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Thermally driven collapse of a polymer brush in a polymer matrix

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The segment density profile of end-functionalized deuterated polystyrene (d-PS) brush in a miscible poly(vinyl methyl ether) (PVME) polymer matrix was studied using neutron reflectivity. Brushes were chemically anchored to a silicon substrate. PVME has a favorable interaction with PS at room temperature. As the temperature increases, the interaction between PS and PVME becomes more unfavorable until in the bulk phase separation would occur. From the reflectivity experiments, it was found that the PVME was expelled from the brush as the temperature was increased. This process was reversible for temperatures up to 90 °C; above this the volume fraction in the brush approached unity and macroscopic dewetting occurred. The height of the brush was sufficiently well predicted by a scaling theory, which predicts a cube root dependence on the Flory-Huggins interaction parameter. [S1063-651X(99)08404-4]

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I. INTRODUCTION

The adsorption of polymer chains from solution to surfaces and interfaces is an active subject of study in polymer physics [1–3]. The character of a polymer/polymer or polymer/nonpolymer interface can be altered by the addition of an interface-active component to a polymer phase. The use of ‘‘compatibilizers’’ has become important in improving multi-phase polymer blends with a potential impact on the commercial use of these materials [4–7].

The interfacial agent may be a polymer that is miscible with a polymer matrix and adsorbs preferentially to the interface from one of its ends, forming what is commonly called a polymer ‘‘brush.’’ The study of polymer brushes is important since the molecular weight of the tethered chains and the interaction between the polymer chain ends at the interface can provide the interface with desired features. For example, the brush and its extension in the polymer matrix determines the strength of adhesion between the polymer and nonpolymer phases. Characteristics of the brush profile are influenced by the molecular weight of the attached chains, the molecular weight of the solvent, and the areal density of the brush (defined as the number of molecules per unit area of the interface). The scaling description developed by de Gennes is particularly transparent in showing the influence of the surrounding matrix and areal density of grafted chains on the extension of the molecules from the plane of attachment [8]. Another approach to the study of the density profile of the brush is based on the self-consistent field theory, developed by different authors [2,9–13].

The study of brushes in solution has been pursued in detail in the last few years [14–22], while less attention has been dedicated to polymer brushes in melts. In this case a layer of grafted chains is in contact not with a solvent but with a dense polymer melt. Most of the experimental work in this latter case has been carried out on polymer molecules grafted on solid substrates such as silicon and mica [23–32]. Typically the polymer is grafted to the surface by a short block of adsorbing copolymer or by a functional end-group that exhibits affinity with the surface. The end-adsorbed layer can be obtained by physical or chemical bonding to the surface. In the chemical bonding case, the polymer is grafted onto the substrate via permanent covalent bonds and the surface coverage is fixed.

In a miscible matrix, the brush is quite stretched in the matrix [8], and is laterally uniform. As the interaction between brush and matrix polymer is changed from favorable to unfavorable, for example by changing temperature, the brush first becomes less extended and forms a sharper interface with the matrix. For yet larger degrees of immiscibility, recent computer simulations and theory suggest the possibility of lateral microphase separation within the brush [33,34].

The present paper reports the results of an investigation in which the response of the brush to temperature changes was studied with the neutron reflection technique. Neutron reflection is an ideal technique since the contrast between the hydrogen and deuterated components gives a depth resolution of few Å. The system used was a d-PS brush chemically grafted to a silicon substrate, in a matrix of poly(vinyl methyl ether) (PVME). At room temperature PVME has a favorable thermodynamic interaction with PS. As the temperature increases, the interaction becomes increasingly less favorable. Within the temperature range that χ is negative, these two polymers are miscible for all molecular weights. The phase diagram has a lower critical solution temperature (LCST). Kinetic studies of the brush profile as a function of temperature were performed. The interfacial widths between d-PS/PVME extracted from the fitting of the reflectivity measurements were compared with a scaling prediction.

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II. SCALING PREDICTIONS

In this section, scaling law predictions for the grafted layer in a solvent are outlined. This scaling analysis due to de Gennes [8], and developed by Leibler in the context of block copolymers [35], distinguishes different regimes depending mainly on the grafting density and molecular weights of the polymers.

Grafted polymer chains of degree of polymerization N_B, attached by one end to a surface, are considered. The statistical segment length of the tethered molecules is a and the brush is in contact with a surrounding polymer matrix of degree of polymerization N_A.

Two related quantities are normally used to characterize the number of molecules in the adsorbed layer. The first is the interfacial excess, defined in terms of the brush volume fraction with the following expression:

$$z^* = \int_0^\infty (\Phi_b(z) - \Phi_\infty)\, dz, \tag{1}$$

where $\Phi_b(z)$ is the brush volume fraction at a distance z from the interface and Φ_∞ is the equilibrium volume fraction of the molecules attached to the surface in the bulk matrix. If strong adsorption is considered, this implies that Φ_∞ is very small, and in the case of a chemically attached polymer brush is zero. z^* is therefore the integral of the brush volume fraction profile. An areal density of the adsorbed molecules can be defined as $\Sigma = z^*/N_B \nu_0$, where ν_0 is the segmental volume. A dimensionless grafting density σ is normally defined as the fraction of surface sites that are occupied by the adsorbing ends of the B molecules. This is the second quantity mentioned above. The expression for σ is

$$\sigma = \frac{z^*}{N_B a}. \tag{2}$$

The chains are surrounded by polymer matrix molecules with degree of polymerization N_A. At low values of the surface excess, each chain is essentially independent of its neighbors, forming what is normally called a ‘‘mushroom,’’ with the radius of the mushroom being $N_B^{3/5} a N_A^{-1/5}$ for $N_A < \sqrt{N_B}$. In the case $N_A > \sqrt{N_B}$ the mushroom reaches the ideal unswollen random walk $N_B^{1/2} a$ due to the chain screening effect. This region is defined by an upper limit on the grafting density σ of N_B^{-1}. As the grafting density increases, the anchored chains start to interact and if $N_A \sim N_B^{1/2}$, the chains are then stretched in an attempt to minimize the unfavorable interactions.

For grafting density $\sigma > N_B^{-6/5}$, a ‘‘mushroom-brush’’ transition occurs. In the brush phase, the height of the brush is given by the balance between the stretching energies and the excluded volume interactions between the chains of the brush. The height is therefore larger than the radius of gyration of the brush molecules and is given by

$$h \sim N_B a \sigma^{1/3}. \tag{3}$$

If the matrix degree of polymerization is much higher than that of the brush, screening effects are important and the brush height is still characterized by the ideal random walk size. When the degree of polymerization of the matrix increases and becomes larger than that value of the brush chains, it is expected that the polymer matrix chains are expelled from the brush, leading to the ‘‘dry brush’’ regime. When the coverage satisfies $\sigma > N_B^{-1/2}$, the profile is insensitive to the solvent molecular weight and the height of the polymer brush scales as

$$h \sim N_B a \sigma, \tag{4}$$

corresponding to the brush forming an unmixed layer at the interface. The density profile is however, not expected to be of a step kind; some penetration of the brush by the matrix chains still takes place.

The case of a nonzero χ situation was extended by Brown, Char, and Deline [36]. The mixing free energy per brush chain is given by

$$\frac{F_{mix}}{kT} = \frac{hD^2}{a^3 N_A} \phi_{N_A} \ln \phi_{N_A} + \chi N_B \phi_{N_A}, \tag{5}$$

where h is the brush thickness, D the distance between attachment sites for the brush and is given by $a\sigma^{-1/2}$, and ϕ_{N_A} is the volume fraction of the solvent in the brush. The brush height h is given by minimizing the total free energy $F_{mix} + F_{el}$, where the term F_{el} represents the elastic energy that resists the brush stretching. The condition $\phi_{N_B} = 1 - \phi_{N_A}$ is considered. The elastic energy assumed by de Gennes takes the form

$$\frac{F_{el}}{kT} = \frac{h^2}{R_o^2} + \frac{R_o^2}{h^2} \tag{6}$$

with $R_o = N_B^{1/2} a$. In the dilute brush case (ϕ_{N_B} is small), considering that for large solvent chain often $-\chi \phi_{N_A} \gg 1$, and for significant stretching $[(R/h)^4 \ll 1]$, the brush height h is found to scale as

$$h \sim \left(-\frac{\chi}{2} \right)^{1/3} N_B a \sigma^{1/3}, \tag{7}$$

where N_B is the degree of polymerization of the brush chains, χ is the interaction parameter, σ is the grafting density, and a is the step length. The height of the brush then scales as $\chi^{1/3}$ and $\sigma^{1/3}$.

III. EXPERIMENTAL SECTION

Carboxy-terminated deuterated polystyrene [d-PS-(COOH)] of molecular weight (MW) equal to 100 000 and polydispersity M_W/M_N of 1.1 was obtained from Polymer Laboratories. Deuterated PS was chemically attached to a silicon surface. The aim of the chemistry was to covalently bond d-PS molecules via their ends to a silicon surface. This process is known as ‘‘grafting’’ and the polymer chains attached to the surface as ‘‘grafted’’ polymer. To chemically graft mono-carboxy-terminated deuterated polystyrene [d-PS-(COOH)] onto silicon substrates the following procedures have been applied [24]. The carboxy-terminated PS needed to be modified to a different end-group capable of reacting with the silicon substrate. A chemical reaction was therefore used to change the mono-carboxy terminated PS into triethoxysilane-end-capped polymer chains that react at a silicon oxide surface to form covalent bonds. The silane group combines the organic chemistry of organofunctional groups with inorganic chemistry of silicates, being in this way the bridge between mineral substrate and organic material. The reaction was performed in the following steps: 0.25 g of 2-chloro-1-methylpyridinium iodine (CMPI), 0.5 ml of tributylamine, 0.5 ml of N,N′-dimethyl-1,3-propanediamine, and 1 ml of (3-isocyanatopropyl) triethoxysilane, each in 100 ml of dichloromethane, were deposited in separate reaction vessels. d-PS-COOH (0.25 g) was dissolved in dichloromethane in another reaction vessel. A 1 ml aliquot of each of the CMPI, tributylamine, and diamine solutions were added and the mixture was stirred and allowed to react overnight. Then 2 ml of the isocylate solution was added and the mixture allowed to react for a further 2 h. The modified polymer was then precipitated out with methanol and centrifuged. The supernatant liquid was then removed and the precipitate washed and redissolved in toluene. The modified solution obtained in this way, was then spun-cast onto a native oxide silicon surface, forming normally a layer of thickness 300–500 Å. The SiO_2 thickness was between 20 and 30 Å for all samples, and this was measured with ellipsometry. The samples were annealed in vacuum at a temperature well above the bulk T_g, for varying lengths of time. The annealing temperatures used were 130 °C and 180 °C. The polymer not grafted was removed with toluene, by immersing the substrate in a volume of solvent typically 10^6–10^7 times larger than the volume of the dry excess polymer layer. The thickness of the grafted polymer was checked at various stages of the immersion of the sample in toluene, until no more changes of thickness were found (this was done with ellipsometry). The grafted layers obtained in this way had thicknesses ranging from ~70 to ~100 Å. Normally, it was found that for longer heat treatments, a greater number of chains were grafted to the surface and thus produced thicker films. The film thicknesses were measured with ellipsometry. On top of the grafted layer, the PVME was spun-cast obtaining a thickness of approximately 5000 Å. The PVME was obtained from Scientific Polymer Products and had a MW of 99 000 with a polydispersity of 2.12. Some samples were prepared using a PVME obtained from Polysciences that had a similar MW but higher polydispersity, equal to 3.1 (as we have determined using Gel Permeation Chromatography).

The PVME was supplied as 50% solution in water, and it was necessary to evaporate the water and to dissolve the polymer in toluene. This was accomplished by the use of a rotary evaporator where removal of most of the water was followed by addition of acetone to lower the viscosity to assist removal of more water. Excess toluene was then added and evaporation continued to ensure removal of acetone and any water and to reach an appropriate solid content for the toluene solution.

IV. RESULTS

In a favorable interacting matrix such as PVME, d-PS brush chains are expected to stretch out into the bulk and the volume fraction of the polymer matrix is expected to be much higher than the case of an immiscible matrix, such as PMMA. Neutron reflectivity experiments were performed on this system using the reflectometers CRISP and SURF, at the Rutherford Appleton Laboratory.

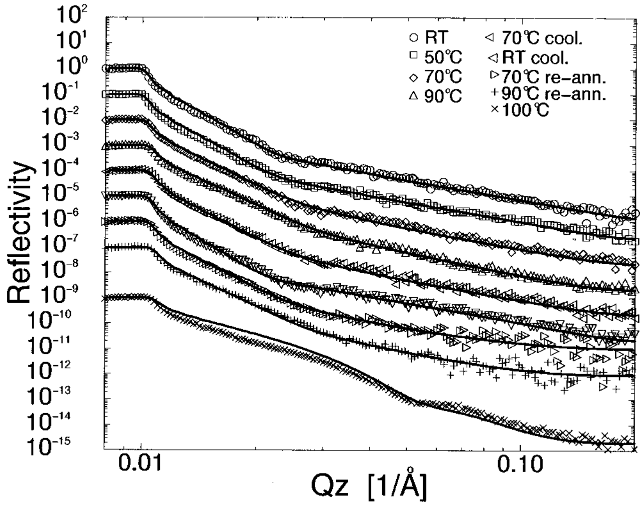

FIG. 1. Reflectivity curves for a d-PS brush of MW = 100 000 in a PVME matrix of MW = 99 000 at different temperatures for a sample with initial d-PS brush thickness of 85 ± 6 Å. The fits to a hyperbolic tangent function are also displayed as solid lines. The reflectivity curves have been scaled by factors of 100 from each other for clarity.

The experiments were conducted at different temperatures. A hot stage was positioned on the reflectometer plate and the sample mounted on it. The temperature was controlled with a Linkam Controller where the heating and cooling rates can be selected. At a fixed temperature, the reflectivity curve was measured. The heating rate was fixed to a value of 20 °C/min (when this rate was changed to a lower value, the same result were obtained for the reflectivity measurements).

Different samples were prepared with the 100 000 d-PS polymer. Before spin-casting the PVME solutions on top of the d-PS grafted films, the thicknesses of the brushes were measured with ellipsometry. Different film thicknesses were obtained after annealing the samples at different temperatures and for different length of time. The thicknesses for the various samples were between 70 and 100 Å.

The reflectivity curves for the sample with a d-PS film thickness of 85 ± 6 Å (measured before the deposition of the PVME layer) are shown in Fig. 1. The q range of the reflectivity is between 0.004 and 0.2 $Å^{-1}$. The PVME was quite thick (~5000 Å). The first four reflectivity curves correspond to the measurements taken at temperatures of 25 °C (RT), 50, 70, and 90 °C. An increase of the reflectivity occurred as the temperature was increased.

These changes appear to be reversible and this can be considered to represent an equilibrium situation. In fact, the sample was cooled at the same rate and reflectivity curves were taken at 70 °C and RT, and are also shown in Fig. 1. After reaching RT, the sample was re-annealed again and the reflectivity measured at 70 and 90 °C, showing again the complete reversibility. The next reflectivity curve was taken after annealing the sample at 100 °C. This measurement is shown as the bottom reflectivity curve in Fig. 1. Clearly in

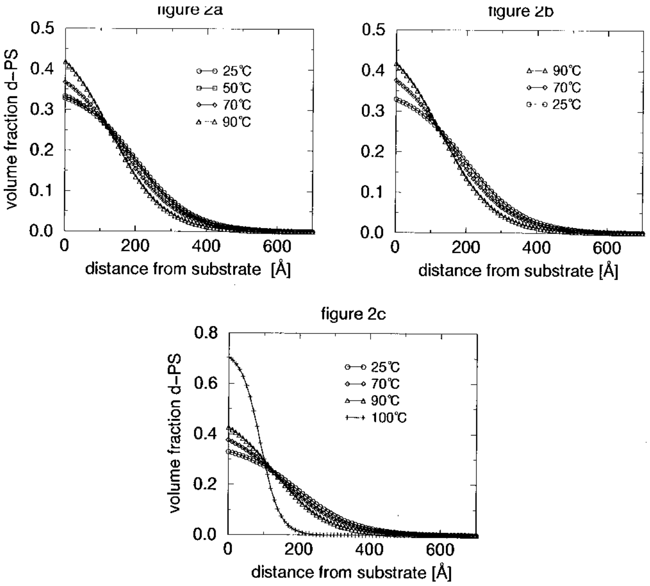

FIG. 2. Brush density profiles extracted from the fitting of the reflectivity curves of Fig. 1. (a) corresponds to the annealing measurements from 25 to 90 °C, (b) corresponds to the cooling from 90 to 25 °C, and (c) is for the reannealing cycle from 25 to 100 °C.

this case, some fringes are visible with a period corresponding to around 100 Å.

The fits to the reflectivity curves were obtained using a hyperbolic tangent profile of the form

$$\Phi(z)=\tfrac{1}{2}(\Phi_b+\Phi_s)+\tfrac{1}{2}(\Phi_b-\Phi_s)\tanh\left(\frac{z}{w}\right), \tag{8}$$

where z is the distance from the interface, Φ_b and Φ_s are the volume fractions in the bulk and at the surface, respectively, and w is the thickness of the broad interface. An SiO_2 layer was also included in the model, with a thickness equal to that extracted from the ellipsometry measurement. The fit to the reflectivity data was obtained with the constraint of constant amount of d-PS for all temperatures. This interfacial excess was derived from the ellipsometry measurements carried out prior to the deposition of the PVME. The results of the fits are shown as solid lines overlapping the reflectivity curves in Fig. 1. While the fits are good to up 90 °C, it was difficult to fit the reflectivity for the 100 °C measurement, and the best fit with the model used is shown in the figure. Clearly a dramatic collapse of the brush is visible at this temperature.

The density profiles extracted from the fitting are shown in Fig. 2, where the annealing [Fig. 2(a)], cooling [Fig. 2(b)] and reannealing [Fig. 2(c)] profiles are displayed in separate plots. These clearly illustrate the reversibility of the curves. In Fig. 2(c), the density profile for the 100 °C measurement is also reported.

As is clear from the profiles, in the PVME matrix the brush chains extended several hundred Å into the bulk and were highly stretched. The d-PS volume fraction at the substrate for the unannealed sample was around 0.32 and decreased very quickly as the distance from the substrate increased. The height of the profile, defined as the distance from the substrate at which the slope of the profile is steepest, was around 220 Å. As the temperature increased the brush collapsed, since the interaction between the two polymers became more unfavorable. The volume fraction at the substrate for the 90 °C profile was ~0.42 and the height of the brush was around 150 Å. When the temperature was decreased, reversibility was observed, as clearly shown in Fig. 2 when the density profiles of the annealing and cooling measurements are compared. Again when the temperature was increased, the same phenomenon was observed, indicating clearly that what was seen did represent the collapse of the brush in response to poorer thermodynamic interactions.

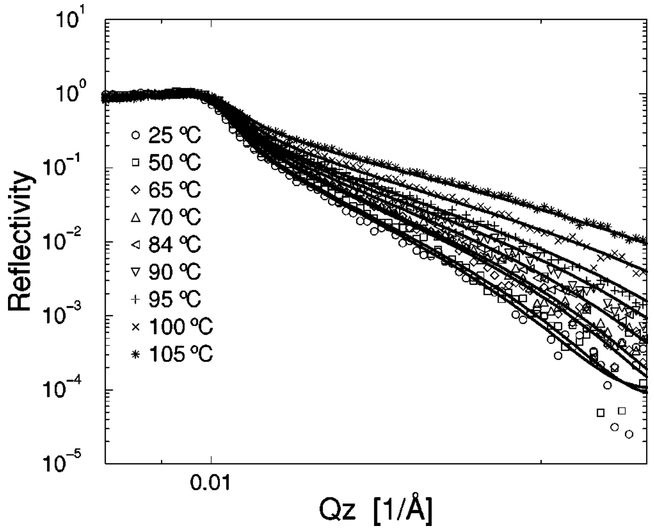

FIG. 3. Reflectivity curves at different temperatures for a sample with initial d-PS brush thickness of 66±6 Å. The fits to an hyperbolic tangent function are also displayed as solid lines. The reflectivity curves have been displayed up to $q_z=0.03$ Å^{-1} for clarity.

As the temperature was increased beyond 90 °C, the brush collapsed further. At 100 °C the d-PS volume fraction at the substrate became ~0.7 and the height of the brush approximately 95 Å, as clearly observed in Fig. 2(c). Increasing the temperature further, the PVME macroscopically dewetted.

Also for the other samples measured, the reflectivity experiments were performed changing the temperature, as in the previous case. As another example, Figs. 3 and 4 show the reflectivities and the d-PS density profiles extracted from the reflectivity fits, respectively, for a sample with initial d-PS thickness of 66±6 Å. The PVME overlayer was quite thick (5000 Å). For clarity, in Fig. 3 the reflectivities are shown only to q_z of 0.03 Å^{-1}.

As in the previous cases, a gradual collapse of the brush was observed when the temperature was increased. At 100 °C the collapse was more severe and macroscopic dewetting took place. The volume fraction at the solid surface was slightly smaller than the previous samples, and for the unannealed case was around 0.29 while the height of the brush was around 200 Å. For the sample with initial d-PS thickness of 66 Å (Figs. 3 and 4), the reflectivities were measured from RT to ~100°C, until dewetting took place. If annealing is not carried until the stage at which dewetting takes place, then the conformational changes in the brush are fully reversible. This is illustrated in Fig. 5, which shows the d-PS brush height as a function of the temperature for a sample that had a d-PS thickness of 84±6 Å. Both the

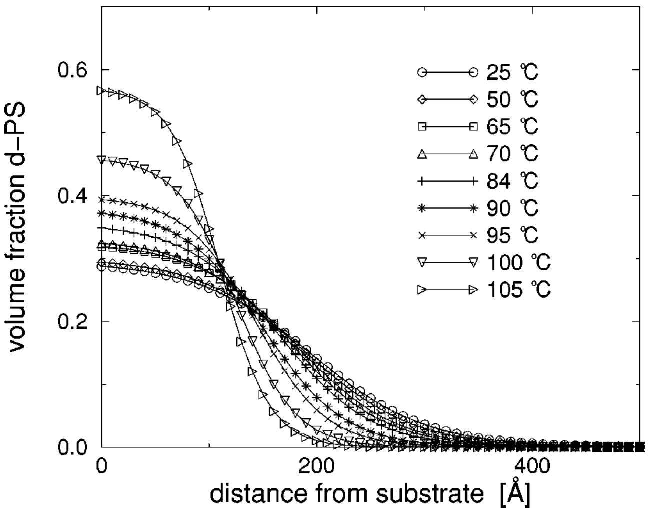

FIG. 4. Brush density profiles extracted from the fitting of the reflectivity curves of Fig. 3. A gradual collapse of the brush is observed when the temperature is increased.

annealing and cooling cycles are displayed in the figure clearly showing the reversibility of the process under annealing.

V. DISCUSSION

The PS/PVME system has a lower critical solution temperature (LCST). As the temperature is increased, the interaction between PS and PVME becomes more unfavorable and this leads in the bulk to phase separation [37–49]. For the brush, when the temperature is increased, phase separation is also expected.

Neutron reflectivity experiments showed consistently for all samples measured (with slightly different grafting densities), an increase of the reflectivity as the temperature increased. The brushes were quite extended in the matrix at room temperature with the height of the profile ~210 Å. The increase of the reflectivity indicated clearly that the PVME was expelled from the brush and that the interface became narrow, as expected since the LCST is approached and the χ interaction becomes less favorable. Up to 90 °C, this change was completely reversible, as observed when the temperature was changed from 90 °C to room temperature. In this range no significant off-specular scattering was observed. This suggested that the interaction was still not unfavorable enough to produce lateral phase separation, as has been predicted in poor solvent conditions by computer simulations and theory. At higher temperatures, the brush collapsed even further, suggesting complete phase separation of the two polymers. The temperature at which this was observed was approximately 100 °C. This change was not reversible. A quick macroscopic dewetting took place in the temperature range 100–110 °C and after annealing the samples to higher temperatures. This macroscopic dewetting may be qualitatively understood as a result of the increasing interfacial energy of the brush/matrix interface as the brush/matrix interaction becomes more unfavorable. As introduced in Sec. II, the scaling law predicts that the height of the brush depends on χ parameter and the grafting density with a 1/3 exponent law.

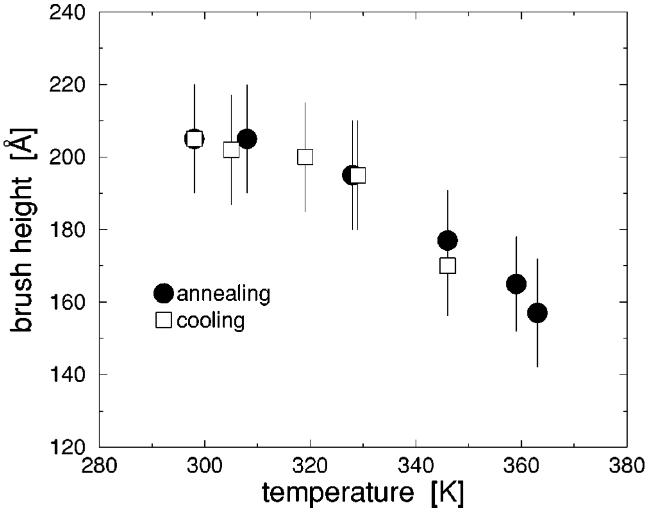

FIG. 5. Brush height as a function of the temperature for a sample with d-PS thickness of 84±6 Å. Reversibility upon annealing is clearly observed.

TABLE I. Different samples, interfacial integral excess z^*, and grafting density σ. The molecular weight of the d-PS brush was 100 000. The errors on z^* and σ are ~6 Å and ~0.002, respectively.

Sample	z^* (Å)	Grafting density σ
1	85	0.015
2	78	0.014
3	84	0.015
4	85	0.015
5	66	0.012
6	100	0.018

The grafting density σ can be calculated directly from the thickness of the d-PS layer as measured with ellipsometry before the PVME was spun-cast on top. The grafting density is given by

$$\sigma=\frac{z^*}{N_B a} \tag{9}$$

with z^* the interfacial excess, which in the case of a strong adsorption (such as the case under study since the brush is chemically attached to the silicon) corresponds to the integral of the brush volume fraction profile. This is known from the value of the thickness of the d-PS layer. Table I reports interfacial integrals and grafting densities for different samples measured.

The brush height depends on the interaction parameter χ. Some studies by Hammounda, Briber, and Bauer [48] and Han *et al.* [49] reported the behavior of the χ parameter as a function of the temperature for the PS/PVME system, using small angle neutron scattering measurements (SANS). A wide range of compositions and MW of the PS/PVME system were studied with SANS. The results of both works are in good agreement and predict the following behavior of the PS/PVME interaction parameter:

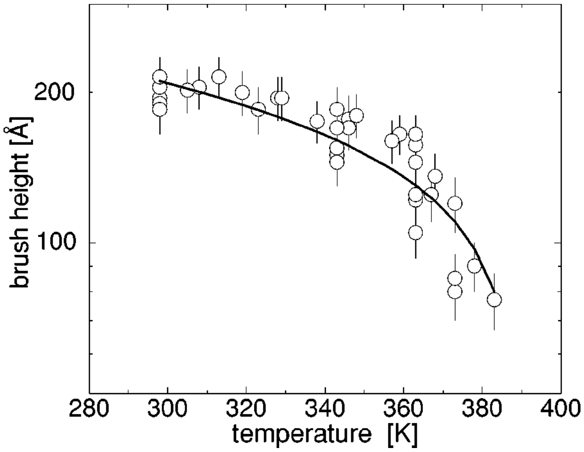

FIG. 6. Brush height extracted from the fits of the reflectivity curves as a function of temperature for all the samples measured. The solid line is a fit to the data using expression (11) in the text.

$$\frac{\chi}{\nu_o}=A-\frac{B}{T} \tag{10}$$

with A and B of the order 10^{-3} and 0.43, respectively, T in K, and ν_o the molar volume. χ/ν_o goes from $\sim -4.2\times10^{-4}$ at room temperature and increases up to $\sim -1.6\times10^{-4}$ for 90 °C. Figure 6 shows the brush heights for all the data collected, including the various annealing and cooling cycles. The brush height seems to follows for all samples the same behavior; a decrease of the height with the temperature is evident, and this becomes even more dramatic at approximately 380 K. Considering expression (10), Eq. (7) becomes of the type

$$h=C\left(-\frac{(A-B/T)\nu_o}{2}\right)^{1/3}\sigma^{1/3}N_B a, \tag{11}$$

where C is a constant. The only parameter different for the various measurements at different temperatures, and for various samples, is the interaction parameter. The degree of polymerization N_B and the statistical length a are the same for all the samples, and an average value of 0.015 was considered for the grafting density. The solid line in Fig. 6, is the best fits to the data using the above equation, where the variables fitted were A, B, and C. The χ parameter extracted from the fit is given by

$$\frac{\chi}{\nu_o}=11.65\times10^{-4}-\frac{0.453}{T}. \tag{12}$$

This expression is quite similar to the one derived for the PS/PVME polymer mixture of different compositions and MW, reported in the literature. With this interaction parameter, the gradual collapse of the brush is then sufficiently well predicted, with the curve following the data even to temperature of ~380 K. The value of χ/ν_o extracted from the fit is around -7.5×10^{-5} for the 90 °C, and decreases to $\sim -4\times10^{-5}$ for 100 °C. It becomes positive at a temperature around 115 °C. Also from the fit, the constant C was estimated to be of 0.7 ± 0.2. A good agreement is therefore obtained between the prediction of the scaling law and the experimental result.

VI. CONCLUSIONS

In conclusion, the interface between a d-PS brush and the miscible PVME matrix have been studied with neutron reflection. The brushes were obtained by chemically attaching d-PS(COOH) chains to the silicon substrate via permanent covalent bonds. In this way the surface coverage was fixed. d-PS brush of MW=100 000 with various thickness of the brush were prepared. PS and PVME are miscible at room temperature and the brush extends several hundred Å into the matrix. When the temperature is increased, the interaction becomes more unfavorable. This was indeed observed from the analysis of the reflectivities measured at different temperatures. As the temperature increased the PVME was expelled from the brush and the interface became sharper. This was reversible up to 90 °C, clearly showing that what was observed did indeed represent the collapse of the brush under poorer thermodynamic conditions. In this range no significant off-specular scattering was observed, indicating that the temperature was not still so unfavorable as to lead to a lateral phase separation in the brush (as predicted by recent computer simulations and theory on the response of a brush to a poor solvent). At higher temperatures a further collapse of the brush was observed, followed by macroscopic dewetting. This macroscopic dewetting frustrates our efforts to observe the predicted lateral microphase separation of the brush.

The scaling theory was used to predict the height of the brush in a good solvent matrix. The height depends on $\chi^{1/3}$ and on grafting density $\sigma^{1/3}$. A good agreement between the prediction of the scaling theory and the results was obtained.

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