

# Peculiarities of local chemical structure of PS<sub>39</sub>PEO<sub>61</sub> block-copolymer surface studied by means of AFM and XPS

S.G. Bystrov, A.A. Shakov

Physicotechnical Institute UrB RAS, 132 Kirov St., Izhevsk, Russia, 426001. Tel. (3412)212655, Fax.(3412)250614; e-mail: [less@fti.udm.ru](mailto:less@fti.udm.ru)

## Introduction

Due to the unique characteristics of block copolymers, which are determined by the features of their supramolecular structure, they have always been in the focus of the researches attention [1]. However, a number of questions have remained undetermined, namely, the location of blocks on the polymer surface, the degree of the surface homogeneity, and the changes in the local chemical structure of the block copolymer surface during its thermal treatment. In an attempt to solve these problems we have used the X-ray photoelectron spectroscopy (XPS) and chemical force microscopy (CFM). The task imposed on CFM is to enhance chemical contrast on AFM-images and obtain information on the surface chemical structure of the sample under study. It is well known that not only surface topography contributes into AFM-images, but also force interactions between the tip and the surface [2]. Hence, by measuring the adhesion forces between the tip and the sample surface in different areas, it is possible to obtain a map of the distribution of chemical inhomogeneities across the sample surface.

## Experimental

Block copolymer PS<sub>39</sub>PEO<sub>61</sub> with molecular weight Mn=46 000, Mw/Mn=1.2 was investigated. The samples were prepared by applying copolymer solution in chloroform onto a pyroceram substrate, followed by drying at room temperature for 48 hours and additional drying in vacuum at room temperature for 72 hours until constant mass was reached. Part of the samples thus prepared was annealed in vacuum at 80 and 130°C for 24 hours. Probe microscope P47 from NT-MDT (Russia) was used for AFM-investigations. Silicon probes with tip curvature of no more than 10 nm were obtained from the same manufacturer. Spring constant of cantilevers was 0.1 N/m on average and was additionally specified for each probe. All the measurements were taken in air. The probe-to-sample surface adhesion was measured using force-distance curves. The data obtained were processed using NT-MDT computer software. XP-spectra were taken with the electron spectrometer ES 2401. The methods used for measurements and data processing, were presented in [3].

## Results and discussion

**Table.** XPS-data for PS<sub>39</sub>PEO<sub>61</sub> - initial and annealed at different temperatures

Bulk composition of block copolymer (mol.%PS)	Surface composition of block copolymer according to XPS (mol.%PS)		
	Initial	Annealed at 80 °C	Annealed at 130 °C
39	11	82	82

The data presented suggest that the surface of the initial block copolymer is enriched in PEO-blocks. Such a structure can result from quick evaporation of a solvent. In this case the block copolymer surface can “freeze” in its nonequilibrium state. After annealing at 80°C (temperature higher than melting temperature for PEO) PEO-blocks drift into the bulk, with the new surface structure including mainly PS-blocks. Such a change in surface composition of the material under study results from a difference between surface energies of PS- and PEO-blocks (36 and 44 dyne/cm) and is in accordance with literature [4]. No changes in XP-spectra were observed after annealing of the samples at 130°C (temperature higher than glass-transition temperature of PS).

It was initially necessary to determine if standard silicon probes possessed selectivity. To do this interaction forces between the probe and surfaces with different chemical natures were measured. Namely, we measured the adhesive force between the tip and non-polar (PS) and polar (PMMA) surfaces in different media. The results obtained show that a standard silicon probe is selective enough in regard to surfaces with different chemical nature and can well be used in XPS-measurements.

AFM-images taken from the initial block copolymer and that annealed at 80°C indicate a lamellar structure of the surface. This is especially clearly seen at the images taken in friction forces. Lateral sizes of lamellas in the initial sample are 40 nm on average, the height of lamellas is in the order of 10 nm. After annealing lamellas become larger (with their width equal to 80 nm). Also, height differences on the image increase to 30 nm. These changes are apparently caused by restructuring of the block copolymer supramolecular structure in the process of annealing.

Based on XPS-results and taking into account that the average thickness of a layer analyzed by means of XPS for such samples is in the order of 5 nm [2], two ways of blocks location in the surface layer under analysis can be assumed. First, the sample surface only can consist of blocks with similar chemical composition. Another layer, located under the top one, would consist of blocks of the other type. In this case the thickness of these layers would be proportional to the production of molar concentration and molar volume of this type of blocks. Second, the surface can have island structure, when different blocks are simultaneously present on the surface. Note here that the areas of block islands can vary in a wide range. Molar volumes of monomer PS and PEO would relate as 2.6:1 (99 cm<sup>3</sup>/mole и 38.9 cm<sup>3</sup>/mole, respectively). In this case, based on estimation calculations, the area of PS-islands on the surface of the initial block copolymer can vary from 27% of the total surface area (if PS-blocks are located as vertical bars) to 100% (if PS would be located as a surface monolayer). In case of the sample annealed at 80°C the area of PEO-islands can vary from 7 to 100% (two surface monolayers).

On Fig. a) and b) given is the AFM-image of the initial block copolymer surface, measured in topography mode and a map of adhesion forces between the tip and the sample surface. The image was taken with a resolution of 64x64 pixels. The adhesion force was measured in every point. Darker spots correspond to areas with larger adhesion. We found earlier that the adhesion of a silicon tip to polar surfaces was larger than to non-polar ones. Therefore, the surface areas with PS-blocks will look lighter on the map of adhesion forces than those including PEO-blocks.

According to measurements the adhesion force for the given sample varied from 34 nN to 60 nN. Such a limit considerably increases the error ( $\pm 1,7$  nN), which evidences the presence of different kinds of blocks on the surface. On Fig. b) displayed are the areas of the initial block copolymer surface (light areas). It is in these areas that PS-blocks can most probably be present. The marked areas make up in the order of 24% of the total image area, which is in correspondence with the calculated minimum PS-blocks concentration on the surface.

Similar measurements were taken with the block copolymer annealed at 80°C (Fig.c,d). The adhesion force values for this sample are in the range of 31 to 55 nN, which also indicates the presence of blocks with different chemical nature on the surface. On Fig.d marked are the regions with minimum adhesion force between the tip and the surface (dark areas) with the area of 8% of the total image area. In all probability it is in these surface regions that PEO-blocks are located.

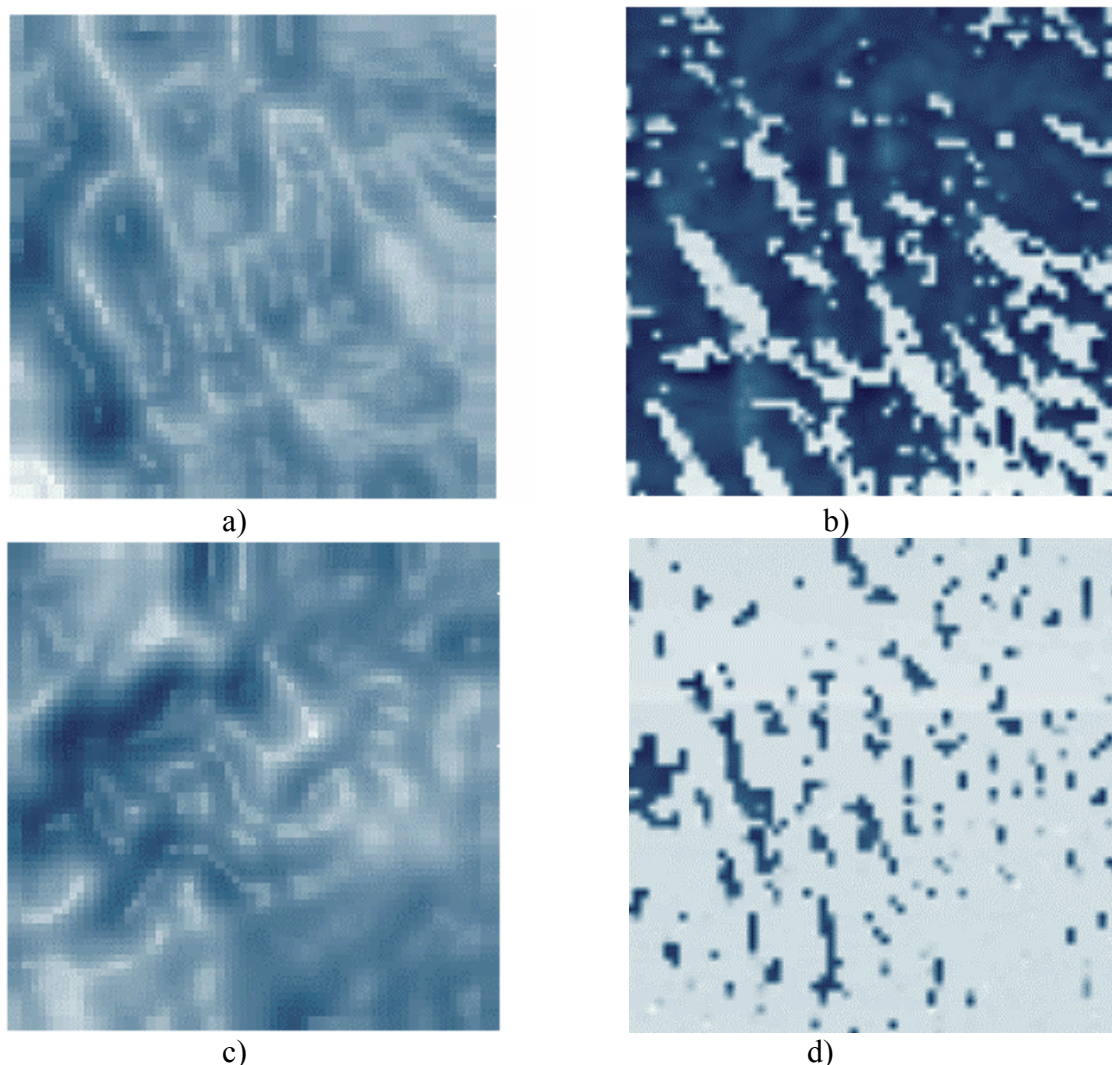
### Conclusion

It has been shown that standard silicon probes are selective by adhesive forces to sample surfaces with different chemical structure. By means of XPS it has been stated that the surface layer of the initial sample is rich in PEO-blocks. After annealing at 80°C the surface layer becomes rich in PS-blocks. AFM has depicted folded surface topography of sample surfaces.

The folds are apparently formed by lamellas of certain blocks. The data on the sizes of these species have also been obtained. CFM has shown that the sample surfaces are inhomogeneous. Also, surface distribution of different kinds of blocks has been determined.

#### Acknowledgements

The authors are grateful to V.V. Shilov for the samples and the help in research task setting. The paper has been supported by the RFFI (project №01-03-96461).



**Fig.** AFM-images of PS<sub>39</sub>PEO<sub>61</sub> surface (contact mode, image size 1000x1000 nm, resolution 64x64 pixels).

a) surface topography of initial block copolymer; Z-direction height difference is 50 nm;

b) map of force distribution when tip adheres to initial sample surface. Z-direction adhesive force varies from 34 nN (light areas) to 60 nN (dark areas).

c) surface topography of block copolymer after annealing at 80°C; Z-direction height difference is 32 nm;

d) map of force distribution when tip adheres to sample surface after annealing at 80°C. Z-direction adhesive force varies from 31 nN (light areas) to 55 nN (dark areas).

1. L.Zhu, S.Z.D.Cheng, B.H.Calhoun, Q.Ge, R.P.Quirk, E.L.Thomas, B.S.Hsiao, F.Yeh, B.Lotz. Polymer 42 (2001) 5829-5839.
2. S.N.Magonov, Myung-Hwan Whangbo. Surface analysis with STM and AFM. VCH, Weinheim (1996).
3. S.S.Mikhailova, O.M.Mikhailik, A.M.Dorfman, V.I.Povstugar// SIA, v29, 519-523 (2000).
4. K. Ishizu. Polym-Plast. Technol. Eng., 28(5&6), 601-630 (1989)