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Self-Organization of Polymer Brush Layers in a Poor Solvent


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Abstract. — Synthesis of densely grafted polymer brushes from good solvent polymer solutions is difficult when the surface interaction is only weakly attractive because of the strong steric repulsion between the polymer chains. To circumvent this difficulty we graft polymer layers in a poor solvent to exploit attractive polymer-polymer interactions which largely nullify the repulsive steric interactions. This simple strategy gives rise to densely grafted and homogeneous polymer brush layers. Model end-grafted polystyrene chains ($M_w = 105,000$) are prepared in the poor solvent cyclohexane (95 °C) where the chains are chemically attached to the surface utilizing a trichlorosilane end-group. Polished silicon wafers were then exposed to the reactive polymer solutions for a series of “induction times” $\tau_1$ and the evolving layer was characterized by X-ray reflectivity and atomic force microscopy. Distinct morphologies were found depending on $\tau_1$. For short $\tau_1$, corresponding to a grafting density less than 5 mg/m$^2$, the grafted layer forms an inhomogeneous island-like structure. At intermediate $\tau_1$, where the coverage becomes percolating, a surface pattern develops which appears similar to spinodal decomposition in bulk solution. Finally, after sufficiently long $\tau_1$, a dense and nearly homogeneous layer with a sharp interface is formed which does not exhibit surface pattern formation. The stages of brush growth are discussed qualitatively in terms of a random deposition model.

1. Introduction

The control of the self-assembly of organic layers forming smooth and stable films with different wetting and mechanical characteristics is essential for many technological applications [1]. The defect structure of the mature films often reflects the growth history of the film [2] so that a better understanding of the various stages of film self-organization is needed to obtain films of high quality.

There are different strategies for making self-assembled organic layers. In small molecule layers it is usual to rely on the chemical bonding or weaker physisorption of part of the molecule...
onto the surface. The formation of self-assembled monolayers (SAMs) from alkylsilanes and alkylthiols through binding to silicon, mica, gold or some other surface provides a classic and well studied example of this type of self-assembly process (Fig. 1a) [1e, 1f]. Experimental studies show that the growing morphology depends on the strength of the binding onto the surface, the interaction between the adsorbed particles and the mobility of the adsorbed particles on the surface. For example, for octadecyltrichlorosilane (OTS) layers growing on mica surfaces, where surface mobility seems to be high, the early stage growing layer develops a diffuse fractal island structure [2]. Unlike mica, the growing monolayer of OTS on silicon, where the binding is stronger, obtains a much more uniform growth coverage [3]. The uniform growth habit is typical of a random deposition onto a surface with volume exclusion between the adsorbing elements where there is little rearrangement once chemical binding has occurred (see below). The fractal growth habit, as seen for SAMs on mica on the other hand, is natural for the case where there is considerable mobility for the bound chain to diffuse on the surface until encountering other adsorbed chains at which point sticking occurs [2a, 4]. This amounts to two dimensional diffusion-limited aggregation-like process [5] with the complication of further deposition onto the interior of the growing aggregates from the dimension normal to the growing monolayer at the interface [2]. There is a third scenario which has been seen recently in butanethiol SAMs growing on a gold interface [6]. Experiment shows the development of compact island structures in these SAMs which is apparently a consequence of the mobility of the bound butanethiol chains on the surface, and a weaker surface interchain interaction than OTS on Si. The weaker interparticle interaction seems to allow the growing clusters to coarsen into a more compact form. This tendency is also evident in diffusion limited aggregation studies with imperfect particle sticking where a change to a more compact cluster growth is obtained for sufficiently imperfect particle sticking [7]. The variety of growth habits obtained in SAMs illustrates the delicate interplay between the interactions of the adsorbing molecules and the surface, and the interactions between the adsorbed molecules in the growth of the self-organizing layer.

The self-organization of grafted layers of polymer chains is governed by the same forces as small molecules SAMs and similar variations in the morphological development depending on the relative strengths of the polymer-polymer and polymer-surface interactions can be expected. A novel feature of the polymer layers is the strong steric interference between the chains (see Fig. 1) which is strongly dependent on the polymer-solvent interaction. There are natural polymer analogs of small molecule films. Surfactant adsorbed films [8] correspond to block-copolymer layers [9] (see Fig. 1b) where one block is adsorbed to the surface while SAMs [1–3] have their analog in end-grafted polymer layers (Fig. 1c). Many recent experimental and theoretical studies have studied the swelling of the grafted polymer layer whose thickness can vary by a factor on the order O(10) through a variation of solvent quality [10]. This situation is contrasted with the limited expansion possible in SAM layers. Considerable variations in the lateral density of polymer brush layers is also possible through a variation of solvent and this effect is considered in the present experimental study.

The self-organization of a dense grafted polymer layer ("brush") requires attractive polymer-polymer or polymer-surface interactions to drive the layer formation as in SAMs. It is evidently a simple matter to bring the layer of end-group reactive polymers to an attractive surface through polymer adsorption. A drawback of this approach is that grafting of the chain ends to a highly attractive surface can be rather inhibited in the resulting high polymer concentration adsorbed layer. These layers characteristically develop much more rapidly than the end-linking of the chains onto the surface so that the formation of homogeneous grafted layers should be difficult under these circumstances. Unreacted polymer can simply wash off the surface when exposed to pure solvent if the end grafting does not occur. Grafting polymer layers inside pores
Fig 1. — a) Illustration of formation of self-assembled monolayers (SAMs) of alkylsilanes and alkylthiols through binding to silicon, mica, gold or other surfaces. b) Adsorption of an asymmetric diblock copolymer, such as PS-P(2VP) on mica, where the non-solvated and adsorbing P(2VP) can act as an anchor to the mica surface. c) Grafted polymer layers are formed by a similar grafting chemistry as SAMs. High density grafted layers (polymer "brushes") differ from SAMs in their capacity to exhibit large variations in thickness and lateral homogeneity through variations of solvent quality. The formation of dense grafted layers on weakly attractive surface is facilitated by a poor solvent where interchain interactions are mediated by the solvent. In contrast, the grafting of chains to a weakly attractive surface in a good solvent leads to polymer layers having a low grafting density. These low density layers are expected to be relatively uniform, however (see Fig. 2a).

by Auroy et al. [11], where the surface was rather attractive and the solvent was good, required vigorous synthesis conditions and the process was time consuming. Zhao et al. [12] found that layers prepared by melt spin coating can lead to non-uniform grafted polymer layers which reflect the sluggishness of grafting in dense polymer layers. The growth of grafted polymer layers on weakly attractive surfaces is also problematic in good solvents because of the strong steric interactions between the grafting chains and these interactions cause the formation of layers having low grafting densities (see below). These difficulties motivate the utilization of a sufficiently poor solvent (attractive polymer-polymer interaction sufficient to cause the second virial coefficient of the polymer in bulk solution to be less than or equal to zero [13]) so that the repulsive interchain interactions are largely nullified. Of course, if the solvent is so poor that polymer collapse occurs, then inhibited grafting may again be expected as in the case of a strongly adsorbing surface. On the basis of these qualitative considerations, we then expect a weakly attractive surface and a poor solvent (specifically a temperature near the cloud point temperature of the polymer solution) to provide optimal conditions for the growth of uniform brushes which have a uniformity comparable to SAM layers.

Recently, the self-organization of protein layers has been successfully modeled by an idealized model of random sequential adsorption [14,15] of discs onto a plane where the discs are
Fig. 2. — a) The random sequential adsorption of non-overlapping discs at 50% surface coverage. The non-overlapping disc model is suggested to be similar to deposition of grafted polymers in a good solvent where there are strong steric repulsions between the polymer chains. The discs correspond to the individual chain domains in this simple deposition model.

b) The random adsorption of overlapping discs near the percolation threshold (coverage is 70%). The absence of a constraint against overlap leads to large fluctuations in the coverage concentration at lower coverage. Excluded volume repulsions between the polymer chains are naturally suppressed in a poor solvent so the overlapping disc model is a reasonable "cartoon" model of the chain domain deposition under these circumstances.

deposited one by one so that the locations are chosen randomly except for the constraint that the placement cannot be made onto a previously occupied domain [14].

Polymer chains in a good solvent, despite their low average local monomer density, repel other chains from their molecular domain so that the layer grown by random sequential adsorption of chains from solution likewise has a low density [16]. Figure 2a shows a realization of random sequential adsorption of discs onto a plane where the discs are deposited one by one so that the locations are chosen randomly, except for the constraint that the placement cannot be made onto a previously occupied domain on the surface. We notice that the volume exclusion constraint tends to make the coverage rather uniform [17]. It is known that complete coverage \( \theta \) of the discs onto the surface can not be obtained for this model and a "jamming" coverage of 0.549 is obtained [15]. The synthesis of an end-grafted chain layer in a good solvent should lead to an array of essentially isolated chains or chain clusters rather than a "brush-like" morphology where there are strong interchain interactions (See below). This factor was not appreciated in earlier grafting studies [18] in good solvents (for example, grafting polystyrene from its toluene solution) where it was found that only low grafting densities could be formed in the case where the interaction between the surface and the polymer is only weakly attractive. In hindsight the difficulty of forming "brushes" in a good solvent is evident.

As discussed above, the obvious means of reducing the steric interaction between chains, which limit the grafting densities of polymer layers, is to graft in poor solvents where the interchain repulsion is greatly diminished. This simple observation was essential for the synthesis of "brush" layers used in our previous studies of brush swelling [10].

Apart from the increased grafting density, growth of the grafted polymer layer in a poor
solvent should be essentially different than a grafted layer in a good solvent because of the greatly diminished interchain interaction. Such differences may be important since they also affect the mechanical properties of the grafted layers [19]. As an idealization of this kind of polymer layer self-organization process we consider in Figure 2b the random sequential adsorption of discs (polymer chains) onto a surface where there is no volume exclusion between the discs. Observe that the coverage is much more inhomogeneous in the case where there is no exclusion so there is a tendency of the regions to clump. In the overlapping disc case the coverage goes to 100%. It is well known that the average fraction $\theta$ of the surface coverage obeys the relation [14]

$$\theta(t) = 1 - e^{-t/\tau} \quad (1)$$

for overlapping discs where $t$ depends on the rate of deposition [assumed constant in Eq. (1)] and $\tau$ depends on the relative area of the discs to the plane area being covered.

The rate of polymer deposition to the adsorbing layer can be diffusion-limited [20] under certain conditions so that effective deposition rate becomes time dependent. The combination of diffusion and deposition random processes (adsorption kinetics is assumed to be independent from the surface coverage kinetics) leads to a stretched-exponential [21,22] kinetics for $\theta(t)$ rather than the exponential kinetics indicated by equation (1) [14]. The simple disc deposition model of polymer grafting suggests that the morphology of the grafted layer, its density and the time development of the coverage is governed by excluded volume interactions mediated by the solvent. In the present paper we consider the growth of the grafted chain layer with reference to this idealized random deposition model.

A basic and unusual feature of phase separation in high molecular weight fluids is that the theta temperature, where volume exclusion between chains is small, and the critical temperature for phase separation of the polymer and solvent are close to each other [23]. This means that if the solvent is sufficiently poor (temperature is somewhat below theta temperature of the solution) then, the grafted layer should also undergo phase separation to form periodic modulations of the surface morphology under appropriate conditions. Of course, this phase separation process is limited due to the surface grafting constraint and only a *macrophase separation* on a scale determined by the grafting density and other chains molecular parameters is possible. This interesting effect is indicated in Monte Carlo [24] and molecular dynamics studies [25] of model grafted brushes where it is found that the transition does not occur if the grafting density is too high [24]. Our experiments below accord with these simulation studies. It is also clear that phase separation can not occur unless there is sufficient polymeric material on the surface for long wavelength fluctuations to “percolate”. This effect is well known in the bulk where phase separation is suppressed when dilution is made below a critical percolation concentration [26]. Our experiments show that the appearance of the long wavelength phase separation fluctuations arise at a critical coverage of polymer which happens to be close (perhaps fortuitously) to the percolating coverage of overlapping discs 68% [27] (see Fig. 2b). Clearly the existence of long wavelength fluctuations requires a critical amount of polymeric material and at high grafting density it is energetically very costly to form concentrations variations in the plane of the brush so that other types of grafting morphologies may be anticipated at either very low or very high grafting density. The microphase separation of end-grafted chains is found to be restricted to an intermediate range of grafting densities.

2. Experimental

Self-assembled films of trichlorosilane terminated polystyrenes ($\text{PS-SiCl}_3$) were anchored on polished silicon wafers. Samples of polystyrene with $M_w = 105,000 (M_w/M_n < 1.05)$ were
prepared in the following way [21]. Filtered solutions of $\approx 1.4 \text{ mg/ml}$ PS-SiCl$_3$ in cyclohexane (Aldrich Chemicals) were prepared in a moisture controlled glove box from air tight sealed bottles of the dry polymer. After filtration through a 0.2 $\mu$m Millex PTFE filter, the solution was removed from the glove box in a closed container and refrigerated at 9.5 °C. The critical temperature $T_c$ for unfunctionalized PS of molecular weight 110,000 is about 21 °C and the critical volume fraction is about 8% [28]. These conditions correspond to a poor solvent regime at a temperature about 10 °C below $T_c$. A 100 mm diameter by 0.5 mm thick silicon wafer with \{111\} orientation, polished on one side was cleaved into several square pieces of $\approx 25$ mm sides. These pieces were cleaned in an oxidizing bath of 70% H$_2$SO$_4$/30% H$_2$O$_2$ at an elevated temperature of $\approx 80$ °C for an hour. Subsequently, the wafers were thoroughly rinsed under flowing deionized water ($> 10^{18}\Omega$/cm) and dried under a jet of dry nitrogen and immediately immersed in the prepared solution. Wafer pieces were extracted from the solution at different “induction times” $\tau$, rinsed in an excess of toluene, acetone, and dichloromethane to remove any loosely attached polymer. While our earlier measurements on grafted PS [10] indicate a small attraction for PS to the silicon oxide surface, we perform measurements here to show that ungrafted homopolymer PS can be washed off completely in a good solvent, toluene. Thus, it should be appreciated that we are only measuring the chains that are actually bound to the surface. The samples were then baked in a vacuum oven at 110 °C for an hour to remove any moisture that may have condensed on the film surface after rapid evaporation of dichloromethane from the film after extraction from solvent. Finally, the wafers were rinsed again in toluene and dried in air. The baking procedure and second rinsing were only performed as precautions to ensure contaminant (e.g. moisture, ungrafted chains) free samples. Test AFM measurements performed on samples before and after these precautionary procedures were very similar.

X-ray reflectivity measurements were performed on a 2kW Scintag fixed anode (CuK$\alpha$, $\lambda = 0.154 \text{ nm}$) instrument, equipped with a scintillation detector. The nominal depth resolution of the instrument is $\approx 5$ Å. Data were obtained over a range $0 < q < 0.05 \text{ nm}^{-1}$ where $q = 4\pi \sin \Theta/\lambda$, where $2\Theta$ is the scattering angle and $\lambda$ is the wavelength. The AFM images of the surface at ambient temperature in a contact mode were obtained with an atomic force microscope [19], the Nanoscope II (Digital Instruments, Inc.) using a pyramidal Si$_3$N$_4$ tip in air and in water according to a common procedure. For some specimens, the AFM images were obtained in a non-contact mode using “tapping” operational mode of the Nanoscope III. The AFM images obtained in the various modes are very consistent and confirm the stability of the surface morphology studied and its independence upon scanning mode. Scanners J, D, and A were used for scanning on scales from 100 nm to 100 nm with applied force in the range of 10 to 40 nN in air and 0.2 to 3 nN in water and in “tapping” mode. Typical scanning areas for which average roughnesses are reported in this paper measured 1 $\mu$m x 1 $\mu$m. The scanning rate was kept in the range of 0.1 to 2 Hz for various scan sizes. Images were obtained from 10-15 different areas on 2-3 different pieces of silicon. All AFM images are presented as obtained.

3. Results and Discussion

Figure 3a illustrates X-ray reflectivity data from samples corresponding to increasing induction times. This set represents typical stages of self-assembly under poor solvent conditions. Samples prepared identically on different pieces of silicon wafers were virtually identical. The robustness of the grafted films was checked by immersing the samples in toluene for additional periods of 24 to 36 hours. Stability of the films and the absence of desorption were demonstrated by the constancy of the parameters derived from X-ray reflectivity. All reflectivity
Fig 3 — a) X-ray reflectivity from sample 1 of end-grafted PS-\text{SiCl}_3\ measured in air for various induction times, $\tau_I$. The solid lines are calculated reflectivity curves based on model step-like density profiles as shown in Figure 3b. b) Volume fraction profile of the grafted brush layer for the longest induction time $\tau_I = 2885$ min
curves show a rapid decay which falls off faster than $q^{-4}$ as can be expected from theoretical considerations [29]. For geometrical reasons the reflectivity below the critical wavevector ($q_c$) of silicon is less than unity for samples having small areas.

The rapidly decaying reflectivity for all samples in Figure 3a is modulated by damped oscillations originating from the presence of the thin polymer films with varying degrees of roughness in the air-polymer interface. The periodicity of these modulations depend upon the thickness of the organic layer normal to the surface, while the damping of the modulations depends on the detailed nature of the surface roughness. We have determined that at low grafting densities, the roughnesses measured by X-ray reflectivity and AFM quantitatively match, but as the grafting density increases, there is a noticeable quantitative discrepancy between the two. These different measurements still track each other qualitatively, however. We expect the developing film exhibits significant lateral density fluctuations and therefore roughnesses as measured by fitting specular X-ray reflectivity data are less accurate than the rms roughness ($r$) measurements obtained by AFM, where $r$ is defined as in reference [30]. Thus, we only refer to $r$ values (see Tab. I) obtained by AFM which are more reliable than X-ray rms estimates of $r$. The layer thickness $d$ values are obtained from X-ray reflectivity. We believe that layer thickness, $d$, can be measured more consistently by X-ray reflectivity, while AFM measurements can underestimate actual thickness of soft polymer layers [19c]. (One of the reasons for underestimation of $d$ is likely the local deformation of soft layers under high local pressure produced by the stiff AFM tip. A discussion of elastic properties of the grafted layer will be discussed elsewhere [19b]) A nominal rms roughness of 0.5 nm taken from typical X-ray and AFM data was assigned to the silicon oxide-polymer interface. We have fit the reflectivity data assuming a simple uniform film model with a gradual variation of the density at the air-polymer interface in the form of a symmetric error function. The film thickness ($d$), density ($\rho$) of the film and the width of the air-film interface are fitting parameters [10,21] in this model (See Tab. I). The density $\rho$ of the films were in the range of 85% to 95% of the bulk density of PS. It is difficult to estimate the density accurately at the lower grafting densities due to the relatively small polymer to silicon signal ratio, especially at the lower coverages The consideration of more complicated models is not justified by the data in hand and the fits obtained by the model profile seem quite reasonable.

A number of qualitative features are apparent from Table I and Figure 3. First, we observe that the polymer film thickness increases with $\tau$ and $d$ seems to approach a saturating value $d(\tau \rightarrow \infty) = d^* = 16.1$ nm after about 8 hrs (Fig. 3a). The oscillations in the reflectivity data with increasing $\tau$ correspond to the evolution from a diffuse to a sharp interface. Little insight into the inhomogeneity in the plane of the grafted layer can be obtained from specular X-ray reflectivity data, however. The density profiles for the saturated brush ($\tau \rightarrow \infty$) correspond

<table>
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<tr>
<th>Sample</th>
<th>Induction Time, $\tau$ (min)</th>
<th>AFM Film Thickness $r$ (nm)</th>
<th>XR Film Thickness $d$ (nm)</th>
<th>$r/d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0.30</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>0.60</td>
<td>1.1</td>
<td>0.546</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>0.90</td>
<td>8.2</td>
<td>0.110</td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>0.30</td>
<td>8.0</td>
<td>0.038</td>
</tr>
<tr>
<td>5</td>
<td>507</td>
<td>0.20</td>
<td>16.1</td>
<td>0.012</td>
</tr>
<tr>
<td>6</td>
<td>2885</td>
<td>0.15</td>
<td>16.1</td>
<td>0.009</td>
</tr>
</tbody>
</table>
to the typical behavior for a dry brush where $\rho(z)$ varies in almost a step-like fashion (Fig. 3b) at the interface height.

Since our synthesis of a high density grafted chain layer in a poor solvent relies on a greatly diminished interchain repulsion, it is interesting to investigate the dependence of the grafted layer thickness on molecular weight. It is well known that the repulsive interchain interactions cause the chains to swell when exposed to a good solvent [10, 11b, 24, 25, 31] so that the thickness scales as $d \sim M$. For an ideal flexible chain in the absence of interchain interactions $d$ scales as $d \sim M^{1/2}$ which is strikingly different (see below). To examine the extent of swelling under poor solvent conditions, where interchain interactions might be expected to be largely compensated, we consider the ratio of the film “thickness” $d$ (the first moment of the polymer concentration profile) to the “unperturbed” chain radius of gyration $R_g$ measured in the melt,

$$\delta = d/R_g$$

(2)

$\delta$ provides an indirect measure of chain stretching within the brush layer. Using the melt dimensions of PS as a reference scale [23] in (2) we find that for three molecular weights between 8k to 105k that $\delta = 1.85 \pm 0.2$. An exact calculation of the first moment of the monomer density profile for a Gaussian chain attached to an impenetrable surface (“non-interacting” or “adsorbing” boundary condition) gives $\delta = 5\pi^{1/2}/4 \approx 2.22$ [34], while the $\delta$ corresponding to an attractive surface interaction (near the absorption transition) equals, $\delta = 4\pi^{1/2}/3 \approx 0.752$. $R_g$ of an isolated flexible chain attached to a non-adsorbing surface is little influenced by the surface or its interaction if the interaction is not sufficiently attractive to adsorb the chain [32,33]. Our observations for $\delta$ then seem to be qualitatively consistent with chains having a limited interchain excluded volume interaction which are terminally attached to an energetically neutral, but impenetrable boundary. (It is also notable [35] that $\delta$ for polystyrene layers adsorbed onto Cr in a theta solvent is also near 2 for concentrations in the semi-dilute to concentrated range.) Our preliminary experimental study of brush swelling in a poor solvent then suggests that excluded volume interactions are substantially screened as in a concentrated bulk polymer solution.

A comparison of our data to recent polymer brush theories [31] provides further insight into the near constancy of $\delta$. The standard brush theory [10c,31b] predicts that the thickness of the brush layer $d$ scales as $d \sim M \sigma$ in a poor solvent. This finding seems difficult to reconcile with our measurements, until it is realized that $\sigma$ itself depends strongly on $M$. The brush scaling relation $d \sim M \sigma$ and a constant ratio $\delta$ are compatible only if the surface grafting density $\sigma$ scales as $\sigma \sim M^{-1/2}$. Indeed, a comparison with our limited data for $\sigma$ shows qualitative agreement with this scaling for $\sigma$ so that our experiments are also consistent with the predictions of brush theory. However, it is apparent from this comparison that an understanding of the absolute molecular weight variation of the brush layer thickness $d$ requires a specification of the dependence of $\sigma$ on $M$. The dense grafted layers in a poor solvent correspond to a density comparable to a polymer melt and it seems likely that the variation $\sigma \sim M^{-1/2}$ derives from space filling constraints and kinetic processes associated with the layer growth. At any rate, it is artificial to treat $\sigma$ as a free variable which can be arbitrarily fixed in modeling the thickness of brush layers. Apparently, the $\h \sim M \sigma$ scaling of brush theory does not necessarily imply that the chains are highly stretched and further theoretical and experimental (chain labeling) studies of the chain conformation within the brush layer should be undertaken to better specify the extent of chain swelling within the brush layer.

The monotonic time evolution of thickness from the uniform film model and the X-ray data possesses an interesting feature in the interval 20 to 40 minutes where the average film thickness is seen to stagnate at 8.1 nm (see Fig. 4b). The reality of this feature is supported by the non-
Fig. 4 — a) Time evolution of grafted layer thickness $d$ as measured by X-ray reflectivity. Observe the development of plateau-like regions after about $\tau_1 \approx 40$ min and 500 minutes. The filled circles and open squares correspond to independent measurements on two different samples. b) Time evolution of absolute rms roughness $r$ of the grafted layer as measured by AFM. The roughness decreases sharply at $\tau_1 \approx 40$ min corresponding to the first plateau in Figure 4a and decreases slowly thereafter. The roughness seems to plateau after about 500 min, which corresponds to complete formation of the dense brush. c) The "relative roughness" ($r/d$) of the grafted layer decreases monotonically with time as apparent in the raw X-ray data in Figure 3

monotonic behavior of the roughness $r$ within this time interval (Fig. 4a). From an initially small value ($r \approx 0.3$ nm) the roughness increases sharply to 0.9 nm at 20 minutes (1.6 nm at 15 min for sample 2) and falls below 0.3 nm for longer times. Observe that the oscillations are significantly damped at $\tau_1 \approx 20$ min indicative of large scale roughness, while at $\tau_1 \approx 40$ min the oscillations have larger amplitude corresponding to a smoother surface. However, the oscillation periodicity, which is a measure of film thickness, is unchanged. In the discussion below we denote the characteristic induction time to form the plateau as $\tau_1^* \approx 40$ min. There is a later "aging time" $\tau_1^{**}$ where the evolution of the surface thickness value saturates which is on the order of 500 min. The surface is quite smooth at these time scales ($r \sim 0.3$ nm). These characteristic times appear to demark characteristic stages in the morphological evolution in the end-grafted layer. Figure 4c shows that the ratio of the absolute scale of film roughness $r$ to film thickness, $r/d$, ("relative roughness") decreases rapidly and monotonically to a very small value at large $\tau_1$. This behavior is qualitatively apparent in the reflectivity data in
Fig 5 — AFM image of the surface of sample 1 of the PS-SiCl₃ grafted layer ($r_1 = 6$ min). Note island-like structures [36a]. Full length of figure corresponds to 1000 nm.

Figure 3. The plateau after $\tau^*_1 \approx 40$ min. roughly corresponds to the time where the ratio of $r/d$ dramatically flattens out to approach its asymptotic value. Thus, $\tau_1 \approx 40$ min indicates a cross-over to a regime where a connecting layer forms. This layer gradually fills in to become homogeneous at $\tau^*_1$. Other experimental methods are required to determine more about the morphologies involved and we need to turn to AFM [19] data to more precisely describe this structure.

As known, AFM provides the possibility for direct observation of surface morphology with nanometer resolution at ambient conditions and for modification of the surface by mechanical interactions with the AFM tip. The very local probing capability of the AFM technique provides complementary information to scattering techniques. In Figure 5 we show a typical morphology for a short induction time ($l_1 = 6$ min) obtained from AFM. The coverage is inhomogeneous in the plane of the grafted layer at this early stage. The chains evidently attach to the surface in a random deposition process to form islands as in the random covering process shown in Figure 2b.

A different pattern is apparent in the grafted layer after longer times $\tau_1 \geq \tau^*$ where the grafting density becomes higher (Fig. 6). The grafting density then becomes sufficient for the collective fluctuations to "percolate". We tentatively interpret this pattern as the polymer phase separation (polymer is bright field feature) from the solvent so that a spinodal-like [36] pattern is formed (Fig. 6c). The growth of this pattern is inhibited by the chain end-grafting so that only microphase separation (surface pattern formation) can be obtained. The situation is also quite similar to diblock copolymer fluids where the interchain junction causes a correlation hole effect leading to bicontinous type patterns in the disordered phase [37]. We expect the scale of the surface phase separation pattern (defined by a characteristic $q^*$ corresponding to a maximum scattering intensity), to directly reflect the induction time $\tau_1$. Indeed, we observed significant variations of $q^*$ within a narrow time interval but we have not pursued a quantitative examination of this effect in the present paper. We suspect that the surface
Fig 6 — a) AFM image of the surface of sample 1 of the PS-SiCl$_3$ grafted layer ($\tau_1 = 10$ min). Note similarity of surface pattern to “spinodal-type patterns” observed in bulk fluid phase separation and bicontinuous patterns seen in disordered block copolymer fluids [36-38]. Full length of figure corresponds to 4000 nm. b) Three-dimensional plot of the surface of the grafted layer ($\tau_1 = 10$ min) at higher magnification. Full length of figure corresponds to 650 nm. c) 2-D Fourier transform of AFM image in a) which shows a diffuse halo at a characteristic $q^* = 0.042$ nm$^{-1}$, reflecting the average size of the real space pattern with average spacing $d \approx 150$ nm.

Pattern scale can be “tuned”, at least through some limited range, through a variation of $\tau_1$. It should also be possible to modify the pattern significantly by exposing the layer to a good solvent to redissolve the grafted layer if the lateral spinodal decomposition interpretation of the surface layer is correct (see Discussion). On the other hand, if the pattern does not dissolve in the good solvent then the correlation hole interpretation of the pattern would be favored.

After a longer time $\tau_1 \gg \tau^*$ another limiting region is apparent in the AFM images. For $\tau_1 \sim O(500 \text{ min})$ the AFM images of the grafted layer is almost featureless, indicating the formation of a homogenous “brush” layer. The formation of concentration fluctuations in the plane of the layer becomes suppressed by the high elastic energy which must be expended to
deform the high density brush. From the present standpoint this final regime is less interesting, but such layers are the starting point of our previous studies on swollen brushes [10].

4. Discussion

We have observed the variations in surface morphology which arise when increasing amounts of polystyrene are end-grafted onto a silicon surface under poor solvent conditions. X-ray scattering and AFM methods provided complementary and consistent information to reveal the details of a series of morphological transitions in the self-organizing grafted polymer layer. The X-ray data allowed us to follow the evolution of the film thickness while AFM revealed more detailed information about the surface roughness and inhomogeneity in the plane of the grafted polymer layer. We find three rather distinct stages in the self-organization of the grafted chain layer. After a short induction time \( \tau \) of end-grafting PS chains from solution a morphology is formed which has an inhomogeneous island structure. These island structures roughly resemble structures obtained by random deposition of circular discs (overlapping) on a plane surface [14, 15]. After longer \( \tau \) the surface concentration becomes sufficiently high for long wavelength concentration fluctuations in the chain graft layer to “percolate”. Since the solvent is poor the layer exhibits phase separation subject to the constraint of the end-junction which inhibits long wavelength phase separation. The microphase separation pattern resembles the transient intermediate stage spinodal decomposition pattern [38] found characteristically in bulk phase separating fluids and microphase separation patterns seen in disordered block copolymer materials. After still longer induction times the polymer layer attains a high polymer concentration and becomes uniform. The high polymer density no longer allows for concentration fluctuations in the plane of the grafted layer and the thickness of high density brushes in poor solvents seems to be consistent with tethered chains having weak interchain excluded volume interactions. Specifically, the thickness of the dense brush layer is found to be roughly twice the radius of gyration of the chain in the melt (this should be comparable to the chain dimensions at the theta point in solution).

Several other mechanisms of the formation of heterogeneous in-plane morphology were investigated, but rejected, as inconsistent with our observations. Dewetting is known to induce “cellular” surface morphology in spin-coated ultrathin polymer films at elevated temperatures [39]. However, even after prolonged thermal treatment above the glass transition temperatures, X-ray and AFM studies showed that none of the surface morphologies changed significantly. To test if the patterns could be produced by inhomogeneous dissolution of unattached polymer, a spin coated film of regular PS was exposed only partially to toluene by dipping part of the wafer in toluene for a relatively short period of time. The AFM shown in Figure 7 shows that the undipped PS covered regions is very smooth, a rough boundary with scattered islands of polymer is visible and at some distance away from the boundary where the film was exposed completely to toluene, a smooth surface of silicon wafer is observed bearing no tracks of polymer film indicating complete dissolution of spin coated polymer film.

Future experimental studies should explore the extent to which the scale of the surface pattern in the intermediate grafting density regime can be controlled by varying \( \tau \) (i.e., the surface grafting density) and the solvent quality. The disc random deposition model indicates that the coverage of grafted chains should be much more homogeneous and the grafting density lower for grafting from good solvent and this prediction should be examined in the future. Recent experiments by Kent et al. [40] for diblock copolymers of polystyrene and PDMS at the air surface and ethyl benzoate (a good solvent for PS) gives a rms thickness \( d_{\text{rms}} \) of the PS layer extending into the solvent, corresponding to \( \delta \) in the range (1.5-2.2) for the entire range of surface concentrations. This observation also seems to be consistent with a rather
Fig. 7. — Edge relief of a spin-coated (non-grafted) homopolymer PS layer whose boundary was formed by dissolution of polymer in a good solvent, toluene. The boundary separates regions of a uniform polymer layer and mostly exposed silicon surface. Full length of figure corresponds to 2.5 μm.

small interchain interaction as in our poor solvent grafted layers and we expect to see similar behavior in grafted layers (arguably “brush” is an inappropriate terminology for such layers) formed in good solvents. Experiments of this kind for end-grafted layers in good solvents are planned, but the experiments are complicated by the requirement that the AFM measurements must be performed in solution. The AFM measurements in the good solvent should also allow us to examine the change of the surface patterns obtained in the intermediate coverage regime. We expect the redissolution of the layers should yield a much more homogeneous layer, but the inhomogeneity in the chain grafting under poor solvent conditions might persist to some degree. It should also be possible to open and close the fine pin-hole structures in the high grafting density brush through a variation of solvent quality which could provide a “switch” on transport through the brush layer. We also plan to examine grafting polymer brushes from a polymer melt of end-functionalized polymers at high temperatures (high temperatures will hopefully solve the problem of sluggish kinetics in the melt film) since this situation should similarly involve excluded volume screening. The arguments of the present paper suggest that this procedure might provide an alternative strategy for synthesizing dense uniform brushes of high quality. Finally, the elasticity of these grafted layer should be examined carefully. Measurements of this kind could be made at a macroscopic scale with the surface force apparatus [41] in conjunction with local measurements of force-distance behavior using AFM [19].

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References


[16] The disc model of a flexible polymer chain captures many salient features of polymer solution properties. The radius of gyration, hydrodynamic radius and intrinsic viscosity of a thin disc all scale as $M^{1/2}$ in three dimensions as for the case of random coil polymers and the relation between disc and random coil properties holds more generally in d-dimensions. This relation exists because the disc and the random coil polymer both have a "fractal" (Hausdorff) dimension of 2.


[19] a) Certain commercial materials and equipment are identified in this paper in order to adequately specify the experimental procedure. In no case does it imply recommendation or endorsement by the
National Institute of Standards and Technology nor does it imply that the material or equipment identified is necessarily the best available for this purpose; b) Karim A., Tsukruk V.V. et al. in preparation (We probe using AFM the mechanical stability or the shear modulus of the grafted polymer layers discussed in this paper); c) Tsukruk V.V and Reneker V.V., Polymer 6 (1995).

[24] a) Lai P. and Binder K., J. Chem. Phys. 97 (1992) 589. References b) - d) correspond to analytic studies of phase separation in end-grafted polymer layers. The conditions considered do not correspond to the present kinetic study of brush layer self-organization, however b) Carignano M.A. and Szleifer I., J. Chem. Phys. 100 (1994) 3210. c) Yeung C., Balazs A.C. and Jansnow D., Macromolec. 26 (1993) 1914, d) Marko J.F. and Witten T.A., Phys. Rev. Lett. 66 (1991) 1541 This work considers phase separation of an end-grafted polymer blend. Recently, we have also considered phase separation where only one component of the blend is end-grafted and have found the wetting characteristics of the boundary can be completely modified by this procedure.
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[34] Lepine Y. and Caille A., Canad. J. Phys. 56 (1978) 403. Bill McMullen (Texas A&M University) has recently indicated to us that the value of \( \delta \) for an adsorbing boundary is actually \( 3 \pi^{1/2} / 4 \approx 1.329 \) so the corresponding result of Lepine and Caille seems to be incorrect. This discrepancy does not alter our qualitative conclusions in the text, however.