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Affinity of Polystyrene Films to Hydrogen-Passivated Silicon and Its Relevance to the T_g of the Films

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ABSTRACT: Qualitatively different thickness dependences have been observed in the glass transition temperature, T_g, of polystyrene (PS) films supported by hydrogen-passivated silicon (H−Si). It has been suggested that upon annealing at high temperatures in air, the polymer/substrate interface of these films (i.e., PS/Si), though buried underneath the PS layer, might be oxidized, rendering the films a different polymer/substrate interface (i.e., PS/SiO$_x$−Si), which may account for the different thickness dependences of the T_g observed. In this experiment, we examine if the buried substrate interface of PS/H−Si films can indeed be oxidized by annealing the films at 150 °C in air. Our result shows that a residual film does form on top of the H−Si surface, but it is a bound layer of PS. X-ray photoelectron spectroscopic (XPS) analyses and independence of the residual film on the initial PS thickness evidence that the H−Si substrate buried underneath a PS film is not oxidized by annealing. We discuss a possible explanation to how the different thickness dependences may be observed in the T_g of these films.

Introduction

As the interests in making nanoscale devices grow, numerous questions concerning the properties of materials under nanoconfinement have emerged. For polymers, a great number of measurements demonstrated that their structural[1−6] and dynamical properties[1,6−12] can be significantly different from those of the bulk when the polymers are confined in thin films with thickness on the order of nanometers. Despite the efforts made by a large number of researchers in the past 2 decades, the mechanism underpinning the unusual properties of polymer nanometer films remains elusive. One major obstacle arises from the inconsistent pictures brought about by different experiments about the properties of these films. A well-known example is the contradictory results found of the thickness dependences of the glass transition temperature, T_g, of polystyrene (PS) supported by hydrogen-passivated silicon (H−Si), which refers to silicon substrates where the native oxide capping layer has been removed by submerging them in an aqueous solution of hydrogen fluoride. Keddie et al.[13] found that the T_g of these films decreased with decreasing film thickness, h, and was reduced by more than 20 °C from the bulk value of ∼100 °C when h was decreased to 10 nm. On the other hand, Wallace et al.[14] found that the T_g of these films increased with decreasing h, and appeared to become more than 50 °C above the bulk T_g at $h = 9.1$ nm. It has been suggested[14] that the former result might be caused by the oxidation of the buried H−Si interface during the T_g measurement, which was carried out in air, whereby the result might actually mirror the T_g of PS supported by silicon covered by an oxide layer (denoted PS/SiO$_x$−Si below);[7−9] and PS/SiO$_x$−Si may have a different $T_g(h)$ than that of PS supported by H−Si (denoted PS/Si) as the polymer/substrate interactions in the former are broadly considered to be weaker. The proposed scenario, if valid, can have important implication about the

stability of polymer films. Specifically, result from van der Waals (vdW) potential calculation[15] shows that PS/Si films are stable, but PS/SiO$_x$−Si films are not, irrespective of how thin the oxide layer is. The question we want to address is whether the surface of an H−Si substrate buried underneath a PS film can be oxidized by annealing the PS/Si films in air. Such pursuit concerns broader questions about the thermal stability of polymer films besides the inconsistent results found by Keddie et al.[13] and Wallace et al.[14] on the T_g of PS/Si films.

Experimental Section

Polystyrene with weight-average molecular weight, M_w, ranging from 13.7 to 940 kg/mol and polydispersity index, $M_w/M_n \leq$ 1.16, were purchased from Scientific Polymer Products (Ontario, NY) and used without purification. We use Si (100), diced into 1.0×1.0 cm^2 pieces, as substrates. If SiO$_x$−Si substrates are desired, we submerge the as-purchased substrate in a piranha solution, i.e., H$_2$SO$_4$:H$_2$O$_2$ (7:3) preheated to 90 °C for 10 min. Afterward we thoroughly rinse the substrates in excessive deionized water and dry them with 99.99% nitrogen. This process removes the organic contaminants, leaving the silicon surface a native oxide layer covered with the Si−OH groups.[16] If H−Si substrates are desired, we submerged the substrates, precleaned by piranha as above, in a 2% aqueous solution of HF for 2 min and then rinse and dry them as described above. This procedure removes the native oxide layer and leaves the silicon surface terminated with Si−H groups.[17] The change in the chemical constituency is easily recognizable from the substrate surface changing from being hydrophilic to hydrophobic. The polymer films are spun cast from solutions of PS in toluene. The film thickness, varied by adjusting the solution concentration and spinning speed, is determined by ellipsometry. To determine if the PS/Si interface under the cover of the PS layer can be oxidized, we anneal the films at 150 °C for different times in air. Afterward we remove the polymer by rinsing the films in copious amount of toluene, which is a good solvent of PS then leave them submerged in a beaker of 100 mL of toluene for 10 min. We repeat this rinsing

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process two more times. We use ellipsometry to determine the thickness, $h_{residue}$, of any residual film remaining on the silicon. We check that $h_{residue} = 0$ for PS/Si films that have not been subjected to any annealing, confirming our rinsing procedure to be effective in removing the polymer from the substrate. To study the surface morphology of the residual film, we use tapping-mode atomic force microscopy (AFM). To characterize the chemical and molecular structure of the residual layer, we use X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF−SIMS). The XPS measurements were performed on a PHI 5800 ESCA system equipped with a monochromatic Al Kα X-ray source. All core-level spectra were referenced to the Carbon 1s hydrocarbon peak at 285.0 eV. The emission angle of the photoelectrons (i.e., the angle between the sample surface normal and the axis of the analyzer) was 45°, corresponding to a sampling depth of approximately 4.5 nm. The ToF−SIMS spectra were taken from a Physical Electronics PHI 7200 ToF−SIMS spectrometer. The primary Cs⁺ ion source was operated at 8 kV and the scanning area was 200 μm × 200 μm. The total ion dose for each spectrum was less than 4×10^{11} ion/cm^2. Charge compensation was realized by low-energy (0−70 eV) electron flooding. The mass resolution (M/ΔM) was about 5000 in the films studied.

Results and Discussions

In Figure 1, the solid circles represent the thicknesses of the residual films, $h_{residue}$ obtained from PS/Si films with $M_w = 44.1$ kg/mol and initial thickness, $h_0 = 200$ nm, plotted as a function of annealing time, t. The open circles represent the thickness of the residual film founds on bare H−Si substrates (for which $h_0 = 0$) subjected to the same annealing and rinsing procedure. While a residual film clearly develops in both samples, the former is more than six times thicker than that of the latter. In addition, the residual film from the PS/Si continues to grow until about 50 h before it saturates, but that from the bare H−Si saturates much sooner after only about 4 h. These results are inconsistent with the notion that the $h_{residue}$ originates from the growth of an oxide film on top of the H−Si substrate. Instead, because the residual film grows more prominently in the presence of a PS film, this suggests that the residual film from PS/Si most probably bears its origin from the polymer. We make preliminary verification on whether the residual film grown from the PS/Si is silicon oxide or organic by submerging it in an aqueous solution of HF (a solvent of silicon oxide) and then piranha (a solvent of organic substances). The film survived the former, but not the latter, demonstrating its organic nature. Figure 2a shows a representative AFM topographic image of the residual films obtained by annealing the PS/Si specimens. As seen, the film surface is uniform across the image showing no sign of dewetting, consistent with the small value of 0.49 nm found of the root-mean-square roughness of the film. We also find that we can scratch part of the film off with a razor blade, as the topographic image (Figures 2b) and cross-sectional profile (Figure 2c) of the resultant film show. The thickness of the film, 5.2 ± 0.1 nm as determined from the cross-sectional profile agrees well with the thickness value obtained by ellipsometry. All these show that the residue films are "soft" and yet stable against dewetting and rinsing by a good solvent.

To determine the chemical composition of the residual film, we use XPS and ToF−SIMS. Shown in Figure 3 is the XPS spectrum of a residual film obtained from a PS/Si annealed in air for 4 h. The prominent peak seen in the spectrum, with a binding energy of 285.0 eV, is identifiable with the C 1s peak typically found in hydrocarbons. The shakeup peak, corresponding to the π−π* transition of the phenyl group with a binding energy between 291.0 and 293.0 eV is also clearly discernible. Figure 4 shows the ToF−SIMS spectrum analyzed from the low-mass fragments
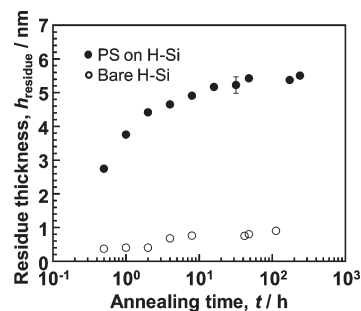

Figure 1. Annealing time dependence of the thickness of the residual film, $h_{residue}$ obtained from PS/H−Si (solid symbols) and bare H−Si (open symbols). The annealing was carried out at 150 °C in air. The PS has $M_w = 44.1$ kg/mol and initial thickness, $h_0 = 200$ nm.
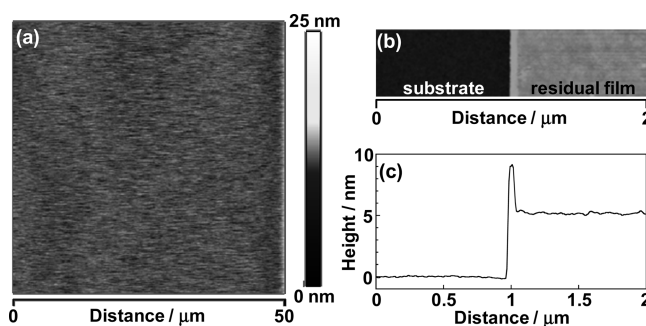

Figure 2. (a) AFM topographic image of a residual film obtained from a PS/Si sample after annealing for 32 h before rinsing by toluene. (b) Topographic image of the same film at where part of it has been scratched by a razor blade. (c) Average cross-sectional profile of part b.
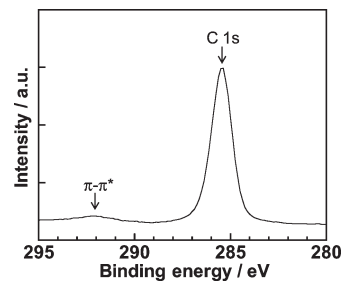

Figure 3. X-ray photoelectron spectroscopic C 1s narrow scan of the residual film obtained from a $M_w = 44.1$ kg/mol PS/H−Si film after annealing at 150 °C for 4 h followed by thorough rinsing in toluene.
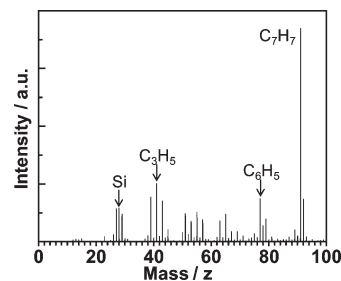

Figure 4. Positive ToF−SIMS spectrum of a residual film similarly prepared as that used in acquiring the XPS data shown in Figure 3.

sputtered from a residual film, similarly prepared as the one studied by XPS. The spectrum is largely consisted of peaks corresponding to hydrocarbon fragments as C$_3$H$_5^+$, C$_6$H$_5^+$, and C$_7$H$_7^+$, which are characteristic of specimens containing
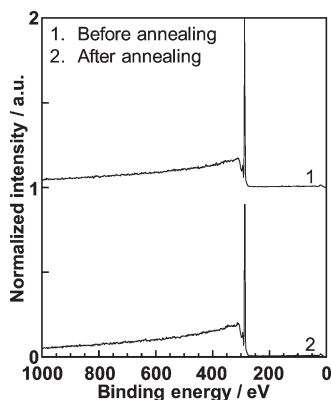
Figure 5. X-ray photoelectron spectroscopic wide scan of a thick PS film (ca. 200 nm) with M_w = 44.1 kg/mol spin-coated on PS/H−Si: (1) before and (2) after annealing at 150 °C for 4 h.

polystyrene.[18] The data of XPS and ToF−SIMS together provide compelling evidence that the residual film is polystyrene.

We have also compared the XPS spectra of a ∼200 nm thick PS/Si film acquired before and after annealing in air for 4 h. Since the escape depth of the C 1s and O 1s photoelectrons is 7.1 and 5.9 nm, respectively,[19] the measurement would reveal if there is any oxidation of the PS from the annealing, without interference of possible signals from the PS/Si interface. The result is shown in Figure 5. There, one can see that the O 1s peak, with a binding energy of 532.0 eV, is not noticeable in either spectrum. More-over, from the narrow scans obtained about the C 1s and O 1s peaks, we find that both have the same C: O atomic ratios of 1: 0.004. These observations show that there is no detectable degradation of the PS films from thermal oxidation in the annealing process. The trace amount of oxygen found is probably due to some oxide contaminants on the film surface.

To verify if the H−Si substrate beneath the PS layer had been oxidized in the PS/Si film examined in Figure 3, we compare the Si 2p and O 1s XPS signals obtained from this film with those of a freshly spun-cast (unannealed) PS/Si film with a similar thickness of ∼4 nm. By using a similar thickness as the residual film, the atomic concentrations of the annealed and unannealed films can be compared directly. Because the film thickness is less than the escape depth of the O 1s and Si 2p photoelectrons (which are 5.9 and 8.0 nm, respectively[19]), the measurement can provide an indication of whether there has been oxidation of the PS/Si interface when the PS/Si film was annealed. We found that the O 1s peak is present in the XPS spectrum of both films; within experimental uncertainty, the Si:O atomic ratios are the same and equal to approximately 3:1. In both films, the PS was spin-coated onto the H−Si substrate within 30 min after the substrate was treated by HF. Our observations thus suggest that oxidization of the H−Si surface took place soon after the substrate was rid of the native oxide coating and exposed to air, but this process was effectively suppressed when a PS layer was deposited on top. We have also checked that the growth of the residual film was unchanged even if the PS/Si films were annealed in vacuum. In addition, variations of the initial PS thickness, h_0, by as much as a factor of 2 (for $h_0 > \sim 1R_g$) has unnoticeable effect on the growth rate or equilibrium thickness of the residual films. Since the diffusional flux of a gas through a porous film is known to fall off as one over the film thickness,[20] if the H−Si interface had been oxidized due to the oxygen diffused through the PS, the growth of the residual film should display a visible dependence on h_0. All of these consistently show that the H−Si interface was not oxidized when the PS/Si films was annealed at 150 °C in air.

To gain some insight about the chain conformation inside the residual film, we examine the M_w dependence of the equilibrium
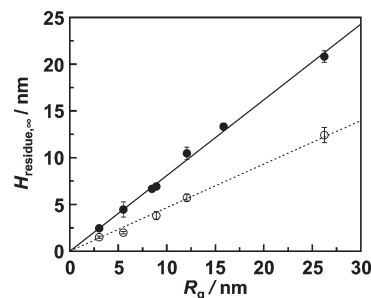

Figure 6. R_g dependence of the equilibrium residue thickness, $h_{residue,\infty}$ for residual films obtained from PS/Si (solid circles) and PS/SiO$_x$−Si (open circles) In this plot, the value of R_g is deduced from the weight-average molecular weight of the polymer.

thickness of the residual film, $h_{residue,\infty}$, namely the asymptotic plateau value of the residue thickness upon long annealing times. In this study, we use initial PS thicknesses, h_0 that exceed $4R_g$, where R_g is the gyration radius of the polymer. Figure 6 shows the plot of $h_{residue,\infty}$ versus R_g (solid circles). We find that the data can be fitted well to the expression, $h_{residue,\infty} = aR_g$, with the least-squares fitted value of a being 0.81. This finding is consistent with the notion that a polymer chain with N segments near a flat impenetrable wall should maintain the reflecting random-walk statistics and makes $\sim N^{1/2}$ contacts with the wall.[21] Persistence of the $h_{residue,\infty} \sim R_g$ dependence from R_g = 2.7 to 25 nm rules out cross-linking of the polymer by thermal annealing as a possible cause for the formation of the residual film for otherwise $h_{residue,\infty}$ should show little to no dependence on R_g. We also do not think that there had been significant chain cessation from thermal degradation as the data follows the fitted curve down to the $h_{residue,\infty} \rightarrow 0$ limit. The fact that the residual films survive rigorous rinsing by a good solvent suggests that the PS chains in the films are not only adsorbed, but are in fact bound to the substrate. For comparison, we carry out similar measurements on PS/SiO$_x$−Si films. Although the polymer/substrate interactions in this system are commonly considered weak or even repulsive,[22] we find that the $h_{residue,\infty}$ of these films is by no means negligible (open circles in Figure 6). Least-square fitting indicates the relation, $h_{residue,\infty} = 0.47R_g$ as represented by the dotted line in Figure 6. This result shows that the value of $h_{residue,\infty}$ for PS/SiO$_x$−Si is 58% of that for PS/Si. The present finding that $h_{residue,\infty}$ scales linearly with R_g in both systems despite of their disparity in the polymer/substrate affinity is in keeping with previous studies by simulation.[23,24]

We are unaware of any published work on the binding of PS homopolymers to silicon. Though relatively abundant studies have been reported on the binding of poly(methyl methacrylate) (PMMA) homopolymer to silica.[21,25−27] Durning et al.[21] mea-sured the residue thickness of PMMA on hydroxylated quartz by neutron reflectivity and found a M_w-dependence similar to the one found here. Infrared vibrational spectroscopy confirmed that the strong affinity of PMMA to quartz was due to hydrogen bonding formed between the carbonyl side groups of PMMA and the surface hydroxyl groups of quartz.[26,27] On the other hand, it is not at all obvious if similar short-range, strong bonds can be formed between PS and H−Si given their chemical structures. The short-range binding found between PS and SiO$_x$−Si is even more surprising. The former is hydrophobic while the latter is hydrophilic. Moreover, SiO$_x$−Si is known to dewet PS. The wetting stability of a thin film system is generally governed by its interfacial potential, $G(h)$. Below we discuss the interfacial potential of the PS/Si and PS/SiO$_x$−Si systems based on our findings.

The value of $G(h)$ at $h \approx 0$ is determined by short-range forces and best described by the spreading coefficient. Pertinent to PS/Si
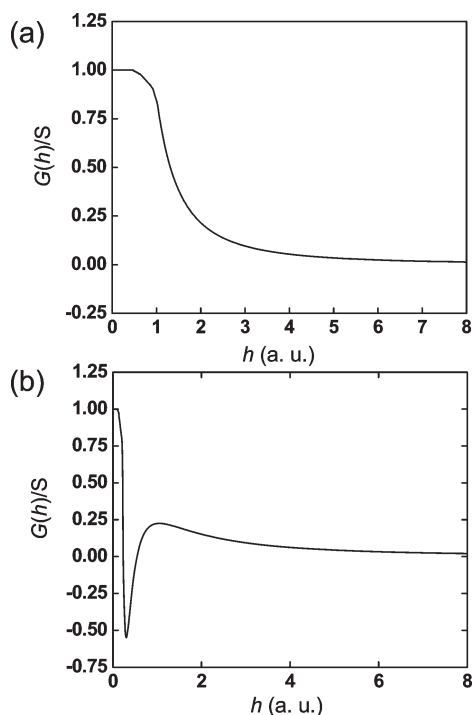
Figure 7. Sketch of the interfacial potential, $G(h)$, normalized by the spreading coefficient, S, of PS/Si (a) and PS/SiO$_x$–Si (b). The spreading coefficient is assumed to be positive in both cases.

and PS/SiO$_x$–Si, the spreading coefficient is given by:

$$S = \gamma_{\text{sub}} - (\gamma_{\text{PS}} + \gamma_{\text{PS/sub}}) \qquad (1)$$

where γ_{sub}, γ_{PS}, and $\gamma_{\text{PS/sub}}$ are the unit-area surface energies (or surface tensions) of the air/substrate, air/PS and PS/substrate interface, respectively. When S is positive, the surface energy of the substrate is bigger than the sum of those of the air/PS and the PS/sub interfaces whereby exposure of the substrate surface by holes formation is energetically unfavorable. The fact that no holes are found in the residue films (e.g., Figure 2) shows that the spreading coefficients in these films are positive. At long-range, namely at distances greater than a few Å, the interfacial interactions are governed by the van der Waals (vdW) potential.[15] Previous studies[15,28] showed that liquid films, irrespective of the sign of the spreading coefficient, are unstable to spontaneous formation of undulations in the film thickness h if the second derivative of the interfacial potential, $G''(h)$, is negative. For PS/Si, $G''(h)$ is positive for all values of h. This, together with the fact that the spreading coefficient is positive suggest an interfacial potential of the PS/Si system as shown in Figure 7a, with which the films would be stable at all film thicknesses. But for the PS/SiO$_x$–Si system, a previous study shows that $G''(h)$ is negative when h is less than about twice the thickness of the oxide layer.[15] Given this, and that the spreading coefficient of this system is positive, the interfacial potential corresponds to the one shown in Figure 7b). Interfacial potentials as such, with a minimum at a finite thickness, are known to render the films unstable to autophobic dewetting.[29] This may explain why oxide coated silicon substrates dewet PS film despite of the strong binding observed here between them. Another point to note is that a full development of the polymer–substrate binding requires several hours to accomplish as the data of Figure 1 shows. If the rupturing rate of a film far exceeds the rate by which the bindings take place, the effect of polymer–substrate binding would be preempted in that film.

In a recent experiment,[5] the viscosity of thick PS/H–Si films ($h > 4R_g$) was found to be the same as the bulk. This suggests that the mobility of the polymer chains is not reduced despite of the fact that their segments can form strong bonds to the substrate. In that measurement, the viscosity of the films was deduced from the time-evolution of their surface structure in the course of 0–4 h since they were prepared from spin-coating. We notice that this duration is of the same order as the time for the residual film to develop (Figure 1), and yet no time-variation in the viscosity was found in the films.[5,30] This observation suggests that binding of the PS to the substrate surface has little to no effect on the overall mobility of the films. This result is in keeping with a recent finding that the T_g of an end-grafted PS brush film was within a few °C of the bulk T_g.[31]

Given our results, it cannot be concluded why the thickness dependence of the T_g of PS/Si attained by Keddie et al.[13] and Wallace et al.[14] should be different. In both experiments, the T_g was determined by intersecting the best fitted straight lines to the data of $\Delta h/h_0$ vs T (where $\Delta h = h(T) - h_0$) below and above the T_g. In the experiment of Keddie et al., ellipsometry was used to measure the film thickness as the temperature was swept at 2 °C/min; in the latter experiment, X-ray Reflectivity was used as the temperature was changed in 10 °C incremental steps with 45 min allowed for the system to equilibrate at each temperature. Previous experiments[32,33] have found that the $\Delta h/h_0$ vs T behavior of PS/SiO$_x$/Si films depends strongly on the thermal history and heating rate. Specifically, the slope of the data (or the thermal expansion coefficient) in the glassy state was found to exhibit negative, zero and positive values depending on the circumstance, which can be attributed to the slow structural relaxations of these films.[32,33] For PS/Si, the glassy thermal expansion coefficient attained at 2 °C/min by ellipsometry was found to increase with decreasing h and approach the value of the liquid state as h approached 10 nm.[34] On the other hand, the same quantity measured at < 0.22 °C/min (= 10 °C/45 min by X-ray reflectivity) was constant, independent of h.[14] We believe that the discrepancy in the thickness dependence of the T_g of PS/Si found between refs 13 and 14 probably has to do with the rate and history dependence of the thermal expansion coefficients of the films.

Conclusion

We have observed the formation of a bound PS layer on both H–Si and SiO$_x$–Si upon annealing the films with initial thicknesses $> 4R_g$ at 150 °C. The thickness of the PS residual films increases with annealing time until it reaches an equilibrium value, $h_{\text{residue},\infty}$. For PS/Si, $h_{\text{residue},\infty}$ varies with the R_g of the polymer according to $h_{\text{residue},\infty} = 0.81R_g$; but for PS/SiO$_x$–Si, $h_{\text{residue},\infty} = 0.47R_g$. X-ray Photoelectron Spectroscopy indicates that oxidation of the H–Si substrate buried underneath a PS film does not take place by annealing the PS/Si film in air. While the binding of PS to the substrate suggests that the mobility of the bound polymer chains should be decreased, the overall mobility of the film may still be enhanced due to dominance of the surface mobile layer, consistent with the reduction of the T_g of PS/Si observed by Keddie et al.[13] The different result found by Wallace et al.,[14] which essentially shows that the PS/Si films display a different thermal expansion behavior when they are heated at a much reduced rate, is probably a result of the slow structural relaxations known of these films.

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