Diblock copolymer ultrathin films studied by high resolution electron energy loss spectroscopy

A.M. Botelho do Rego, O. Pellegrino *, J.G. Martinho, J. Lopes da Silva

Centro de Química-Física Molecular, Instituto Superior Técnico Avenida Rovisco Pais, 1049-001 Lisboa, Portugal

Abstract

Surface segregation of polymers forming thin films is relevant in several industrial applications. This paper studies the influence of preparation parameters on the surface composition of poly(ethylene oxide)–polystyrene diblock copolymer ultrathin films. Silicon wafers were used as substrates. The film preparation method (spin coating vs. casting followed by solvent evaporation), solvent (THF vs. CCl₄), annealing vs. non-annealing and the substrate nature (native silicon oxide vs. silanized substrate) were analyzed. High resolution electron energy spectroscopy in vibrational energy loss range was used to estimate the extreme surface composition. Generally, THF favors the surface segregation of polystyrene. After annealing, whatever the preparation method, the polystyrene preferentially segregates at the surface without forming a pure overlayer. These results were compared with the surface compositions calculated from X-ray photoelectron spectroscopy spectra of the films. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Electron energy loss spectroscopy (EELS); X-ray photoelectron spectroscopy; Surface segregation

1. Introduction

Protein-resistant surfaces are successfully produced by combining PEO block and hydrophobic polymer segments, such as PS. Surfaces composition of PS–PEO has been the subject of several studies [1]. More precisely, surface PS segregation has been evidenced by X-ray photoelectron spectroscopy (XPS) [2–4] and more recently by high resolution electron energy loss spectroscopy (HR-EELS) [5]. The segregation was explained by the lower surface tension of the PS block and it is enhanced by good solvents for PS in the weak segregation limit [1]. Surface studies of other copolymer films also demonstrated the role of annealing [4,6] and the substrate [7,8]. In a previous paper [5], we studied by HREELS the surface composition of PS–PEO diblock copolymer films prepared from tetrahydrofuran (THF) and tetra-chloromethane (CCl₄) polymer solutions upon a hydroxylated native silica surface. HREELS is particularly adequate for studying segregation effects in polymer surfaces [9–12] since it probes depths of analysis of the order of magnitude of a chemical bond length [13] in experimental conditions of impact mechanism (high primary energies and off-specular conditions). Furthermore, the FWHM of the elastic peak (i.e. the spectral resolution) is a decreasing function of the surface roughness for a given set of lenses electrodes voltages [14]. We found [5] that, normalizing pure PS
and PEO copolymer HREELS spectra to the background, instead of the elastic peak, the copolymer spectrum can be obtained from a combination of the pure polymer spectra multiplied by factors varying between 0 and 1 and whose sum was 1. The normalization to the background was already proved by Ibach and Mills [15] to work on the quantitative comparison of spectra obtained in different spectrometers. On the other hand, the assumption that the multiplying factors measured the fractions of the monomers of each polymer at the extreme surface needs to be checked. In this work, this was attempted by XPS on films with smooth surfaces. However, the results are not directly comparable since XPS probes a much larger depth than HREELS [16] and the probable contamination of the samples has different consequences on the estimated surface compositions. Nevertheless, the main conclusions obtained by both techniques are identical, in spite of the differences in the numerical results.

2. Experimental

The synthesis and characterization of the PS–PEO block-copolymer was described in detail elsewhere [17–19]. The weight-average molar weight of the copolymer is \( M_w = 22150 \) (\( M_w/M_n = 1.07 \)), with block weight-average molar masses of \( M_w = 3800 \) and \( M_n = 18350 \), for PS and PEO, respectively. \( \text{CCl}_4 \) and THF both from Merck (Uvasol, spectroscopic grade) were used as received. Silicon substrates with surface silanol groups (hydroxilated substrates) were prepared by the method described before [20]. To prepare the silanized substrates, the surface silanols were removed by dipping the hydroxylated samples into a 0.05 M ethyl–dimethyl–chlorosilane solution during 30 min. Surface hydroxyl groups were controlled by the presence of the hydroxyl stretching vibration band (~3650 cm\(^{-1}\)) in the HREELS spectra. Solvent-cast and spin-coated films were prepared from copolymer solutions of concentration 0.48 g l\(^{-1}\). This concentration was required for preparing cast films ~400 A thick on squared 1.2 \( \times \) 1.2 cm\(^2\) slabs. The films were annealed at 100°C during 24 h under 10\(^{-1}\) mbar.

The HREELS spectra were recorded using a Kesmodel LK 2000R spectrometer in an UHV chamber (\( P < 10^{-9} \) mbar). The incident angle was 60° and the angle of analysis 30° (off-specular conditions). Incident and backscattered electron directions are measured relative to the normal of the sample surface. Experimental resolution taken as FWHM of the elastic peak varies from 13 to ~25 meV, showing a marked dependence on the film preparation. Sweeping steps were about 1 meV. Angle-resolved X-ray photoelectron spectroscopy (ARXPS) analysis was performed with a Kratos XSAM800 equipment, using an unmonochromated MgKα radiation (\( h\nu = 1253.7 \) eV), operating at 13 kV and 10 mA under a pressure lower than 10\(^{-8}\) mbar. Detailed scans of Si 2p, C 1s and O 1s regions were obtained with 10 eV pass energy. Emission angles are relative to the normal to the sample surface. After binding energy correction of the C–C component of the C 1s region to 285.0 eV, a Shirley base line was subtracted. The curve fitting of the C 1s line shapes and the corresponding quantification were performed on a Sun SPARC station 4 using Vision software (Kratos). Voigt profiles were used in the fitting procedure.

The HREELS spectra were recorded without charge compensation, as complete spectra (i.e. for energy loss, \( \Delta E \), ranging from 0 to the primary energy, \( E_p \), 5 eV) exhibit stationary cutoffs near \( \Delta E \approx E_p \), showing that films were thin enough to prevent charge effects [5]. No irradiation damage was noticed in the samples during the time needed to record a HREELS spectrum. Charge shifts on XPS spectra were corrected by setting the C 1s peak at the 285.0 eV binding energy. No X-ray induced sample degradation was noticed during the ARXPS analysis and no electron flood gun was necessary to offset charging.

3. Results

Vibrational electron energy loss spectra (between 0 and 4000 cm\(^{-1}\)) of films prepared upon
silanized substrates from CCl₄ solutions for a primary energy of 5 eV are displayed in Fig. 1.

The arrows stand for the two characteristic bands of the polystyrene at 720 and 3050 cm⁻¹ [5]. The 720 cm⁻¹ band corresponds to the aromatic CH out-of-plane deformation, while the 3050 cm⁻¹ band corresponds to the aromatic CH stretching. In the region from 700 to 1800 cm⁻¹, the HREELS spectrum of PEO shows a single broad band peaking at 1137 cm⁻¹ (assigned to stretching modes in the chain (C–C and C–O) and deformation modes H–C–H, H–C–O, O–C–C and C–O–C), while both PS and contaminant hydrocarbons show a structured band with several peaks, in the same region. In the case of PEO, in the tail of this last band, a broad band between 2000 and 2700 cm⁻¹ (assigned to multiple excitation of modes responsible by the band peaking at 1137 cm⁻¹) exists [21–23]. The aliphatic CH₂ stretching modes appear in spectra of all compounds in the region of 2900 cm⁻¹.

Table 1 shows the extreme surface PS/PEO monomer amounts obtained by the procedure described in Ref. [5]. The normalized copolymer films HREELS spectra were fitted with a weighed sum of spectra corresponding to pure PS and PEO. Curve fitting was performed over the entire vibrational range (excluding the elastic peak) and over a more restrict range (1950–3450 cm⁻¹). The maximum difference between the results of the two fittings was taken as the accuracy of the method. The PS/PEO monomer composition was calculated by the ratio of the multiplying factors corresponding to PS and PEO. As spectra were obtained in off specular conditions, information comes from a depth of the order of 10 Å.

ARXPS needs flat surfaces to give reliable results [24], i.e., to avoid shade effects. Henceforth,
only films with smooth surfaces (the ones which presented narrower elastic peaks in HREELS spectra) were analyzed. A typical C1s spectrum with the components of the different chemical environment (i.e. C1 for the carbon bound to the oxygen in the PEO repeat unit and C2 for the carbon in the styrene unit) is shown in Fig. 2.

The ratios [(area of C2 peak)/8]/[(area of C1 peak)/2] for the films studied by ARXPS are summarized in Table 2.

4. Discussion

From the comparison of the results of Tables 1 and 2, the following conclusions can be extracted:

- the qualitative effects of all the treatments on the surface PS/PEO ratios calculated by ARXPS analysis are similar to the ones estimated by HREELS;
- the PS/PEO surface ratios calculated from XPS spectra are always greater than the ones from HREELS.

Table 2 shows that for some films (cast from CCl4, without annealing and independently of the substrate), the ARXPS relative intensities with the analysis angle are invariant suggesting constant concentration profiles. For these films, hence, the ratio PS/PEO from HREELS and XPS should be similar. Nevertheless, the PS/PEO ratio is ~1.8
larger from XPS than from HREELS. This is understandable: indeed, it was assumed that the multiplying factor of each pure polymer HREELS spectrum needed to fit the copolymer spectrum was proportional to the number of monomers of each block in the copolymer. This assumption was based on the reasoning that a monomer of PS should have a C–H stretch intensity similar to the one in PEO. This cannot be the case since the number of C–H oscillators in a monomer of PEO is larger than the same number in PS (4:3). Moreover, bond angles H–C–H are different in PS and PEO and, hence, the vibration transition moments are also different leading to different intensities. The combination of these two factors can lead to a PS/PEO ratio > 1, for equal C–H stretch intensities. On the other hand, in XPS, the contribution of hydrocarbon contaminants to the C 1s spectra will be mixed with PS signal from their alike chemical environment, whereas, in HREELS, the C–H stretching mode of the hydrocarbon contaminant will be essentially mixed with PEO signal since the CH₂ groups in PEO are aliphatic. The presence of contaminants, even in small amounts, leads then to (PS/PEO)_{HREELS} < (PS/PEO)_{XPS}. For instance, for a surface composition of 10 monomers of PS and 90 monomers of PEO (260 carbon atoms), 11 atoms of contaminants (∼4%) are enough to give a ratio, \( r = (PS^{mon}/PEO^{mon})_{XPS}/(PS^{mon}/PEO^{mon})_{HREELS} = 1.2 \). For the same level of contamination, \( r \) decreases till the composition in monomers 50:50 and increases again for larger PS surface concentrations (\( r = 1.3 \) for the composition in monomers 80:20). Hence, the quantitative disagreement between HREELS and XPS results is certainly due to the combination of these effects. We want also to stress that in ARXPS, the extreme surface composition was calculated from models of concentration profiles since the analyzed depth is 10–30 atomic layers thick. In HREELS, and in off-specular conditions, it is a direct measurement since the analyzed depth is two to three atomic layers thick. Finally, results can be summarized as follows:

- the PS surface concentration is larger for films prepared from THF than from CCl₄ as solvent, irrespective of the substrate and preparation method (casting or spin coating);
- before annealing, the percentage of PS at the extreme surface of the films is higher for solvent-cast than for spin coated films for the hydroxylated substrate; the opposite is observed for the silanized substrate;
- for annealed films, PS percentages are very insensitive to the solvent and preparation method; however, films on silanized substrates have lower PS/PEO ratios (1.70 ± 0.05 for the hydroxylated silicon substrate and 1.13 ± 0.05 for the silanized one).

The results clearly evidence the influence of the nature of the substrate and the importance of film preparation method on the PS segregation to the extreme surface. Modifications of surface properties of PS-containing polymer thin films were already observed as being due to the interaction of PS with various silicon-based substrates. For instance, phase-separation-induced surface patterns of dPS/poly(vinyl methyl) ether polymer blend films on hydroxylated or silanized Si-based surfaces were shown to depend on the interfacial tension ratio to the surface tension [7]. For PS films on Si–H surface or Si native-oxide surface,
variations up to several tens of degrees on the glass transition were observed. This was attributed to changes on the entropy of the copolymer induced by the interactions with the substrate [8].

In what concerns the solvent, CCl₄ presents a lower affinity to the silanols and a greater affinity to the silanized substrate relative to THF. However, favorable THF–silanol interactions clearly promotes greater surface PS concentration than the CCl₄–silanized substrate interactions.

The relative constancy of the surface PS concentration after annealing for a given substrate clearly indicates the relevance of the interactions with the substrates. Therefore, as the surface PS/PEO ratios are much higher than the bulk ones (≈0.09), a strong PS segregation towards the extreme surface exists, although without forming a pure surface overlayer of PS in agreement with other surface studies [2–4]. Furthermore, the slightly lower surface PS segregation for the silanized substrate than for the hydroxylated one can be explained by the weaker interaction of the PEO block with the silanized substrate compared with the preferential interaction of PS. Nevertheless, the lower surface tension of PS is still enough to assure the PS segregation towards the surface.

5. Conclusions

PS fractions at the extreme surface of PS–PEO diblock copolymer films cast upon hydroxylated and silanized native silica were obtained from vibrational HREELS and ARXPS. This work shows that for all films the PS/PEO monomer fraction ratio in the surface is higher than the stoichiometric value (0.09). Non-annealed films have richer PS surfaces when prepared from THF solutions than those prepared from CCl₄ solutions. Contrarily to the hydroxylated substrate, the silanized one favors the PS segregation to the surface in spin coating irrespective of the solvent. The influence of the substrate is also found after the annealing treatment. Lower surface PS/PEO ratios were observed for the silanized native silica than for the hydroxylated substrate (1.13 ± 0.05 vs. 1.70 ± 0.05).

Acknowledgements

The authors thank M.A. Winnik for the gift of the block copolymer polymer. O.P. thanks FCT and PRAXIS XXI for a fellowship (PRAXIS XXI BPD/14157/97).

References


