mode (FMM) to study distribution of the stiffness on the surface of polymer films deposited from mixed polymer solutions. In the latter case, polymer sample was mounted on top of a piezotransducer, and sound waves of the frequency of 60 kHz were generated across the substrate with a function generator. An additional 2 kHz modulation in conjunction with a lock-in amplifier was used to detect a signal responsible for the elastic reaction of the sample surface to the sound waves propagating through the polymer film. The thickness of polymer films was also measured from AFM experiments. For this, scratches were intentionally produced on the

sample surface down to the substrate surface, and the thickness was then extracted from an AFM scan cross sections as a relative elevation of the film surface against the bottom of the scratch.

Surface root mean square roughness (RMS) of the films has been measured at various scan sizes (typically, 10×10, 5×5, and 1×1 μm^2) to perform surface fractal analysis as discussed below.

Results and discussions

The experimental data on adsorption of PS, PBMA, and their mixtures from solutions are given in Table 1. The values of the thickness of the adsorption layers for PS, PBMA, and their mixtures at various solution regimes are presented in Table 2. The average dimensions of the molecular clusters of polymers and their mixtures formed at the solution concentration above C^* [16] are given in Table 3. These values were found experimentally from the light scattering data [18]. Before, it was shown that in case of polymer adsorption at concentrations above C^*, the clusters are adsorbed along with individual coils [12]. Under such conditions of the adsorption, the value of the adsorption and the layer thickness should be higher whereas the fraction of the bound segments is lower. The fraction of the surface-bound segments is therefore an important characteristic of the polymer adsorption and has been determined by infrared spectroscopy technique according to well-established Fontana–Thomas method [19].

Figure 1 shows the dependence of the fraction of the surface-bound segments, p, for pure components and for the same components in the mixture (1:1 ratio of the components) on the equilibrium concentration [16]. As can be seen from the figure, the transition to the semi-dilute regime leads to the decrease of p as a result of simultaneous adsorption of molecular clusters.

Table 1 Concentration dependence of adsorption from binary and ternary systems

Binary systems				Ternary system PBMA–PS–CCl_4		
C_e, g/100 ml	Region of C	(PBMA–CCl_4) A_{PBMA}, g/g	PS–CCl_4 A_{PS}, g/g	C_e, g/100 ml	A_{PBMA}, g/g	A_{PS}, g/g
0.02	$C<C^*$	0.03	0.02	0.002	0.02	0.01
0.05		0.05	0.04	0.05	0.04	0.02
0.16		0.09	0.09	0.16	0.07	0.03
0.86	$C=C^*$	0.23	0.22	0.90	0.19	0.06
1.10		0.24	0.23	1.10	0.20	0.03
2.25	$C>C^*$	0.22	0.20	2.00	0.14	0.02
2.60		0.20	0.15	2.50	0.12	0.02

C_e Equilibrium solution concentration, A adsorption

Table 2 Concentration dependence of the adsorption layer thickness on silica under adsorption from binary and ternary systems

C_e, g/100 ml	Region of C	Binary systems		Ternary system (PBMA–PS–CCl_4)
		PBMA–CCl_4 δ, nm	PS–CCl_4 δ, nm	δ, nm
0.05	$C<C^*$	19	20	32
0.20		28	30	34
0.50		35	30	46
0.90	$C=C^*$	54	44	60
1.10		60	54	55
1.50	$C>C^*$	55	50	45
2.00		50	45	40

C_e Equilibrium solution concentration, δ adsorption layer thickness

The thickness of the adsorption layers was estimated in two different ways: The first [16] one is based on the data on the specific surface of an adsorbent and the amount of the polymer, which was adsorbed. The layer thickness is taken as a ratio of the volume of adsorbed polymer to the adsorbent surface. It was accepted that the density of a polymer in the surface layer was the same as in the bulk. For the adsorption from the mixed systems, the total thickness was taken as the ratio of the sum of volumes of each adsorbed polymer to the surface area. These calculations are based on the following considerations: It is known that the adsorption from very dilute solutions leads to a saturation of the adsorbent surface at very low concentration. Meanwhile, after such saturation, the following increase in solution concentration brings about further increase in adsorption value due to reorganization of the structure of the adsorption layer. Increasing solution concentration brings about the changing of the dimension of the adsorbed entities (separated coils, molecular cluster). We believe that all the processes of the reorganization in the adsorption layer proceed when the surface is already a fully covered, adsorbent surface. This assumption gives

Table 3 Dependence of PBMA and PS cluster dimensions on the solution concentration and components ratio obtained from the light scattering experiments

Binary system			Ternary system	
C, g/100 ml	PBMA–CCl_4 r_w, nm	PS–CCl_4 r_w, nm	C_{PBMA}/C_{PS}, g/100 ml	PBMA–PS–CCl_4 r_w, nm
0.50	40	35	0.50/3.00	30
0.75	60	45	0.75/2.75	30
1.00	70	50	1.00/2.50	25
1.50	90	55	1.50/2.00	20
2.00	140	60	2.50/1.00	20
2.50	190	65	2.75/0.75	25
3.00	250	70	3.00/0.50	30

r_w Cluster dimension

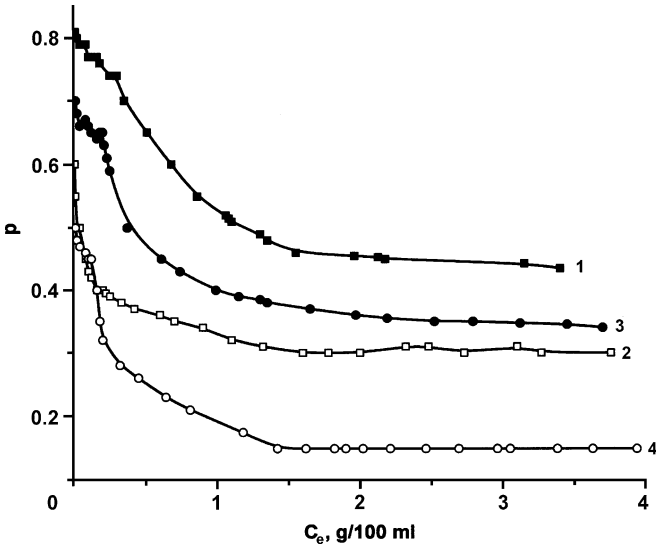

Fig. 1 Dependence of the fraction of bound segments, p, on the equilibrium concentration for PBMA (**1**) and PS (**2**) and for the same polymers PBMA (**3**) and PS (**4**) as components of the 1:1 mixture

basis for calculation of the thickness of the layer at any equilibrium concentration of the solution.

As is seen from Table 1, the values of adsorption both from binary and ternary solutions depend strongly on the concentration regime of the solution, being higher above C^*. These data demonstrate that the calculated thickness of the adsorption layer, δ, increases with concentration both for each individual polymer and for their mixture. All the values of the thickness are on average in the range of 20–50 nm. As follows from Tables 1 and 2 in case of solution concentration above C^*, the dimensions of the clusters increase with concentration for pure polymers whereas for the mixtures, they almost do not depend on concentration. The latter effect is the result of diminishing the dimensions of coils of both polymer components due to their incompatibility in solutions. The thickness of the layers formed from binary or ternary systems above C^* is approximately 2–2.5 times higher as compared with those formed at $C<C^*$ and is comparable with the polymer cluster dimensions. Based on the data given in Tables 2 and 3, one can draw a conclusion that the transition through C^* leads to the increase in the thickness of the adsorption layer. This effect is explained by adsorption of macromolecular clusters.

Presented results allow some speculations as for the self-assembly process of polymer layers by adsorption from polymer solutions. First of all, the layer thickness for pure polymers and their mixtures depends on the solution concentration. As the saturation of the surface by polymer adsorption usually takes place at a very low concentration, we may suppose that the increase in solution concentration is accompanied by the continuous reorganization of the adsorption layer, i.e., by changing the structure of adsorbing entities. That means that the self-assembly conditions are determined by the solution regime. Thus, variation of the thickness corresponds to a different structure of the adsorption layer. This is especially clearly seen for the adsorption layers obtained at concentrations above C^*. Higher thickness in this case seems to be connected exclusively to a transfer of clusters already existing in the polymer solution to the adsorbent surface. In the ternary systems, the clusters of both types of polymers may be present. The common clusters cannot be formed as the given pair of polymers is not thermodynamically compatible in solution. The data on the thickness of the layers in the ternary systems allow speculation that the effect of the incompatibility may play a role in the arrangement of the adsorbed molecules and clusters in this case. The incompatibility implies that the surface of adsorbent has a mosaic structure with alternation of the regions formed by each polymer component.

Now let us consider the data on the structure of the adsorbed layers obtained using AFM method. Table 4 shows the thickness and the surface roughness values measured by AFM for adsorbed polymer films from binary and ternary systems. The thickness of the adsorbed films is about 20 nm for polymer films deposited from diluted solutions ($C<C^*$) but increases to higher values in case of concentrated solutions. Even higher values of the thickness (δ) are registered for mixed films [15].

Figure 2 shows typical AFM images of PS and PBMA films adsorbed from diluted and concentrated solutions. The films are smooth and almost featureless in accordance to their amorphous nature. The observed granular structure

Table 4 AFM results for the adsorption layer thickness and RMS roughness measured at various scan sizes for adsorbed polymer layers on SiO_2

Polymer system	$C<C^*$				$C>C^*$			
	RMS roughness, nm			δ, nm	RMS roughness, nm			δ, nm
	10×10 μm^2	5×5 μm^2	1×1 μm^2		10×10 μm^2	5×5 μm^2	1×1 μm^2	
PS	4.4	4.1	3.1	25	3.5	0.5	0.3	59
PBMA	2.6	1.8	0.4	22	3.9	2.6	1.5	35
PS/PBMA=1/1	3.9	0.7	0.6	50–170	1.0	0.6	0.2	~1,000
Si substrate	0.7	0.5	0.4	N/A	0.7	0.5	0.4	N/A

δ Adsorption layer thickness

on the scale of several nanometers is typical for amorphous polymers [20]. Surface RMS roughness is in the order of a few nanometers for 10×10 μm^2 scan size (Table 4) and is just slightly exceeding the roughness of the substrates being used for polymer adsorption. On contrary to individual polymers, the mixed films possess more developed surface. AFM and FMM images of mixed polymer films (the initial ratio of the components in the polymer solution PS:PBMA=1:1) are presented in Fig. 3. The vertical scale of the topography image is represented in angstroms while on FMM image, it is given in arbitrary units (voltage measured by the AFM photodetector). Higher contrast and resolution are typical for FMM images. As follows from the images consideration, ternary polymer systems form heterogeneous films during adsorption on the solid substrate. These films are characterized with a mosaic structure constituted with nanosized domains of presumably individual polymers. The higher contrast is due to the difference in stiffness for polymer components [21]. PS component with glass-transition temperature, T_g=95°C, is slightly stiffer than PBMA (with T_g of about 60°C) providing better media for sound waves propagation and therefore appears brighter in FMM images. One can estimate from the images the average size of individual domains as being equal to about 200 nm. This value is consistent with the cluster size formed in concentration solution regime (see Table 3). Similar mosaic structure with alternation of the components is typical for the morphology of blends of incompatible polymers. However, the mosaic structure in adsorption polymer nanolayers formed by two polymers is observed and reported for the first time.

It is generally accepted now that amorphous polymers can be considered as fractals. In accordance to such approach, they are characterized with a special and important structural parameter, the fractal dimension, D_f, which can be introduced through the following relationship between the mass, M, (or some other macroscopic physical properties of the system) and the scale of observation, L:

$$M(L) \propto L^{D_f}.$$

Thin polymer films formed from the solution state are fractal objects [21]. Therefore, interesting additional information on the structure of the adsorbed polymer layers can be extracted from a fractal analysis of their surfaces.

The fractal analysis based on the AFM data can be done in our case through a Hurst approach [21]. In accordance to the Hurst equation [22], an average surface roughness is related to the lateral scale on the sample surface as:

$$<|h(x_i)-h(x_j)|>_{|x_i-x_j|=x} \sim x^{(d-D)}$$

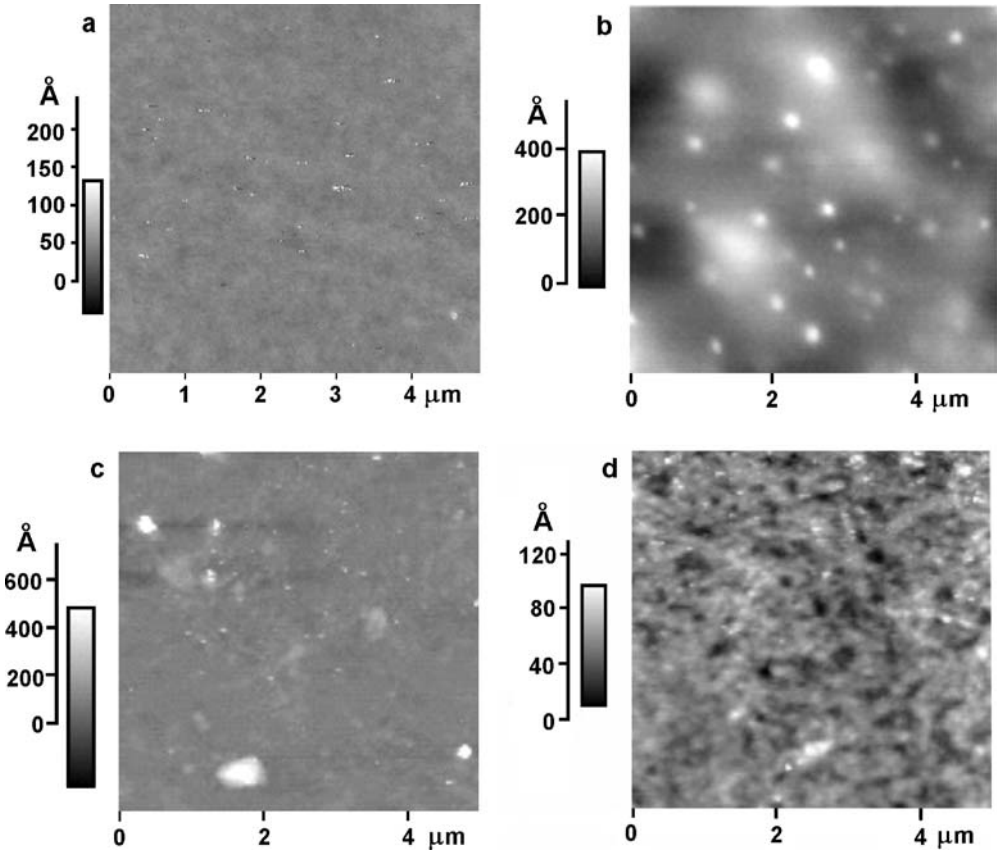

Fig. 2 AFM images of adsorbed polymer films of PS ($C<C^*$) (**a**), PS ($C>C^*$) (**b**), PBMA ($C<C^*$) (**c**), and PBMA ($C>C^*$) (**d**)

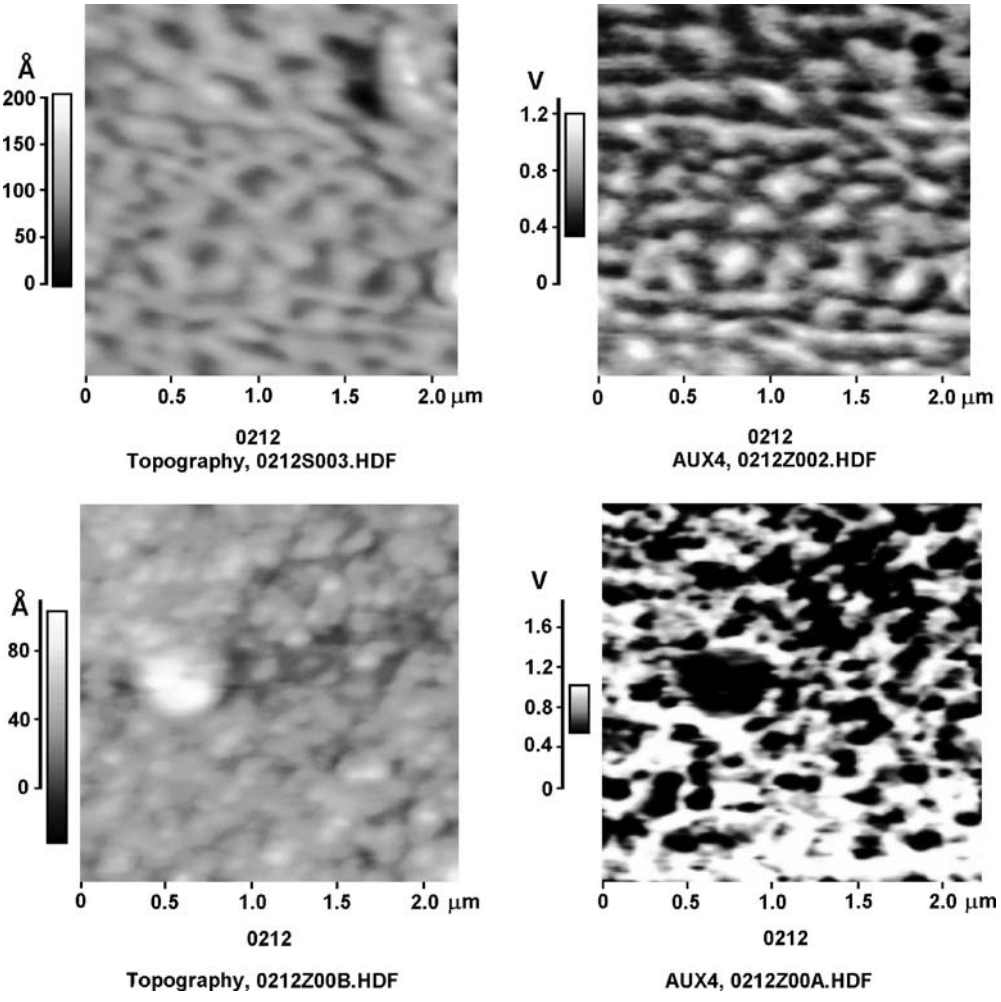

Fig. 3 AFM images of topography (*left*) and FMM images (*right*) of the surface stiffness distribution for PS/PBMA=1/1 films adsorbed on Si at $C<C^*$ (*top images*) and $C>C^*$ (*bottom images*)

where $h(x_i)$ and $h(x_j)$ are relative attitudes for two arbitrary points on the surface located on a distance x apart, sign $< >$ means averaging over different points on the surface, d is dimension of space (3 in our case), and D is a fractal dimension of the surface of interest.

We applied such approach to calculate D for the adsorbed polymer films considering x as different scan sizes of AFM images being used for surface RMS roughness estimation.

A different behavior was revealed for PS and PBMA. Thin PS films deposited from very dilute solutions possessed the fractal dimension of 2.85 which decreased to a value of 2.04 with an increase of the solution concentration over C^*. In contrast, PBMA samples were characterized with lower D for the case of the diluted solution deposition (2.17), but this value increased to 2.6 for high solution concentration. Mixed PS/PBMA films revealed some intermediate fractal dimension of 2.3, which was eventually independent on the solution concentration regime.

The above consideration of the fractal dimension changes with concentration supports the discussed features of the conformation behavior of polymer chains during adsorption. PS chains can form special conformational features (loops and mushrooms) in a regime of dilute solution adsorption, which are then replaced with ordinary random coil conformation of entangled polymer chains under increase of the concentration. PBMA as a polymer, which is characterized with chains having more "bulky" substitutes, cannot adopt so closely packed conformation as PS. At high concentration regime of adsorption, this leads to formation of a film with more defect (more developed) morphology and, therefore, higher fractal dimension D (more intrusions into the third dimension). Mixed polymer films should then possess the morphology and fractal dimensions in-between of those of the individual components as really revealed from our AFM data.

Conclusions

The thickness of the adsorption layers formed by adsorption of polymers and their mixtures on the solid surface depends strongly on the adsorption conditions (dilute or semi-dilute solution regime). The structural features of the adsorbed polymer films are conditioned by various possible conformational states of the adsorbing entities: isolated coils for dilute solutions or macromolecular clusters for semi-dilute solution. Above the critical concentration of the coils overlapping, the macromolecular clusters are formed and their adsorption brings higher thickness of adsorption layers. The estimations of this thickness were made independently from the adsorption isotherms and the atomic force microscopy images agree rather satisfactorily.

As follows from the AFM data, the adsorbed polymer layers have a fractal nature with fractal dimensions being dependent on the adsorption conditions.

The adsorption layers formed under adsorption from solution of the mixture of two polymers have a mosaic structure with characteristic domain size of ~200 nm. Such structural peculiarities appear as a result of thermodynamic incompatibility of the two polymer components in the solution state, which is then preserved under their adsorption to a solid interface and formation of the film. It should be noted that the dependence of the adsorption layer properties on the adsorption conditions (i.e., on the route of the process) testifies thermodynamically nonequilibrium state of the final polymer film. Nevertheless, formation of nanoscale polymer layers on solid surfaces of interest by the adsorption process allows fine control of their thickness and structural characteristics depending on the adsorption conditions.

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