Notes

Surface Analysis of PS–PEO Diblock Copolymer Films by HREELS[†]

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1. Introduction

The surface composition of block copolymer films is relevant in several fields, in particular to solve biological compatibility problems. Poly(ethylene oxide) (PEO) is particularly adequate for this purpose since it is highly soluble in water. Simultaneously it presents a low tendency for protein adsorption.[1] Diblock copolymers of PEO and polystyrene (PS) are specially interesting due to the fact that the blocks are mutually incompatible. In a selective solvent for one of the blocks, they aggregate in solution, forming micelles.[2–5] In the bulk, they adopt several morphological structures depending on the volume fraction of each component:[6,7] for volume fractions of one component lower than 0.2, the minor component forms spherical domains in a matrix of the major component, while for identical volume fractions of each block the structure is formed by alternating lamellae. Bulk and surface compositions in thermodynamic equilibrium should be different due to the lower solid-state surface tension of PS (36 mJ/m^2) compared to the PEO (44 mJ/m^2) value.[8] This constitutes the driving force for polystyrene enrichment of the surface as was confirmed by Thomas and O'Malley for several PS–PEO diblock[9] and PEO–PS–PEO triblock[10] copolymers films cast from different solvents, studied by the use of X-ray photoelectron spectroscopy (XPS). In addition, they found that the PS surface enrichment relative to the bulk also depends on solvent affinity to polystyrene.

In this work, the surface composition of PS–PEO diblock copolymer films prepared from THF and CCl$_4$ polymer solutions was studied by HREELS. This technique was found to be particularly adequate for extreme surface studies.[11,12] In fact, the depth of analysis, although varying with the primary energy, E_p, and the surface characteristics, namely the number of excitation channels available at E_p, is always on the order of magnitude of a chemical bond length,[13] especially if the experimental conditions favor the impact mechanism (high primary energies and off-specular conditions). In addition, the spectra resolution, measured by the fwhm of the elastic peak, provides qualitative insights about the surface roughness[14] (resolution becomes worse with increasing roughness). We found that the extreme surface film composition depends on the preparation method, solvent, and annealing. Annealing produces identical smooth surfaces for both solvent-cast and spin-coated films irrespective of solvent. Roughness and composition of the nonannealed films depend on both solvent and preparation method.

2. Experimental Section

The synthesis and characterization of the PS–PEO block-copolymer was described in detail elsewhere.[15–17] The weight-average molar mass of the copolymer is $M_w = 22\ 150$ ($M_w/M_n = 1.07$), with block weight-average molar masses of $M_w = 3800$ and $M_w = 18\ 350$, for PS and PEO, respectively. Tetrachloromethane (CCl$_4$) and tetrahydrofuran (THF), both from Merck (Uvasol, spectroscopic grade), were used as received. The silicon wafers were etched with hydrofluoric acid,[18] treated with H$_2$SO$_4$ + H$_2$O$_2$ solutions, and thoroughly rinsed in deionized water to ensure the presence of silanol groups at the silicon surface. Both solvent-cast and spin-coated films were prepared from 0.48 g/L copolymer solutions. This concentration was required for preparing cast films ~400 Å thick on squared 1.2 cm × 1.2 cm slabs. The annealing treatment was performed in an oven at 100 °C during 24 h under 10^{-3} mbar of pressure.

The HREEL spectra were recorded using a Kesmodel LK 2000R spectrometer in an UHV chamber (10^{-10} Torr). The incident angle was 60°, and the analyzing angle was 30° (off-specular conditions). Incident and backscattered electron directions were measured relative to the normal of the sample surface. Electron primary energies, E_p, ranged from 0 to 10 eV. 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.

Although spectra were recorded without charge compensation, complete spectra (energy loss, ΔE, ranging from 0 to E_p) exhibit stationary cutoffs near $\Delta E \approx E_p$, showing that films were thin enough to prevent charge effects. This does not ensure that no charge develops on the surface but only that its value is stationary (see section 3). No irradiation damage was noticed in the samples under study during the time needed to record a spectrum.

[†] In memory of Dr. Jorge d'Oliveira, deceased in 1996.

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(1) Garbassi, F.; Morra, M.; Occhiello, E. *Polymer Surfaces From Physics to Technology*; John Wiley & Sons: Chichester, England, 1998.

(2) Xu, R.; Winnik, M. A. *Macromolecules* **1991**, *24*, 87.

(3) Vagberg, L. J. M.; Cogan, K. A.; Gast, A. P. *Macromolecules* **1991**, *24*, 1670.

(4) Xu, R.; Winnik, M. A.; Riess, G.; Chu, B.; Croucher, M. D. *Macromolecules* **1992**, *25*, 644.

(5) Farinha, J. P. S.; d'Oliveira, J. M. R.; Martinho, J. M. G. *Langmuir* **1998**, *14*, 2291.

(6) Crystal, R. G.; Erhardt, P. F.; O'Malley, J. J. In *Block Copolymers*; Aggarwal, S. L., Ed.; Plenum Press: New York, 1970; p 179.

(7) Bates, F. S. *Science* **1991**, *251*, 898.

(8) *Polymer Handbook*; Brandrup, J., Immergut, E. H., Eds.; John Wiley & Sons: New York, 1989.

(9) Thomas, H. R.; O'Malley, J. J. *Macromolecules* **1979**, *12*, 323.

(10) O'Malley, J. J.; Thomas, H. R.; Lee, G. M. *Macromolecules* **1979**, *12*, 996.

(11) Botelho do Rego, A. M.; Lopes da Silva, J.; Rei Vilar, M. *J. Electron Spectrosc. Relat. Phenom.* **1997**, *85*, 81 and references therein.

(12) Pireaux, J. J. In *Surface Characterization of Advanced Polymers*; Sabbatini, L., Zambonin, P. G., Eds.; VCH: Weinheim, Germany, 1993; Chapter 2.

(13) Sanche, L.; Michaud, M. *Chem. Phys. Lett.* **1981**, *80*, 184.

(14) Ibach, H.; Mills D. L. *Electron Energy Loss Spectroscopy and Surface Vibrations*; Academic Press: New York, 1982.

(15) Marti, S.; Nervo, J.; Riess, G. *Prog. Colloid Sci.* **1975**, *58*, 114.

(16) Riess, G.; Nervo, J.; Rogez, D. *Polym. Eng. Sci.* **1977**, *17*, 634.

(17) Riess, G.; Rogez, D. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1982**, *23*, 19.

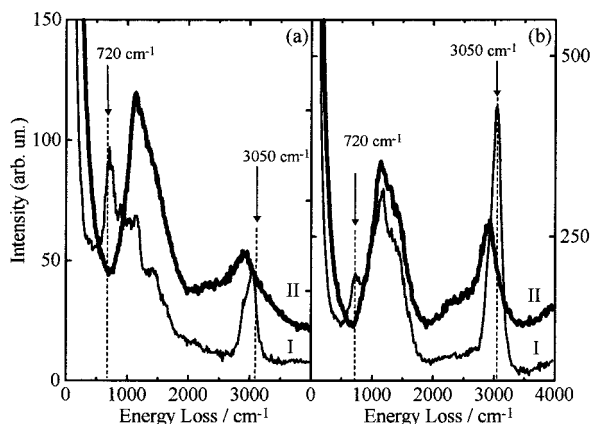(18) Kern, W.; Puotinen, D. A. *RCA Rev.* **1970**, *June*, 187.

Figure 1. HREEL spectra of films of pure polystyrene (I) and pure poly(ethylene oxide) (II) cast from CCl_4 on a silicon wafer covered by its native oxide. The incident angle was 60° and the analysis angle 30°. Arrows indicate the most typical vibrational out of plane deformation (720 cm^{-1}) and stretching (3050 cm^{-1}) modes of benzenic CH bonds: (a) primary energy of 1 eV; (b) primary energy of 5 eV.

3. Results and Discussion

Vibrational electron energy loss spectra (between 0 and 4000 cm^{-1}) of pure PS and PEO for two different primary energies, 1 and 5 eV, are shown in Figure 1.

The HREELS vibrational spectra of polystyrene has two characteristic bands at 720 and 3050 cm^{-1}, shown by arrows in Figure 1, that are not present in the PEO spectrum and will be here used to qualitatively estimate the variations of PS amounts at the surface from film to film. The 720 cm^{-1} band corresponds to the CH out-of-plane deformation, while the 3050 cm^{-1} band corresponds to the aromatic CH stretching. The differential cross sections of the HREELS bands display distinct power law with the primary energy, E_p, depending on the interaction mechanism. The HREELS 720 cm^{-1} band displays a dipole interaction mechanism (differential cross section proportional to E_p^{-1}) while the other bands show an impact behavior (differential cross sections proportional to E_p) or a hybrid character[11] (differential cross sections proportional to E_p^α with $0 \leq \alpha \leq 0.6$). These different laws of variation of the intensity with the primary energy imply a large spectrum shape change with E_p (see Figure 1).

The primary energy, E_p, is related to the nominal energy, E_n, by

$$E_p = E_n + e\Phi_{ct} + e\Phi_c \qquad (1)$$

where Φ_{ct} is the contact potential and Φ_c is the charge potential. Polymeric films always charge under electron irradiation. For very thin films, with thickness around a few hundreds of angstroms, this surface charge attains an equilibrium value very rapidly, and so the unique consequence is the primary energy dependence on the final charge (see eq 1). However, the variation of the primary energy results in distinct intensity changes for the transitions induced by the dipolar and the impact mechanisms, differences being more important for low nominal energies. To reduce this effect, all the spectra were acquired at a high incident energy of 5 eV, where charge effects are minor and the impact mechanism is favored. The relative importance of this mechanism was further enhanced by recording the spectra in off-specular conditions.

The HREEL spectrum of PEO shows two broad bands one around 2900 cm^{-1} assigned to the CH$_2$ stretching modes and another one between 700 and 1800 cm^{-1}
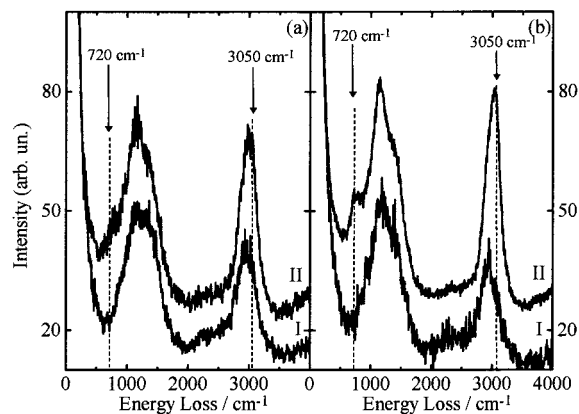

Figure 2. (a) HREEL spectra, taken at an incident energy of 5 eV, incident angle of 60°, and analysis angle of 30°, of PS–PEO diblock copolymer films spread from CCl_4 solutions: (a) cast followed by solvent evaporation; (b) spin-coated; (I) spectra immediately taken after solvent evaporation; (II) spectra taken after film annealing at 100 °C for 24 h.

peaking at 1137 ± 10 cm^{-1}. This last one is a mixture of several stretching and deformation modes of the chain (C–C, C–O, C–O–C, C–C–O) and also the deformation modes of the CH$_2$ groups. The CH$_2$ stretching band of PEO is similar to the HREELS band of an aliphatic hydrocarbon but the other band is completely different. An aliphatic hydrocarbon HREEL spectrum has three unresolved bands[19] with one of the valleys just where the PEO single band has a maximum. This maximum is usually assigned to the C–O–C stretching,[20] obviously absent in an aliphatic hydrocarbon.

Figure 2 shows the spectra of copolymer films prepared from CCl_4 solutions recorded immediately after film deposition (I) and after annealing (II). Figure 2a presents the spectra obtained from cast films, while Figure 2b shows the corresponding spectra of films prepared by spin-coating.

For both solvent-cast and spin-coated films, the spectra change significantly with annealing, being the percentage of polystyrene at the extreme surface higher for annealed films as shown by the increase in intensity of both the out-of-plane and the stretching modes of the aromatic CH bonds. The nonannealed solvent-cast and spin-coated films have different amounts of polystyrene at the surface, being the amount of polystyrene higher for cast films.

Figure 3 shows similar HREEL spectra for films prepared from THF polymer solutions. The main influence of the solvent is observed for the solvent-cast film where a similar high percentage of polystyrene was observed before and after annealing. Contrarily, for spin-coated films the polystyrene fraction increases with annealing as observed previously for films prepared from CCl_4 solutions.

To quantify the polymer composition at the extreme surface, a curve fitting of the block copolymer spectrum with a weighed sum of spectra corresponding to pure PS and PEO spectra was made. Figure 4 shows the spectra (2500–3500 cm^{-1}) normalized to the baseline, of PS and PEO homopolymer films obtained under the same experimental conditions as that of the block-copolymer film.

(19) Botelho do Rego, A. M.; Lopes da Silva, J.; Rei Vilar, M.; Voltz, R. *J. Electron Spectrosc. Relat. Phenom.* **1998**, *87*, 221. Botelho do Rego, A. M.; Lopes da Silva, J.; Rei Vilar, M.; Gonçalves da Silva, A. M. *Thin Solid Films* **1994**, *243*, 521. Pireaux, J. J.; Thiry, P. A.; Caudano, R.; Pfluger, P. *J. Chem. Phys.* **1986**, *84*, 6452.

(20) Bower, D. I.; Maddams, W. F. *The Vibrational Spectroscopy of Polymers*; Cambridge University Press: Cambridge, England, 1989.
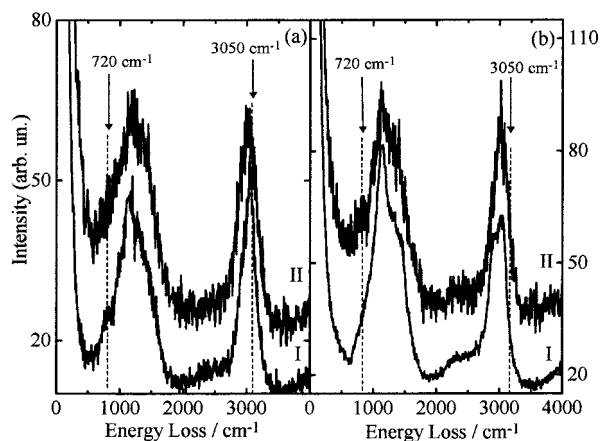
Figure 3. (a) HREEL spectra, taken at an incident energy of 5 eV, incident angle of 60°, and analysis angle of 30°, for a PS−PEO diblock copolymer film spread from tetrahydrofuran solutions: (a) cast followed by solvent evaporation; (b) spin-coated; (I) spectra taken immediately after solvent evaporation; (II) spectra taken after film annealing at 100 °C for 24 h.
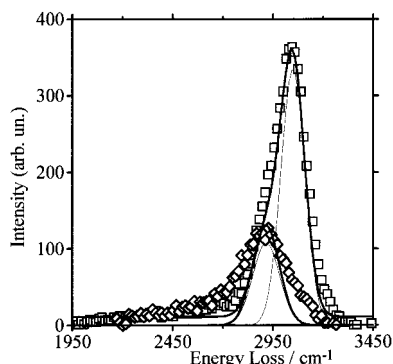

Figure 4. Curve fitting (bold line) of HREEL spectra of pure PS (open squares) and pure PEO (open diamonds), in Gaussian curves (solid lines) centered in the CH_2 chain stretching (2920 cm^{-1}) and the CH ring stretching (3060 cm^{-1}) vibrational modes.

The polystyrene spectrum was curve fitted with two Gaussian functions corresponding to the aliphatic CH stretching and the aromatic CH stretching vibrational modes. The bands of PEO and PS around 2900 cm^{-1}, attributed to the aliphatic CH stretching modes, have the same order of magnitude, reflecting that normalized spectra should correspond approximately to the same number of monomers in both polymers. In fact, and in what concerns the aliphatic groups, one of the polymers presents a CH_2 and a CH groups per monomer whereas the other one has two CH_2 groups. Considering the spectrum of the block-copolymer as a weighed sum of the spectra of its components, one should assume that the ratio of the fitting factors coincides with the ratio of polymer block monomers present at the extreme surface of the film.

Figure 5 shows the spectrum curve fitting of the spun film prepared from the THF solution, by a weighed sum of PS and PEO homopolymers spectra in the region 1950−3450 cm^{-1}. This curve fitting range was chosen because the PEO spectrum presents a large tail between 1950 and 2700 cm^{-1} (see Figure 1a-II), which allows a clear distinction between the CH stretching in PEO and the same vibration in usual contaminants (aliphatic hydrocarbons) as seen above.

All spectra were normalized to the same baseline and not to the elastic peak due to the fact that the background is much less sensitive to the surface roughness than the elastic peak. The curve fitting procedure allows the
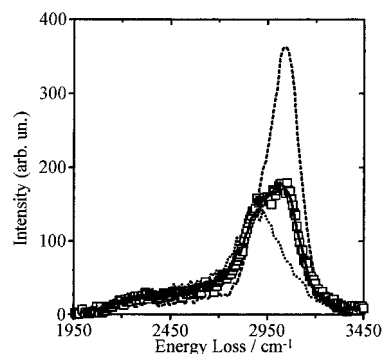

Figure 5. Curve fitting (solid line) of the HREEL spectrum (open squares) of a spun film of the PS−PEO copolymer spread from a THF solution by a weighed sum of HREEL spectra of pure PS (dashed line) and pure PEO (dotted line).

Table 1. Fractions of PS Monomer in the Surface of Block Copolymer Films Calculated by Curve Fitting the Diblock HREEL Spectra with a Weighed Sum of Pure PS and PEO HREEL Spectra[a]

	solvent	annealing	PS monomer fraction (± 0.05)
casting	CCl_4	no	0.32
		yes	0.59
	THF	no	0.77
		yes	0.65
spin-coating	CCl_4	no	0.09
		yes	0.68
	THF	no	0.33
		yes	0.58

[a] The bulk copolymer has a PS monomer fraction of 0.08.

calculation of the PS molar fraction present at the extreme surface, as shown in Table 1.

The curve fitting of the entire spectrum for each sample gives results which are similar to those presented in Table 1. This allows us to withdraw the presence of significant amounts of hydrocarbon contamination since the PEO spectrum at low wavenumbers is completely distinct from that of the aliphatic hydrocarbon. Taking into account that the major source of uncertainty in quantitative treatment of spectra is the background subtraction, we consider only the 1950−3450 cm^{-1} range, where the background is nearly constant. Anyway, the maximum difference between the two PS monomer fraction values (the one obtained by curve fitting from 400 to 3450 cm^{-1} and the one in Table 1) was ± 0.05 and is considered to be a measure of the uncertainty obtained in the final composition.

The results show that, before annealing, the percentage of PS at the extreme surface of films prepared from the CCl_4 solution is higher for solvent-cast films than for spin-coated films. In contrast, the corresponding percentage of PS for films spread from THF solutions is always larger. This shows that solvent influences the composition of the extreme surface. This can be explained by both the competition of the solvent, PEO and PS segments toward the substrate silanol groups and the affinity of the solvent for the PS block. The CCl_4 is a good solvent for both PS and PEO blocks and has a low affinity to the substrate, leading to an interfacial region where the substrate sites are occupied simply by PEO and PS segments. This was confirmed by Tripp and Hair[21−23] using in situ infrared spectroscopy. The CCl_4 is a spherical small molecule that easily escapes through the matrix, not disturbing

(21) Tripp, C. P.; Hair, M. L. *Langmuir* **1993**, *9*, 3523.
(22) Tripp, C. P.; Hair, M. L. *Langmuir* **1994**, *10*, 4031.
(23) Tripp, C. P.; Hair, M. L. *Langmuir* **1996**, *12*, 3952.

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the arrangement of the chains. Indeed, the percentage of PS for spin-coated films (0.09) is very close to the bulk percentage (0.08), showing no segregation of PS at the extreme surface. For solvent-cast films, the PS percentage is higher, reflecting the tendency of PS to segregate toward the surface in conditions closer to equilibrium.

Solvent-cast films spread from THF solutions show a higher percentage of PS (0.77) at the extreme surface (see Table 1). Spin-coated films have a lower fraction of PS at the extreme surface (0.33), which is due to nonequilibrium conditions during film preparation. The high fraction of PS found at the surface of all THF-cast films is attributed to the high affinity of THF to the silanol groups of the substrate surface. The THF fills some of the sites that could be occupied by the segments of PS, and moreover, when it escapes through the matrix, it induces the segregation of PS toward the surface.

The relaxation of the polymer chains in the film by annealing leads to similar percentages of PS at the extreme surface (0.63 ± 0.05) and to a similar roughness of all films. The bulk morphological structure is probably formed of minor PS spherical domains in a matrix of PEO, while at surface the PS spherical domains dominate but do not replace completely the PEO. The formation of a pure surface overlayer of PS was never reached in agreement with the results of Thomas and O'Malley.[9,10]

The topographies of films prepared from CCl$_4$ or THF solutions show different surface changes with annealing. After annealing, the fwhm of the elastic peak decreases for "CCl$_4$" films, while the opposite was observed for "THF" films. This means that the surface of the nonannealed "CCl$_4$" films is rough and the solvent evaporation and chain rearrangements induced by the annealing create a smoother surface. The "THF" films surface of nonannealed films is relatively smooth and is modified by annealing due to the evaporation of a large amount of solvent entrapped in the film. The chains are not able to completely reorganize during annealing, probably due to high cohesion of the PEO blocks (the critical molar mass of PEO entanglement is around 4400[24]).

Finally, irrespective of solvent, the cast films have rougher surfaces than the spin-coated films owing to the higher thickness of the cast films, which makes the chain rearrangements more difficult.

In the whole discussion, we did not mention the possible effect of the high vacuum on the surface morphology. However, high vacuum cannot explain the differences among samples since the pressure is practically the same for all measurements.

4. Conclusions

The HREELS study of a PS−PEO diblock copolymer films shows that for all films the PS monomer fraction in the surface is higher than the stoichiometric value (0.08). This result agrees with a lower surface energy of PS compared to that of PEO. Nonannealed films have richer PS surfaces when prepared from THF solutions than those prepared from CCl$_4$ solutions. This is attributed to the competition of solvent, PS and PEO segments to the silanol sites of the silica substrate. In the absence of annealing, solvent-cast films have rougher surfaces than spin-coated films and THF produces smoother surfaces than CCl$_4$. Annealing provides films with similar surfaces from the point of view of composition (PS monomer fraction of 0.63 ± 0.05) and roughness, irrespective of solvent and preparation method.

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(24) Wool, R. P. *Polymer Interfaces, Structures and Strength*; Hanser Publishers: New York, 1993.