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Investigation of the Surface Activity of a Poly(styrene-*b*-dimethylsiloxane) Copolymer Blended within a Polystyrene Matrix

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ABSTRACT: The surface properties of thin polystyrene films are deeply modified by the addition of various amounts of a poly(styrene-*b*-dimethylsiloxane) copolymer—or poly(S-*b*-DMS)—as confirmed by a series of analytical methods. In addition to the surface tension which has been estimated from wettability and contact angle measurements, surface composition has been analyzed by X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS). Surface studies have been completed by the analysis of the depth distribution of siloxane from the surface by XPS and SIMS. Finally, the surface activity of poly(S-*b*-DMS) has been investigated in solution. Indeed, changes in the surface tension of polystyrene solutions in THF have been measured in relation to the addition of the diblock copolymer. All the experimental data agree with the complete coverage of the polystyrene films with the poly(S-*b*-DMS) copolymer. This situation already prevails in the solutions prepared as precursors to the thin polystyrene films. Accordingly, surface characteristics of films freshly prepared by solvent-casting are unaffected by subsequent annealing.

Introduction

Nowadays, an increasing attention is paid to the analysis of polymer surfaces and to the deliberate modification of their properties. Indeed, a large range of applications are directly dependent on the surface characteristics of polymeric materials such as friction, permeability, adhesion, biocompatibility, etc.

Chemical, photochemical and plasma treatments are currently used in order to increase the polarity of polymer surfaces.[1a] In contrast, the surface energy of a polymer matrix is efficiently decreased by the addition of silicon- and fluorine-rich low molecular weight compounds, which have a remarkable propensity to surface segregation.[1b,2] The same behavior has been reported for block and graft copolymers which comprise a component miscible to the matrix and a second immiscible component of a low surface energy.[2-6] The low surface tension part of such copolymers is responsible for the surface accumulation of the copolymer, whereas the matrix miscible component acts as an anchoring block and ensures the permanency of the surface modification. This anchoring effect accounts for the superiority of these copolymers over low molecular weight surfactants which are easily exuded or washed out from the surface.

Preliminary papers have focused on the surface activity of poly(styrene-*b*-dimethylsiloxane)—or poly(S-*b*-DMS)—in polystyrene (PS). Evidences were essentially based on measurements of wettability and contact angles and on photoelectron spectroscopy (XPS).[7-9] The purpose of this paper is to report on a more detailed analysis of the segregation of poly(S-*b*-DMS) at the polystyrene surface. Secondary ion mass spectrometry (SIMS) is an up-and-coming method of polymer surface analysis, which makes available not only the very surface composition[10-12] but also concentration profiles in surface layers and chemical surface imaging.[13-15] SIMS data have been reported and compared to classical methods, such as XPS[10,16,17] and contact angle measurements.[1c,18a] Surface accumulation of poly(S-*b*-DMS) at the polystyrene surface has thus been analyzed in detail and compared to the situation which prevails in THF solutions, from which thin films have been prepared by solvent- and spin-casting.

Experimental Section

Materials. The poly(S-*b*-DMS) copolymer was synthesized by sequential anionic polymerization of styrene and hexamethylcyclotrisiloxane (D_3).[9] Styrene polymerization was first initiated with *sec*-BuLi in toluene at 0 °C. The temperature was then raised up to 25 °C for 4 h. D_3 and dry THF were successively added to living polystyrene chains, and the second polymerization step was carried out at 40 °C for 4 h. Block copolymer chains were deactivated by acidified methanol and precipitated into methanol, filtered, and dried "in vacuo".

The molecular weight of each block was predetermined by the monomer to initiator molar ratio. The molecular weight of the polystyrene block was measured by size-exclusion chromatography (SEC) and found to be 5400. $\bar{M}_n$ of the poly(dimethylsiloxane) (PDMS) block was calculated from the molar composition of the copolymer, as determined by ^{1}H-NMR spectroscopy (DMS content = 46 mol %, or 38 wt %), and $\bar{M}_n$ of the polystyrene block; it was thus found to be 3300. The polydispersity of the block copolymer ($\bar{M}_w/\bar{M}_n$) was 1.4.

Homopolystyrene (PS) was purchased from BASF. According to SEC, $\bar{M}_n$ = 81 000 and $\bar{M}_w/\bar{M}_n$ = 2.8.

Film Preparation. Films were prepared by casting 10 wt % solutions of PS plus poly(S-*b*-DMS) in THF. Films were either

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solvent-casted (THF evaporation under 1 atm, at room temperature) or spin-casted (25 °C, at a 2000 rpm rotation speed). Several substrates were used, i.e., clean glass slides, stainless-steel plates, and aluminum foils. Deposited films were finally dried under vacuum for 48 h before analysis. Solvent-cast films were carefully peeled from the substrate in order to measure wettability and contact angles and to record XPS and SIMS spectra not only at the polymer/air interface but also on the substrate side, i.e., at the polymer/glass and polymer/metal interface, respectively. In addition to the analysis of the solvent-cast films after peeling from the substrate, some spin-cast films were analyzed by dynamic SIMS, i.e., by complete erosion from the air/polymer surface down to the polymer/substrate interface. These "in situ" done measurements were considered in order to collect direct information on films contacting the substrate.

Surface Analysis. Wettability. The critical surface tension of wetting of polymer films was assessed by using ethanol–water mixtures of various compositions, such as to cover a range of surface tensions from 22 to 36 mN/m, at 25 °C.[19] The actual surface tension of PS films was straddled by the visual observation of film wettability.[9]

Contact Angles. Surface tension was calculated from the contact angle of water droplets ($V = 5\ \mu L$) deposited onto polymer films at 25 °C and measured by the sessile drop method.[1d,18b] A homemade apparatus consisting of a halogen lamp, a sample holder, and a telelens was used to magnify the drop picture on a screen and to measure accurately the contact angle.

XPS. Photoelectron spectra were recorded by using a Hewlett-Packard 5950 A ESCA spectrometer to determine surface atomic ratios and a Scienta ESCA-300 apparatus for the depth distribution study. The HP 5950 A instrument is equipped with a monochromatized Al Kα X-ray source ($h\nu$ = 1486.6 eV). The analysis chamber was under a pressure of ca. 1 μPa and the sample kept at 25 °C. Spurious charging effects were neutralized by the "electron flood gun" technique (typically, $i = 0.2$ mA and $E = 2.0$ eV). Quantitative analysis of silicon and oxygen (markers of PDMS) compared to carbon was carried out in reference to eq 1,[6,16,20] where X is either Si or O and [ ] stands for the atomic

$$\frac{[\mathrm{X}]}{[\mathrm{C}]} = \frac{S_{\mathrm{X}}{*}f_{\mathrm{C}}{*}t_{\mathrm{C}}}{S_{\mathrm{C}}{*}f_{\mathrm{X}}{*}t_{\mathrm{X}}} \qquad (1)$$

concentration, S the area of the signal, t the related accumulation time, and f a relative sensitivity factor which was calculated from the elemental ratios of standard compounds ($f_{\mathrm{C1s}} = 1.00$, $f_{\mathrm{O1s}} = 2.65$, and $f_{\mathrm{Si2p}} = 0.90$[21,22]).

Depth distribution of the poly(S-*b*-DMS) from the film surface was analyzed by recording XPS spectra at various electron take-off angles. The Scienta ESCA-300 spectrometer, used on purpose, works under the same conditions as the Hewlett-Packard spectrometer, except for the pressure which was maintained at ca. 1 nPa. Since the relative sensitivity factor ($f_{\mathrm{X}}/f_{\mathrm{C}}$) was not available for this very recent equipment, it was approximated from eq 1. This equation was first applied to data collected with the Hewlett-Packard spectrometer at the fixed take-off angle of 38.5°, and the [X]/[C] ratio was accordingly calculated for each sample. Then introducing this [X]/[C] ratio in eq 1 together with the experimental $S_{\mathrm{X}}/S_{\mathrm{C}}$ ratio from the Scienta equipment, $f_{\mathrm{X}}/f_{\mathrm{C}}$ was finally calculated.

SIMS. SIMS analyses were carried out according to three modes, i.e., static, depth profiling, and high spatial resolution imaging. Static SIMS spectra were recorded with a Cameca-Riber Q156 quadrupole spectrometer. On purpose, argon primary ions (4.5 keV and 5 nA/cm^2) were used, whereas high-energy electrons (2 keV) allowed charge effects to be avoided. The analysis chamber was kept at 25 °C under a pressure in the range of 0.1 μPa. In static SIMS, oxygen and silicon were quantified with respect to carbon. Characteristic signals of C$^-$, O$^-$, Si$^-$, CH$^-$, OH$^-$, and SiH$^-$ ions were recorded by static SIMS, and the relative abundance of elements ([Si]/[C] and [O]/[C]) at the film surface was calculated in accordance to eq 2, where [ ] is the atomic

$$\frac{[\mathrm{X}]}{[\mathrm{C}]} = \frac{S_{\mathrm{X}-} + S_{\mathrm{XH}-}}{S_{\mathrm{C}-} + S_{\mathrm{CH}-}} \qquad (2)$$

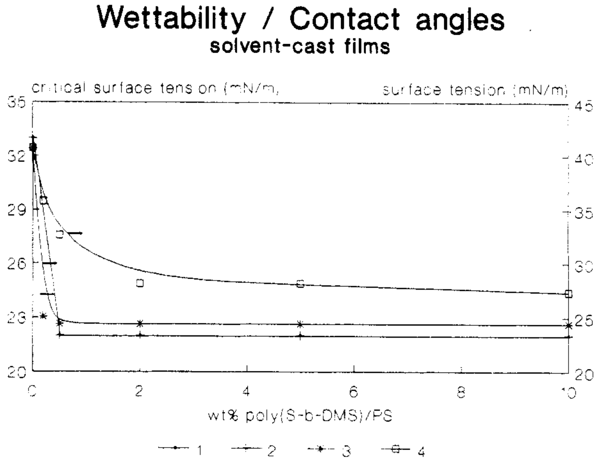

Figure 1. Critical surface tension for solvent-cast films of poly(S-*b*-DMS)/PS blends (mN/m) versus copolymer concentration (wt %). Wettability measurements at 25 °C. (1) Air side. (2) Glass side. Surface tension for solvent-cast films of poly(S-*b*-DMS)/PS blends (mN/m) versus copolymer concentration (wt %). Contact angle measurements at 25 °C. (3) Air side. (4) Glass side.

concentration and S the signal area. Indeed, use of such an equation has already been reported for many polymers.[12] On the other hand, depth profiling was performed by controlled erosion of the samples with the help of argon atom bombardment (7.5×10^{13} atoms/s·cm^2, corresponding to a depth of ca. 9 nm/min in the investigated samples), between static measurements.[23] Silicon and oxygen were also detected by SIMS depth profiling, and quantitative results were obtained by using eq 2 also. Nevertheless, when oxygen is concerned, PDMS profiles of very thin films might be perturbed by the argon ions which could desorb oxygen from the metal support and alter the oxygen distribution within the film. A Cameca IMS-4F magnetic sector microprobe was used for high spatial resolution imaging. Purposely, a cesium microbeam (14.5 keV) was used, whereas low-energy electrons (ca. 1 eV) provided the negative sector with an automatic charge compensation in the negative SIMS mode.

Tensiometry. The surface tension of 10 wt % solutions of poly(S-*b*-DMS)/PS in THF was measured, at 25 °C, by the Wilhelmy plate method[1e,18c] with a Krüss K10 digital tensiometer.

Results and Discussion

Surface Tension of Polymer Films. Figure 1 clearly shows that, whatever the experimental method (wettability or contact angle measurements), the surface tension of solvent-cast polystyrene films on the air side dramatically decreases upon the addition of increasing amounts of poly(S-*b*-DMS). However, beyond a "critical concentration" of ca. 0.5 wt % of diblock, the surface tension of PS films tends to level off at a value which is very close to either the critical surface tension of wetting (γ_c) of PDMS (24 mN/m at 20 °C[1f,2,24]) or the surface tension (γ) of PDMS (20 mN/m at 20 °C[1f,25]). These experimental data reflect the large immiscibility of PDMS and PS, in agreement with a high PS/PDMS interfacial tension (6.1 mN/m[1g,2,25]) and the propensity of PDMS to accumulate uniformly at the PS surface in contact with air. Surprisingly enough, a similar behavior is observed on the glass side, which is a substrate of a higher energy than polystyrene. Although wettability cannot discriminate the air/PS from the glass/PS interface, contact angles show that migration and accumulation of the PDMS block on the glass side are less effective than those at the air/PS interface. The difference is the largest at the lower limit of the aforementioned critical concentration of the diblock. This observation might be consistent with a paper by Shull et al.[26] reporting on the surface activity of poly(styrene-*b*-2-vinylpyridine)

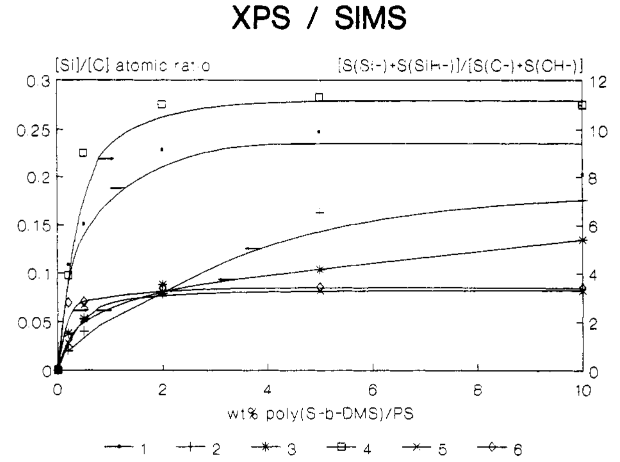

Figure 2. Surface atomic ratio for films of poly(S-*b*-DMS)/PS blends versus copolymer concentration (wt %). XPS analysis: (1) solvent-cast films, air side; (2) solvent-cast films, metal side; (3) spin-cast films, air side. Surface atomic ratio for films of poly(S-*b*-DMS)/PS blends versus copolymer concentration (wt %). SIMS analysis: (4) solvent-cast films, air side; (5) solvent-cast films, metal side; (6) spin-cast films, air side.

in a PS matrix. The diblock copolymer first migrates selectively to the air/PS interface, and then, above a critical concentration, it forms micelles which migrate and accumulate not only at the air side of PS films but also at the interface with a high surface energy substrate.

Surface Composition of Polystyrene Films. The experimental results are remarkably independent of the analytical method (XPS or SIMS) and the PDMS marker (Si or O). Indeed, both XPS and SIMS (Figure 2) data are very consistent with wettability and contact angle measurements, since the PDMS content of the surface increases rapidly with the diblock percentage and tends to level off at a concentration close to that beyond which surface tension is becoming constant. However, the plateau value for the PDMS content on the air side ([Si]/[C] atomic ratio = 0.23 for solvent-cast films and 0.11 for spin-cast films) is not 100% (calculated [Si]/[C] atomic ratio = 0.50 for pure PDMS). In the case of solvent-cast films, this value is definitely larger than the value expected for the nonsegregated pure diblock (calculated [Si]/[C] atomic ratio = 0.09). When a film of the pure diblock is analyzed, the PDMS content on the air side is of the same magnitude ([Si]/[C] atomic ratio = 0.25 for a solvent-cast film and 0.22 for a spin-cast one) as the value reported for the diblock copolymer/PS solvent-cast films in the plateau region. XPS data based on oxygen as the PDMS marker ([O]/[C] atomic ratios) and SIMS data confirm that, in contrast to the solvent-cast blends, the surface of the spin-cast samples in the plateau region is not yet a copolymer-like surface, indicating that a nonequilibrium situation is frozen-in by spin-casting. On the other hand, according to independent SIMS measurements,[27] the air surface of films prepared by solvent-casting, which is a slow process is almost entirely made of PDMS chains, already at a composition of 0.2 wt % diblock copolymer. All in all the experimental data indicate that the phase morphology of the diblock copolymer is not basically different when segregated at the PS surface rather than pure in bulk. The discrepancy in the PDMS content between the PS surface (or the bulk diblock copolymer) and pure PDMS means that the PDMS block extends over a depth smaller than 4 nm, i.e., the XPS-analyzed depth with the Hewlett-Packard spectrometer. It is worth noting that the PDMS content is smaller at the stainless steel/polymer interface compared to the air/polymer interface, which reflects a decreased tendency for the diblock either to accumulate at an interface of a higher interfacial energy or to lead to different interfacial structures at the metal and the air interface, respectively (e.g., micelles versus brushlike structures).

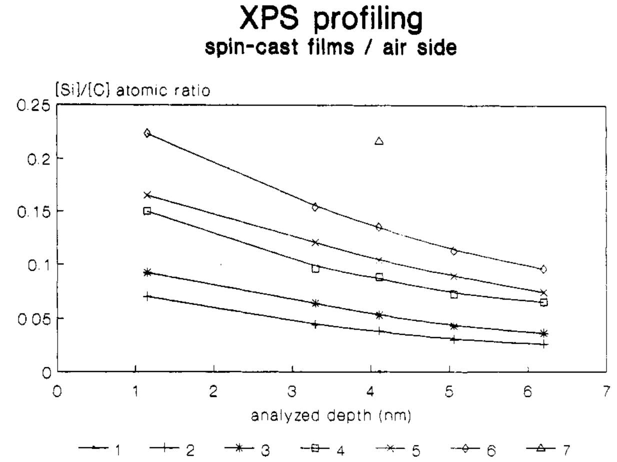

Figure 3. Atomic ratio on the air side of spin-cast films of poly(S-*b*-DMS)/PS blends versus analyzed depth (nm). XPS analysis: (1) pure PS; (2) 0.2 wt % poly(S-*b*-DMS)/PS; (3) 0.5 wt % poly(S-*b*-DMS)/PS; (4) 2.0 wt % poly(S-*b*-DMS)/PS; (5) 5.0 wt % poly(S-*b*-DMS)/PS; (6) 10. wt % poly(S-*b*-DMS)/PS; (7) pure poly(S-*b*-DMS).

Depth Profiles within Polystyrene Films. Cross sections of PS solvent-cast films modified with 5.0 and 10 wt % poly(S-*b*-DMS) have been observed by transmission electron microscopy (TEM), and no phase-separated material has been observed. This result might be accounted for by either a too low PS/PDMS contrast, making micelles of the diblock hard to identify, or the selective accumulation of the diblock at both PS surfaces, the observation of which has been quite a problem. Nevertheless, Rutherford backscattering spectrometry (RBS) has proved that 0.3 and 3.0 wt % block copolymer in PS are located at the surface of PS films.[28]

XPS has provided the concentration gradient of PDMS at the air surface of spin-cast films, from 1 to 6 nm depth (Figure 3). The PDMS profiles fit very well an exponential decrease, according to which most of the copolymer is at the surface to the exclusion of the bulk beyond a ca. 27 nm depth. This value actually corresponds to the highest diblock content (10 wt %). Figure 3 confirms data from Figure 2, according to which the air side of spin-cast films is far from being saturated in PDMS even when PS is modified with 10 wt % diblock copolymer. The effect of annealing will be interestingly discussed later.

The copolymer depth profile of PS films containing poly(S-*b*-DMS) has then been analyzed by SIMS (Figure 4). For solvent-cast films, the depth profiling has been recorded from each surface of the peeled films down to a depth where no PDMS remains detectable (Figure 4a,b), whereas, for some spin-cast films, it has been obtained in situ from the air side down to the metal side, by erosion of the whole thickness of the nonpeeled films (Figure 4c). SIMS data are perfect agreement with both RBS and XPS. Indeed, most of the diblock copolymer is located in the top surface layers at the air/polymer interface (75 and 60% for solvent- and spin-cast films, respectively), whereas the exceeding amount is accumulated at the polymer/aluminum interface, with no copolymer being left in the intermediate bulk. It must be noted that depth profiling of Si as reported in Figure 4a–c is in complete agreement with oxygen-based data. Comparison of parts a and c of Figure 4 confirms that a nonequilibrium situation on the

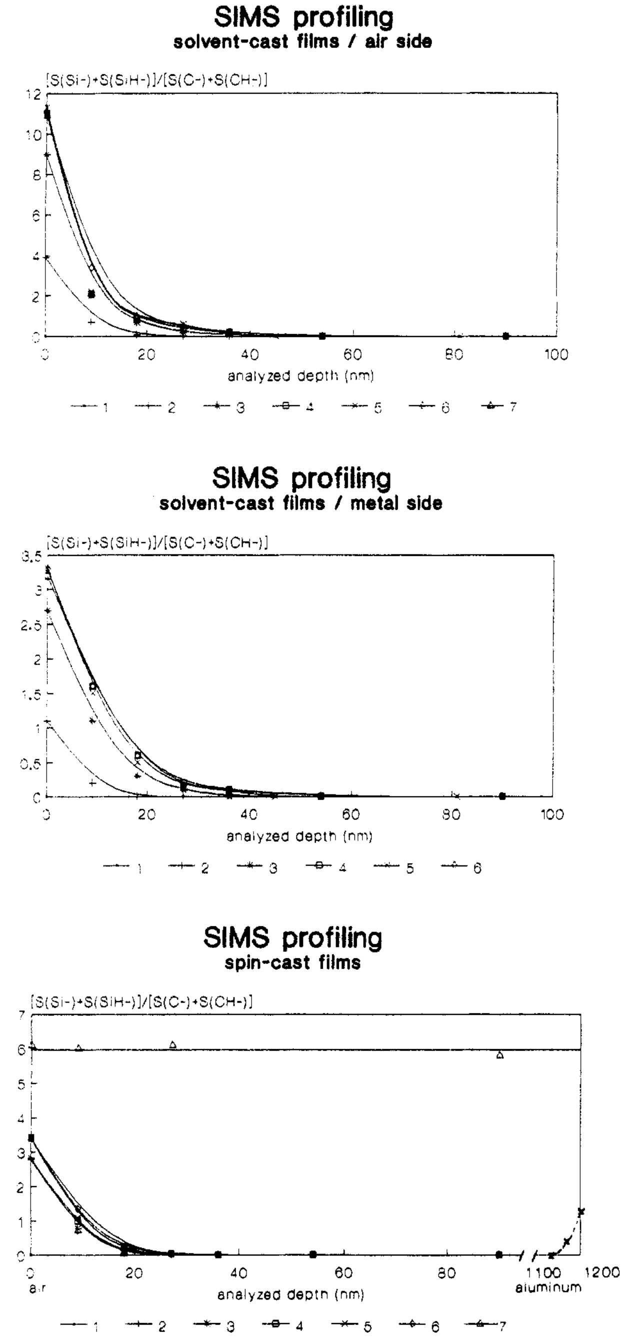

Figure 4. Atomic ratio for films of poly(S-*b*-DMS)/PS blends versus analyzed depth (nm). SIMS analysis: (1) pure PS; (2) 0.2 wt % poly(S-*b*-DMS)/PS; (3) 0.5 wt % poly(S-*b*-DMS)/PS; (4) 2.0 wt % poly(S-*b*-DMS)/PS; (5) 5.0 wt % poly(S-*b*-DMS)/PS; (6) 10 wt % poly(S-*b*-DMS)/PS; (7) pure poly(S-*b*-DMS).

air side is frozen-in by a very fast solvent evaporation (spin-casting compared to solvent-casting), as already highlighted in Figure 2. Depth profiles of the air side and metal side of solvent-cast films show a remarkable parallelism of the diblock accumulation at both interfaces when the copolymer content is increased. The accumulation is, however, 4 times less important on the metal side with respect to air.

Imaging of the Polystyrene Film Surface. The air-side polystyrene surface has been chemically imaged by high spatial resolution ion microscopy (Cameca 4F-ion microscope). The images of Si^- and O^- are quite homogeneous, which shows that no phase separation, micelle, or any other substructure exists at the PS/air interface, at least on a few microns scale. Clearly, imaging substantiates the previous conclusions according to which the PS surface is completely and homogeneously covered with PDMS, on the air side.

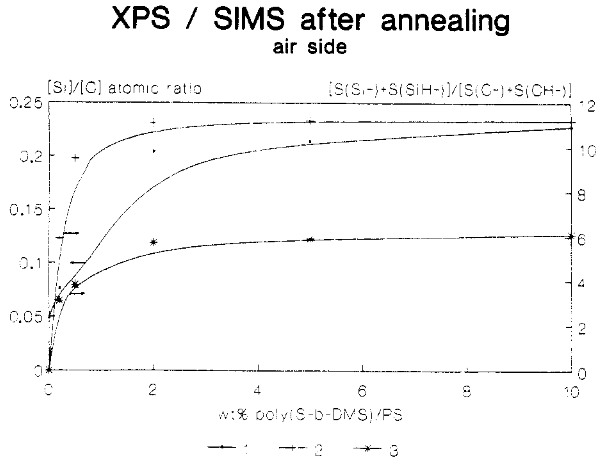

Figure 5. Surface atomic ratio on the air side of films of poly(S-*b*-DMS)/PS blends versus copolymer concentration (wt %). XPS analysis after a 10-h annealing at 200 °C: (1) Spin-cast films. Surface atomic ratio on the air side of films of poly(S-*b*-DMS)/PS blends versus copolymer concentration (wt %). SIMS analysis after a 10-h annealing at 200 °C: (2) solvent-cast films; (3) spin-cast films.

Annealing Effects. Polystyrene films have been annealed at several temperatures (from 120 to 200 °C) for various periods of time (up to 10 h). Whatever the method of surface analysis which has been used (contact angle measurement, XPS, SIMS, or RBS), it is obvious, e.g., from Figures 2 and 5, that annealing has no effect on the surface characteristic features of the air side of solvent-cast films. Undoubtly, an equilibrium state is reached as soon as the film is deposited at room temperature. Otherwise, after thermal treatment, spin-cast films reach the same equilibrium as solvent-cast films as supported by the comparison of Figures 2 and 5 (XPS data). Even though SIMS results confirm this tendency, the PDMS content on the air side remains, however, significantly smaller compared to the surface composition of solvent-cast films. In order to account for this discrepancy between XPS and SIMS data, it should be emphasized that the depth probed by each technique is not the same (ca. 4 nm for XPS and ca. 1 nm in the case of SIMS), together with an accumulation equilibrium which takes place at 25 °C in solvent-cast films compared to 200 °C for the annealed (and rapidly cooled down) spin-cast films. Furthermore, concentration profiles on the air side of annealed solvent-cast films (Figure 7a compared to Figure 4a) confirm the previous conclusion, according to which the equilibrium is reached as soon as the film is solvent-casted at room temperature. When the concentration profile of the spin-cast films on the air side is concerned, the discrepancy between XPS (Figure 6 compared to Figure 3) and SIMS (Figure 7b versus Figure 4a,c) is again obvious, since, in agreement with composition, the same equilibrium as in the solvent-cast films is not observed when probed by SIMS, although it is when investigated by XPS. It is worth pointing out that the experimental depth distribution of the PDMS block from the surface to the bulk (XPS and SIMS) perfectly fits an exponential decrease, which is in a very good agreement with the predictions of the mean-field theory (eq 3[29] and Figure 8), where C_b and C_s are

$$C(z) = C_b + (C_s - C_b)\exp(-z/\zeta) \tag{3}$$

respectively bulk and surface concentrations, z is the depth from the surface, and ζ is a characteristic length.

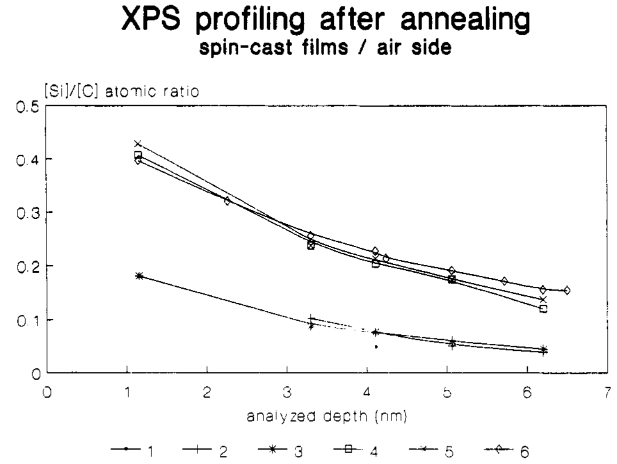

Figure 6. Atomic ratio on the air side of spin-cast films of poly(S-*b*-DMS)/PS blends versus analyzed depth (nm). XPS analysis after a 10-h annealing at 200 °C: (1) pure PS; (2) 0.2 wt % poly(S-*b*-DMS)/PS; (3) 0.5 wt % poly(S-*b*-DMS)/PS; (4) 2.0 wt % poly(S-*b*-DMS)/PS; (5) 5.0 wt % poly(S-*b*-DMS)/PS; (6) 10 wt % poly(S-*b*-DMS)/PS.

Conversely, the three-step power law predicted by the scaling theory (eq 4[30]) completely fails in the theoretical

$$\text{for } z < d, \quad C(z) = C_s$$

$$\text{for } d < z < z_{\max}, \quad C(z) = C_b + (C_s - C_b)(d/z)^{4/3}$$

$$\text{for } z_{\max} < z, \quad C(z) = C_b \qquad (4)$$

description of the experimental PDMS concentration gradient at the PS subsurface (Figure 8), where d is proportional to the chain length and $z_{\max}$ is proportional to the chain radius of gyration.

Finally, it is clear from the concentration profiles obtained after annealing that PDMS quantitatively migrates from the polymer/aluminum interface to a top layer at the air surface (ca. 26 nm thick in blends containing 10 wt % diblock).

Surface Tension of Poly(S-*b*-DMS)/PS Solutions in THF. In order to clarify how the above-mentioned surface equilibrium is achieved during the solvent-cast film deposition, the precursor solutions of poly(S-*b*-DMS)/PS in THF have been analyzed by tensiometry. According to these surface tension measurements (Figure 9), it appears that, even in THF solutions, the block copolymer is located at the surface. So, although THF is a good solvent for both PS and PDMS, reduction in the surface energy is a force strong enough to drive the PDMS block at the surface. Actually, the surface tension of THF is decreased from 26.4 to 24.8 mN/m when 10 wt % PS is substituted by the same amount of a 10/90 poly(S-*b*-DMS)/PS blend. The latter value is very close to that observed for the corresponding solvent-cast film (Figure 1). Thus, whatever the continuous phase (PS matrix, a selective "solvent" for PS blocks; THF, a common solvent for each block), the situation is quite similar: a strong decrease in the surface tension occurs down to a plateau, which would correspond to a "critical micellar concentration" of the copolymer in the range of 0.2 wt % (Figure 1, solid films; Figure 9, THF solutions). It is thus obvious that the surface composition of THF solutions foreshadows the surface situation in the PS films as long as they have been prepared by solvent-casting, which is a slow process preserving conditions close to the equilibrium. In sharp contrast, spin-casting is such a fast process that radial stresses are observed in the films and that accordingly any equilibrium state is prevented from occurring. It might be suggested that block copolymer molecules are tilted with respect to the film surface rather than being perpendicular to the surface as in solutions and solvent-cast films. Then, at a constant depth of analysis, a major part of the PS block could be seen by XPS analysis of spin-cast films in contrast to what happens for the solvent-cast counterparts (Figure 10).

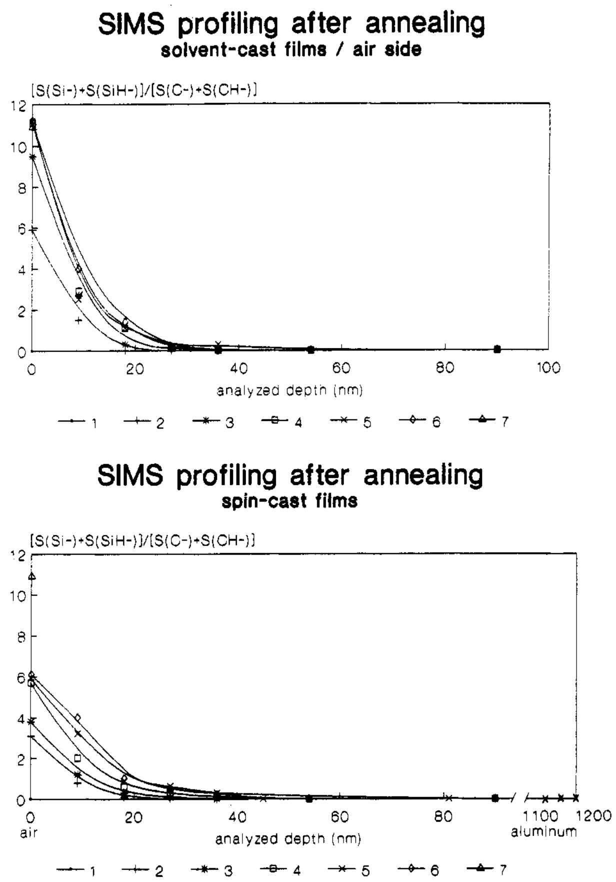

Figure 7. Atomic ratio on the air side of films of poly(S-*b*-DMS)/PS blends versus analyzed depth (nm). SIMS analysis after a 10-h annealing at 200 °C: (1) pure PS; (2) 0.2 wt % poly(S-*b*-DMS)/PS; (3) 0.5 wt % poly(S-*b*-DMS)/PS; (4) 2.0 wt % poly(S-*b*-DMS)/PS; (5) 5.0 wt % poly(S-*b*-DMS)/PS; (6) 10 wt % poly(S-*b*-DMS)/PS; (7) pure poly(S-*b*-DMS).

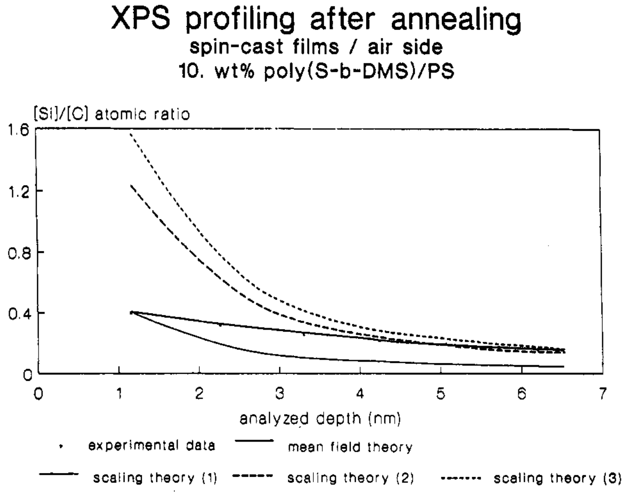

Figure 8. Depth profiles of the copolymer in poly(S-*b*-DMS)/PS blends: comparison of experimental data and theoretical predictions. Mean-field theory: $[\mathrm{Si}]/[\mathrm{C}] = 0.474e^{-z/5.62}$. Scaling theory: (1) $[\mathrm{Si}]/[\mathrm{C}] = 0.477z^{-4/3}$. (2) $[\mathrm{Si}]/[\mathrm{C}] = 1.50z^{-4/3}$. (3) $[\mathrm{Si}]/[\mathrm{C}] = 1.88z^{-4/3}$.

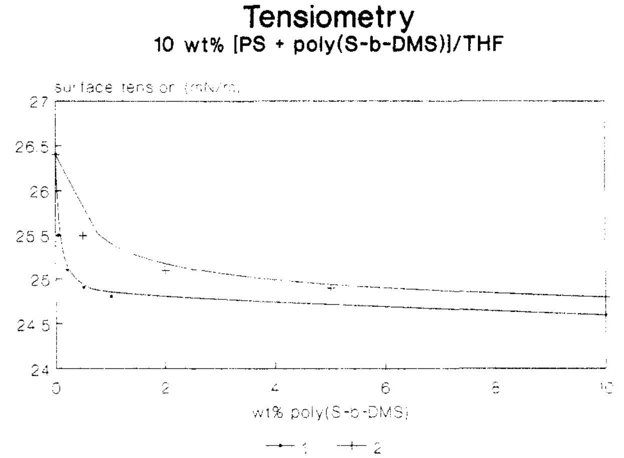

Figure 9. Surface tension of solutions of poly(S-*b*-DMS)/PS in THF (mN/m) versus copolymer concentration (wt %). Tensiometry at 25 °C. (1) wt % poly(S-*b*-DMS)/(PS + THF). (2) wt % poly(S-*b*-DMS)/PS.

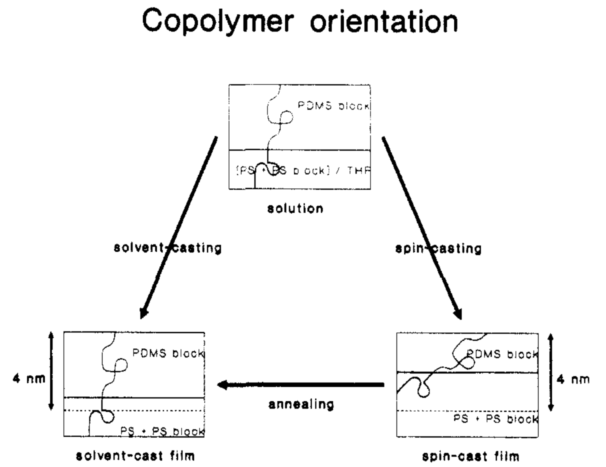

Figure 10. Schematic surface orientation of poly(S-*b*-DMS) in PS/THF solutions and in PS films.

Conclusion

Surface activity of a poly(S-*b*-DMS) copolymer added to a PS matrix has been investigated by various surface analytical techniques. According to both the surface energetics (derived from wettability and contact angles) and the surface composition (obtained by XPS and SIMS), an extreme surface enrichment in PDMS is observed at the air/polymer interface when very small amounts of the block copolymer are used (0.2–2.0 wt %). Accordingly, the PDMS block seems to cover completely the film surface on the air side. Surprisingly enough, the copolymer also accumulates at the interface between PS and the high surface energy substrate (glass, stainless steel, or aluminum) onto which the film has been deposited. The excess of diblock at the PS/substrate interface is, however ,less important than that at the air/PS surface. This work is in complete agreement with data published in the scientific literature about the surface activity of PDMS containing block and graft copolymers, at air/polymer interfaces.[5,8,31–39] This surfactant behavior has been observed to be dependent on the copolymer architecture and the nature of the polymeric partner of PDMS. The complete surface coverage by PDMS occurs at copolymer contents as low as 0.1–2.0 wt %.[33–37] None of the published works has emphasized the accumulation of a PDMS-containing block or graft copolymer at the interface with a high-energy substrate; the pure polymer matrix has anytime been reported to be in contact with this type of substrate.[33,40] What is known is the accumulation of a copolymer containing a polar polymeric component at the interface between a low surface energy polymer matrix and a high surface energy substrate.[40–43] In this respect, the data reported in this paper seem to be original. It must, however, be noted that poly(S-*b*-DMS) in excess at the PS/aluminum interface completely migrates to the air/polymer surface upon an appropriate annealing. Concentration profiles of the PDMS block from the surface confirm results of surface tension and surface composition. They are very consistent with the exponential decrease predicted by the mean-field theory but in complete disagreement with predictions of the scaling theory. Surface imaging (SIMS) of the air side surface of solvent-cast films in the concentration plateau region supports the complete and uniform coverage of PS with PDMS blocks. From the surface tension of the precursor solutions in THF, this particular surface situation already exists in solution and does not change significantly upon the slow solvent evaporation nor during the annealing of the solvent-cast films. Finally, the surface activity of poly(S-*b*-DMS) in spin-cast films is less effective but restored by annealing.

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