

# Wetting Behavior of Graft Copolymer Substrate with Chemically Identical Homopolymer Films

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The wetting behavior of deuterated poly(ethyl acrylate) (dPEA) and polystyrene (PS) homopolymers on the substrates of dPEA–PS graft copolymers with different graft chains (dPEA-*g*-xPS,  $x = 1, 3, 5$ , average number of graft chains) was investigated utilizing scanning force microscopy (SFM). The lateral force and adhesion force measurements of dPEA-*g*-xPS substrates show that the surface molecular mobility of the dPEA-*g*-xPS substrate with the dPEA outermost layer decreases with the number of graft chains because of their different aggregation structure. As the number of PS grafts increases, the wetting behavior of dPEA on graft copolymer substrates changes from wetting to partially wetting. The contact angle measurement at the dPEA homopolymer/dPEA-*g*-xPS substrate interface indicates that the substrate with more PS grafts has a higher interfacial tension with the dPEA homopolymer. The wetting behavior of PS homopolymer on the dPEA-*g*-xPS substrates depends on the viscosity of the substrate, which is expected to be lower than that of the PS homopolymer. The dewetting velocities of the PS homopolymer increase with the increase of PS grafts in the dPEA-*g*-xPS graft copolymers.

## Introduction

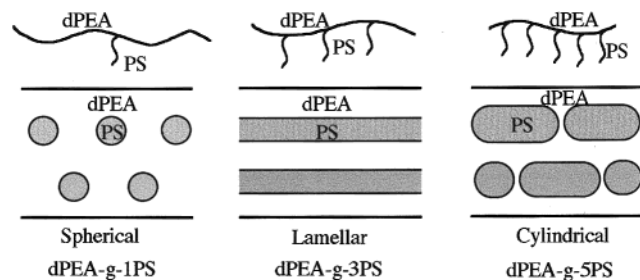
The wetting behavior of polymer thin films has recently received a great amount of attention, because of its importance in practical applications such as paints, adhesives, lubricants, dielectrics, biomedical devices, and nonlinear optics. It has been demonstrated<sup>1–4</sup> that the wetting dynamics and dewetting instability of polymer molecules can be very different from those of simple liquids. The effect of an attractive solid interface on the polymer mobility was investigated and found to decrease diffusion significantly.<sup>5,6</sup> In a number of systems, it was observed that the wettability of the surface is determined by the ability of the polymer melt to penetrate into the restricted polymer substrate such as a densely adsorbed polymer brush,<sup>7</sup> a self-assembled surface of diblock copolymer with chemically dissimilar blocks,<sup>8</sup> or a cross-linked surface.<sup>9</sup> Even if the melt and the substrate are of identical chemical structure, entropy considerations limit the penetration of

the melt chains into the substrate, leading to partial wetting. This phenomenon is referred to as “wetting autophobicity”.<sup>8–14</sup> The physical origins of wetting autophobicity in polymeric systems can be attributed to limitations on the molecular configurations of the restricted polymer substrates. In this paper, we concentrate on the role of the molecular architecture of the substrate. A series of model graft copolymers of constant molecular weight but different number of grafts was used to investigate the dewetting behavior with chemically identical homopolymer films. The graft copolymers consist of a deuterated poly(ethyl acrylate) (dPEA) backbone with one, three, or five pendant chains of monodisperse polystyrene (PS) attached randomly along its length (dPEA-*g*-xPS,  $x = 1, 3, 5$ ). The graft copolymers are ordered on silicon substrates with the lower-energy dPEA backbone at the vacuum interface. The equilibrium structures are shown in Figure 1. The dewetting behavior of dPEA and PS homopolymer films on the ordered graft copolymer

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**Figure 1.** Equilibrium structure of the dPEA-*g*-*x*PS graft copolymer substrates.

**Table 1. Summary of Graft Copolymers Used**

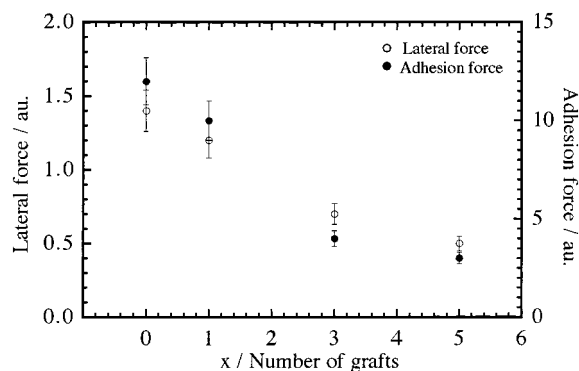
sample	average grafts/chain	$M_{w,PS}$	wt % PS	$M_{w,dPEA}/\text{grafts}$
dPEA- <i>g</i> -1PS	0.9	15 000	9.3	151 000
dPEA- <i>g</i> -3PS	2.8	15 000	24.8	38 000
dPEA- <i>g</i> -5PS	4.8	15 000	48.0	16 000

substrates was then studied using atomic force microscopy (AFM), lateral force microscopy (LFM), and force modulation microscopy (FMM). The equilibrium structure of the microdroplets was then used to determine the interfacial tensions between the graft copolymers and the homopolymers.

### Experimental Section

The graft copolymers used in this study are listed in Table 1. The synthesis procedure was described previously.<sup>15</sup> The total molecular weight of the copolymers was kept constant at  $M_w = 150k$ . Hence, with increasing number of grafts, the mean spacing between grafts decreased. The dPEA backbone (synthesized by free-radical polymerization) had a polydispersity index of  $M_w/M_n = 2.5$ . Monodisperse PS grafts, having a  $M_w = 15k$ , were grafted randomly, whereas the number of grafts per chain was fairly uniform. Thin films of dPEA-PS graft copolymers with different average numbers,  $x$ , of graft chains per copolymer chain (dPEA-*g*-*x*PS,  $x = 1, 3, 5$ ) and with thicknesses ranging from 400 to 1000 Å were spun-cast from toluene solution onto HF-treated polished silicon substrates. These samples were then annealed at  $T = 450$  K for 24 h in a vacuum of  $10^{-4}$  Torr. Because the surface tension of dPEA (37.0 dyn/cm) is lower than that of PS (40.1 dyn/cm), the backbone is known to segregate to the vacuum interface.<sup>16</sup> The annealing time and temperature were chosen so as to enable the copolymer to order in layers parallel to the silicon surface.

dPEA and PS ( $\sim 500$  Å) films were prepared by spin-casting onto glass and floating from water onto the ordered dPEA-*g*-*x*PS substrates. The substrates were only partially covered in order to study relative differences in the scanned images and determine the film thickness of the homopolymer layer. The dPEA/dPEA-*g*-*x*PS and PS/dPEA-*g*-*x*PS bilayers were annealed at 450 K and  $10^{-4}$  Torr for 24 h and rapidly quenched to room temperature. The dewetting characteristics were then studied by scanning force microscopy using an atomic force microscope (AFM, Dimension 3000; Digital Instruments, Co., Ltd. Santa Barbara, CA). The AFM was operated in the constant-force mode in air at room temperature, using a silicon nitride tip on a cantilever with a bending spring constant of  $0.02$  N m<sup>-1</sup>. The imaging force was repulsive, ranging from 0.1 to 1 nN. The surface-phase determination of the binary films after dewetting is based on their surface mechanical properties, lateral force and elastic modulus, as measured by a modified AFM under ambient conditions at room temperature. In lateral force microscope (LFM) experiments, the lateral force is measured during the scanning



**Figure 2.** Lateral and adhesion forces of PEA-*g*-*x*PS substrate.

process with a sharp cantilever tip. To obtain the maximum LFM output voltage as torsional motion, the sample surface was scanned perpendicular to the long axis of the cantilever. The two-dimensional image of dynamic viscoelastic functions was also obtained by utilizing a forced-oscillation AFM, force modulation measurement (FMM) [also called a scanning viscoelasticity microscope (SVM)].<sup>17</sup> The magnitude of strain was modulated by applying a sinusoidal voltage generated by a function generator. A modulation frequency of 4.7 kHz was chosen so that the *z*-piezo could be driven away from the resonance frequencies where the magnitude of the strain was not well-defined.

### Results and Discussions

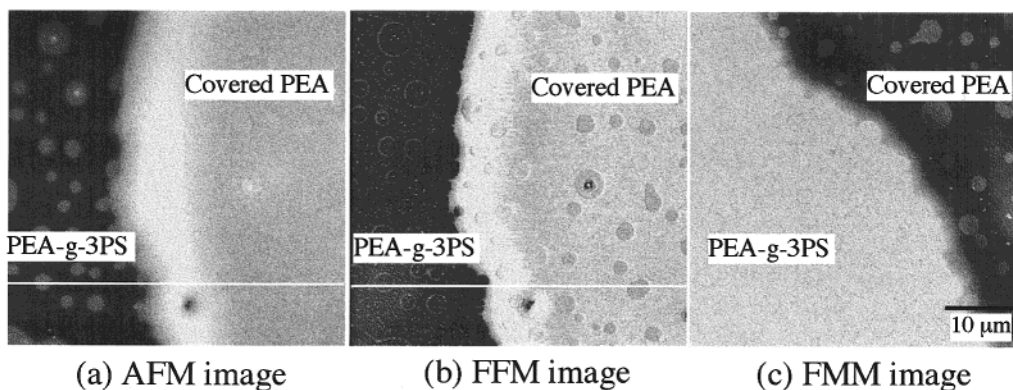
**dPEA/Graft Copolymer Interface.** The equilibrium structures of dPEA-*g*-*x*PS graft copolymer thin films with different average numbers of graft chains per copolymer chain were previously investigated using neutron reflection (NR) and secondary ion mass spectrometry (SIMS).<sup>16</sup> The data showed that, in all cases, the order was induced by the vacuum surface and persisted for at least 20 layers into the film. Because of the lower surface energy of dPEA, regardless of morphology, the first layer always consisted of the dPEA backbone at the vacuum interface followed by a grafted PS layer. The subsequent layers were composed of spherical, cylindrical, or lamellar micelles, depending on whether the copolymer consisted of one, three, or five grafts, respectively. Because the  $T_g$  of dPEA (251 K) is much lower than that of PS (374 K), the surface structure becomes similar to that of an elastomeric gel anchored by the glassy PS legs. The mean distance between anchors can be estimated from the grafting density shown in Table 1 as  $M_{w,dPEA}/\text{grafts}$ . Furthermore, from a comparison of the experimental data measured by NR and theoretical calculations of the lamellar and cylindrical micelle spacing  $h$ , it is clear that the backbone becomes increasingly stretched in a direction parallel to the surface as the number of PS grafts increases. The distorted configuration of the dPEA backbone in the first layer can then alter the surface properties of the film, such as the surface molecular mobility and the surface mechanical properties.

Figure 2 shows the lateral and adhesion forces for the ordered graft copolymer surfaces as a function of the number of grafts. Both the lateral and adhesion forces decrease with increasing number of grafts. For the dPEA-*g*-*x*PS graft copolymer substrates, the outermost layers consisted of the same material, dPEA backbone. The change in the lateral and adhesion forces for these graft copolymer substrates determined by the AFM technique was mainly caused by a change in the contact area between

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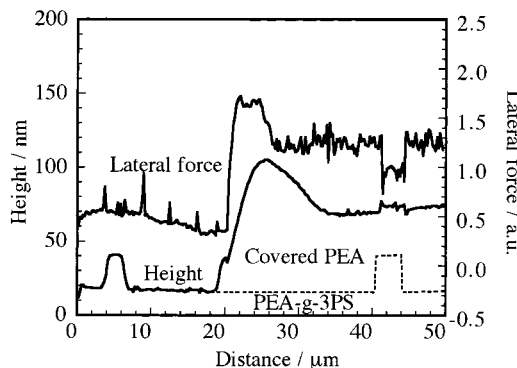


**Figure 3.** AFM, LFM, and FMM images for the dPEA-*g*-3PS graft copolymer film partially covered by unannealed dPEA homopolymer.

the cantilever tip and the material surface or the penetration depth of the cantilever tip into the substrate surfaces. Hence, the difference in the lateral and adhesion forces for these graft copolymer substrates implies a difference in the surface mechanical properties and surface molecular mobility. As the number of grafts increases, the decrease in the lateral and adhesion forces indicates a decrease in the surface molecular mobility.

Figure 3 shows AFM, LFM, and FMM images for the dPEA-*g*-3PS film partially covered by an unannealed dPEA homopolymer film. From the AFM image, we can see that the graft copolymer substrates exhibit island/hole structures similar to those observed previously in linear block copolymers.<sup>8</sup> Similar features were also seen for dPEA-*g*-5PS. When a block copolymer system orients parallel to a surface, the film thickness must correspond to an integral number of oriented layers, and excess material will be pushed out to form islands/holes on the surface approximately one lamella in height.<sup>18,19</sup> Hence, the relatively sharp contour of the islands observed in Figure 3a indicates a high degree of ordering within the copolymer film. The height of islands is found to be  $\sim 250$  Å, in good agreement with previously reported lamellar spacing measured by SIMS and NR.<sup>16</sup> The lateral force and force modulation measurements of the copolymer surface show some slight structure only around the periphery of the islands. The uniform appearance elsewhere confirms that only dPEA is present and that the mechanical response of the dPEA is the same everywhere, including the island surfaces (Figure 3b,c). The slightly higher lateral force and lower force modulation response or stiffness on the island contours might suggest defects around the edges of the islands and somewhat decreased order. Similar defects decorating the edges of islands were previously reported by Liu et al.<sup>8</sup> for a diblock copolymer system.

In the right half of the images in Figure 3, the dPEA-*g*-3PS substrate is partially covered with a dPEA homopolymer film, approximately 500 Å thick. Although this is about twice the height of the substrate's islands, the islands still protrude from the surface with a height of  $\sim 50$  Å. Lateral force measurements reveal a significantly higher lateral force on the homopolymer as compared to that on the graft copolymer substrate. This is not surprising as the glassy PS grafts confine the dPEA backbone on the copolymer surface, thereby restricting its ability to flow when scanned by the moving tip. The dPEA homopolymer on the other hand is free to flow and



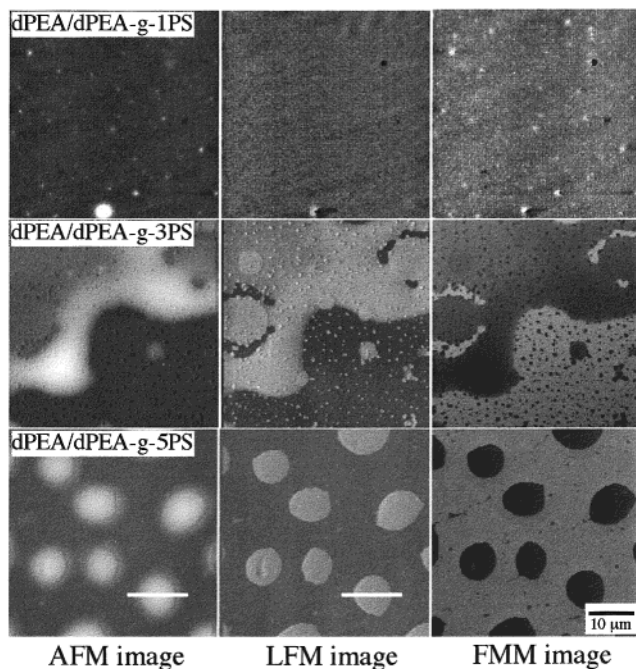
**Figure 4.** Height and lateral force profile along line in AFM image in Figure 3a and b for the dPEA-*g*-3PS graft copolymer film partially covered by unannealed dPEA homopolymer.

thereby provides more drag force to the moving tip. It is interesting to note that the lateral force on the islands is lower than that observed in the valleys in the dPEA-homopolymer-covered area. Because the uncovered islands have the same response as the rest of the surface, this difference must be due to confinement of the homopolymer dPEA on top of these structures. A cross section of the height and force profiles across the dPEA/substrate boundary is shown in Figure 4. From the figure, we can see that the homopolymer layer is thinner at the top of the islands than on the rest of the copolymer surface. In addition, force modulation measurements reveal a higher stiffness on the graft copolymer substrate as compared to the homopolymer. It is considered that the glassy PS grafts confine the dPEA backbone on the copolymer surface and restrict its ability to deform. Furthermore, the higher stiffness on the islands than in the valleys in the dPEA-homopolymer-covered area shows the confinement of the dPEA homopolymer on top of islands where the homopolymer layer is thinner.

Figure 5 shows the AFM, LFM, and FMM images of the dPEA-*g*-1PS, dPEA-*g*-3PS, and dPEA-*g*-5PS graft copolymers covered by the dPEA homopolymer after being annealed at 450 K for 24 h. From the figure, we can see that the dPEA homopolymer completely wets the surface of the dPEA-*g*-1PS graft copolymer, whereas it dewets from the surfaces of the dPEA-*g*-3PS and dPEA-*g*-5PS graft copolymers. The dewetting velocity on dPEA-*g*-5PS is larger than that on dPEA-*g*-3PS. The dewetting reaches an equilibrium state after 15 h of annealing for all the samples. Because all three surfaces are chemically identical, the effect must be caused by the differences in aggregation structure. In all of the ordered samples, the dPEA copolymer backbone layer is at the outermost surface. As the number of grafts increases, the dPEA

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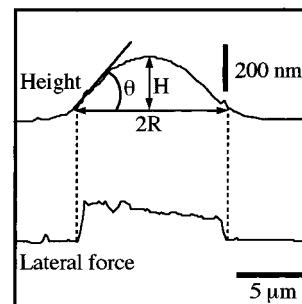
**Figure 5.** AFM, LFM, and FMM images of the dPEA-*g*-3PS and dPEA-*g*-5PS graft copolymers covered by dPEA homopolymer after being annealed at 450 K for 24 h.

backbone increasingly loses its molecular mobility and its ability to swell with the homopolymer. An interface with corresponding interfacial free energy is then established. In contrast to the case of a simple liquid, which will always spread on a free surface of the same composition, auto dewetting of polymeric materials can occur.<sup>8,9</sup> An entropic barrier can be established when the polymer molecules are confined in specific configurations such as a stretched brush or network. When in contact with a free homopolymer layer, the entropic gain in free energy associated with interpretation of the homopolymer chains is offset by the loss in conformational entropy due to distortion of the substrate chains and a well-defined interface is formed. The excess energy associated with this interface can then destabilize the film and induce dewetting. Qualitatively, the higher the density of grafts, the smaller the distance that homopolymer can penetrate into the backbone layer. Hence, the interface between the homopolymer and the graft copolymer layer should become sharper as the interfacial energy increases.

One can measure the interfacial energy between the dPEA homopolymer and the dPEA-*g*-xPS graft copolymer layer as a function of grafting density by measuring the equilibrium contact angle between layers. Because the graft copolymers are ordered and the viscosity of the PS is expected to be much higher than that of the dPEA, the dPEA droplet can only penetrate into the dPEA layer of the ordered substrate. It is reasonable to assume that dPEA and dPEA-*g*-xPS substrates have a nearly flat contact plane. Then, we can use the Young's contact angle instead of full Neuman construction where the angle beneath the vacuum interface is difficult to measure. Young's contact angle can be evaluated from the interface between the droplet and the surface area<sup>20</sup> via

$$\gamma_{\text{dPEA,b}} = \gamma_{\text{dPEA,h}} \cos \theta_e + \Delta F \quad (1)$$

where  $\gamma_{\text{dPEA,b}}$  and  $\gamma_{\text{dPEA,h}}$  are the surface tensions of the dPEA backbone and the dPEA homopolymer, respectively.



**Figure 6.** Height and lateral force profile along line in Figure 5a and b for the dPEA-*g*-5PS film covered by dPEA homopolymer, from which the contact angle is measured.

$\theta_e$  is the equilibrium contact angle.  $\Delta F$  is the interfacial tension between the dPEA backbone layer and the homopolymer, which drives the dewetting process. For small contact angles, the interfacial tension can be written as<sup>8</sup>

$$\Delta F = \frac{1}{2} \theta_e^2 \gamma_{\text{dPEA}} \quad (2)$$

The contact angle can be measured by selecting two points on the surface of a droplet, one at the line of three-phase contact and the other a short distance away on the surface of the droplet. The contact angle is then calculated from the heights and horizontal separation of these points. However, it has been suggested that the detailed shape of the droplet in the vicinity of the contact line can be distorted by local forces. In this case, it is better to obtain the contact angle from the macroscopic height ( $H$ ) and radius ( $R$ ) of the droplet for  $<90^\circ$ . This requires only that the edge of the droplet be well-defined so that  $R$  can be measured accurately. A liquid drop partially wetting a soft substrate induces a deformation of the latter. This is a well-known phenomenon for both liquid and elastomeric substrates.<sup>21,22</sup> To measure the contact angle precisely, we use LFM and FMM to define the edge of the droplet, as shown in Figure 6.  $H$  and  $R$  were measured for at least 30 different circular droplets.  $\theta_e$  was obtained by averaging those different measurements. It should be noted that some imprecision can arise in this method as well because the frictional force is also dependent on the distance of the homopolymer surface from the interface. This phenomenon was previously noted by the frictional contrast seen above islands on the unannealed dPEA samples. The sharp rise in the LFM image of the droplets also designates the region where the homopolymer is free to flow and is not entangled in the dPEA/graft copolymer interface.

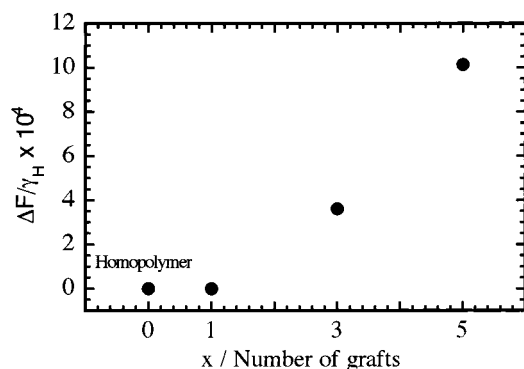
Figure 7 shows the interfacial tension of the dPEA/dPEA-*g*-xPS interface. As expected, the interfacial tension increases as the number of grafts increases. This result is in good agreement with the self-consistent field (SCF) calculation of Balazs,<sup>23</sup> which shows that the interfacial tension between homopolymers increases as the number of grafts of graft copolymer localized at the interface increases. It is clear that the wetting behavior of the graft copolymer substrate with chemically identical homopolymer films is dominated by the surface molecular mobility of the substrates. As the number of grafts increases, the dPEA backbone increasingly loses its molecular mobility

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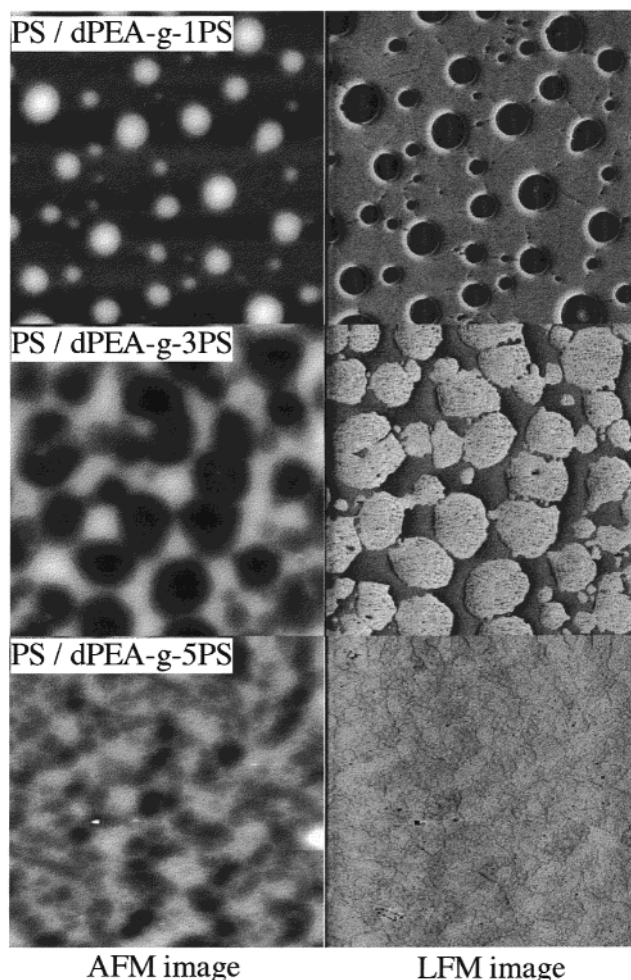
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**Figure 7.** Variations in the amount of interfacial tension between the dPEA homopolymer and the dPEA-*g*-xPS graft copolymer with PS grafts.



**Figure 8.** AFM and LFM images of the dPEA-*g*-xPS graft copolymers covered by PS homopolymer after being annealed at 450 K for 24 h.

and its ability to swell with homopolymer, leading to an increase in the interfacial energy.

**PS/Graft Copolymer Interface.** Figure 8 shows the AFM images of the dPEA-*g*-xPS graft copolymer covered by PS ( $M_w = 90k$ ) after being annealed at 450 K for 24 h. We can see that PS dewets from the surface of the dPEA-*g*-xPS graft copolymer as well. This is not surprising as PS and dPEA are highly immiscible.<sup>16</sup> What is surprising is that the degree of dewetting is now reversed. After 24 h, the largest degree of dewetting is seen to occur on the dPEA-*g*-1PS surface, whereas partial dewetting occurs on the dPEA-*g*-3PS surface, and only minimal dewetting

has occurred on the dPEA-*g*-5PS surface. On a rigid surface, the wetting dynamics is controlled by the viscous dissipation of the excess surface energy in the wedge of the spreading droplet.<sup>24,25</sup> The spreading velocity is thus determined by the viscosity of the liquid. For the case of a highly viscous liquid dewetting from a low-viscosity substrate, the situation is very different. It was found that the viscous dissipation is dominated by the contribution of the lower layer. In the case of a thick lower layer, the dewetting velocity is given by<sup>26</sup>

$$v = \frac{\gamma \theta_e^2}{\eta_B} \quad (3)$$

where  $\eta_B$  is the viscosity of the substrate. The dewetting velocity depends on the substrate viscosity  $\eta_B$  rather than on the viscosity of the top layer. In our case, the viscosity of PS is expected to be larger than that of dPEA. For the dPEA-*g*-xPS graft copolymer, the viscosity would increase with increasing number of PS grafts and fall between those of the dPEA and PS homopolymers. Therefore, the dewetting velocity decreases in the order dPEA-*g*-1PS, dPEA-*g*-3PS, and dPEA-*g*-5PS. This explanation is also consistent with the LFM images of the dewet surfaces. From the LFM images, we can see that the contrast between the dewetting surface and the PS homopolymer film decreases with increasing graft number. The lateral force on the moving tip increases as the viscosity decreases, and the tip is better able to penetrate the sample while scanning. The contrast is maximal for the lower-viscosity sample with one graft and minimal on the stiffest surface with five grafts. Note that, because the viscosity of the graft copolymer substrate is lower than that of the PS homopolymer, the dewetting behavior is more complicated for the PS/dPEA-*g*-xPS graft copolymer system. The local force could distort the contact plane, and even destroy the ordered substrate structure, during the wetting process. In fact, the first layer disappears at the edge when dewetting occurs. The possibility of estimating the contact angle by using the current protocol is not available. The additional experiment was not performed.

## Conclusion

The wetting behavior of deuterated poly(ethyl acrylate) (dPEA) and polystyrene (PS) homopolymer thin films investigated on the substrates of chemically identical dPEA-PS graft copolymer with different graft chains (dPEA-*g*-xPS,  $x = 1, 3, 5$ ) was investigated by atomic force microscopy, lateral force microscopy, and force modulation measurement. We observed that the graft copolymer with more PS grafts per chain has a lower lateral force and higher modulus than that with fewer PS grafts per chain, which falls between that of the dPEA and PS homopolymers. Dewetting of the dPEA homopolymer on the dPEA-*g*-xPS copolymer with a dPEA top surface is caused by the variety of aggregation structures of the substrate surface. The substrate consists of a brush of dPEA-PS graft copolymer with a stretched dPEA backbone into which the spreading homopolymer has difficulty penetrating deeply, so that an interface with the corresponding interfacial free energy be established. The excess energy

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associated with this interface can then destabilize the film and induce dewetting. The contact angle measurements at chemically identical polymer brush and homopolymer interfaces show that the substrate with the more stretched dPEA backbone has a higher interfacial tension with the dPEA homopolymer. For the PS homopolymer, because the viscosity is greater than that of the substrate, the dewetting behavior on the dPEA-*g*-xPS substrate depends on the substrate viscosity. The order

of the dewetting velocity of the PS homopolymer on the graft copolymer was dPEA-*g*-1PS > dPEA-*g*-3PS > dPEA-*g*-5PS.

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