

Morphology and Wettability Of Hybrid Polymer Brushes

John Draper¹, Igor Luzinov¹, Igor Tokarev², Sergiy Minko², and Manfred Stamm²

¹School of Materials Science and Engineering, Clemson University, Clemson, SC 29634

²Department of Polymer Interfaces, Institute für Polymerforschung Dresden, Hohe Strasse 6, Dresden, 01069, Germany

INTRODUCTION

Polymer coatings that are responsive to environmental conditions are of great interest for microelectronics, textile industry, and biomedical applications. The advantage of these "smart" materials is the ability to switch and/or tune the properties of the coatings by applying external stimuli to vary, for example, adhesion, wettability, friction, roughness, reactivity, biocompatibility, selectivity, etc. An example of this type of smart material is a binary (hybrid) polymer brush composed of two incompatible polymers, grafted to a solid substrate. Due to the phase segregation the morphology of the hybrid brushes is sensitive to the surrounding medium.¹⁻⁵ Mixed brushes can be switched between different surface energetic states upon exposure to different solvents.⁶⁻⁷ The interaction of the binary polymer brush with a selective solvent will cause a change of the surface properties of the polymer film because one of the two polymers preferentially occupies the surface layer.⁸

In this paper we report on the surface morphologies of polymer coatings prepared from hybrid polymer brushes of varying composition of grafted chains of polystyrene (PS) and poly(2-vinylpyridine) (PVP). A "grafting to" approach was used to attach the polymer chains to the substrate.

EXPERIMENTAL

Materials. PS-COOH45 $M_n=45900$ g/mol, $M_w=48400$ g/mol and poly(2-vinylpyridine) PVP-COOH; $M_n = 39200$ g/mol and $M_w = 41500$ g/mol were purchased from Polymer Source, Inc. Toluene and tetrahydrofuran (THF) were distilled after drying over sodium. Dichloromethane was dried on molecular sieves. Highly polished silicon wafers (obtained from Wacker-Chemitronics) were first cleaned in an ultrasonic bath for 30 min with dichloromethane, placed in cleaning solution (prepared from NH_4OH and H_2O_2) at 60 °C for 1 h and then rinsed several times with Millipore water (18 $M\Omega \times cm$). 3-glycidoxypropyl trimethoxysilane (GPS) from Aldrich was used as received.

Grafting Procedures. The hybrid brushes were prepared on Si-substrates by "grafting to" methods from carboxyl terminated PS and PVP.⁹⁻¹⁰ The substrate after cleaning was dried under a stream of dry nitrogen, immediately taken into the nitrogen-filled glove box and immersed in an GPS solution (1 vol%) in dry toluene for 16 h. After the deposition was completed, the modified surface was rinsed several times with dry toluene and ethanol in ultrasonic bath to remove unattached silane. A thin layer of PS-COOH was spin coated from 1% toluene solution onto the surface of GPS modified silicon wafers. The thickness of these polystyrene films, as estimated by ellipsometry was 50±5 nm. The silicon wafers with the polystyrene grafted film was placed in vacuum oven at 150 °C to covalently graft PS chains. At high temperature carboxylic groups are able to react with the epoxy and hydroxyl groups of the monolayer.¹¹ The ungrafted polymer was removed by a soxhlet extraction with toluene for 5 h. The second polymer PVP-COOH was spin coated from 1 % THF solution onto the same surface containing PS-COOH, placed in oven at 150 °C to graft it chemically to the epoxy surface and ungrafted polymer was removed by soxhlet extraction with THF for 5 h. Every step of the modification of Si-wafers was controlled by ellipsometric measurements of the layer thickness.

Rinsing Procedure. The final hybrid brushes were each rinsed in THF, and then ethanol. The procedure for rinsing was to attach the

wafer to a dip-coating apparatus at the edge of the wafer using an alligator clip. The wafer was dipped three times on slow speed to a point just prior to the edge of the clip. Each time the wafer was then immediately withdrawn from the solution to air dry. A polypropylene cover was placed over the sample to prevent disruption of sample drying by air currents. After rinsing in each solvent the samples were allowed to dry for a minimum of two hours prior to any sample characterization.

Sample Characterization. Scanning probe microscopy (SPM) studies were performed on a Dimension 3100 (Digital Instruments, Inc.). We used the tapping and phase modes to study the surface morphology of the films in ambient air. Silicon tips with spring constants of 100 N/m were used. Imaging was done at a scan rate of 1 Hz. For "light" and "moderate" tapping modes, the set-point amplitude ratio, $r_{sp}=A_{sp}/A_0$ (A_{sp} is the set-point amplitude used for the feedback control), was selected to be 0.9 ± 0.05 and 0.65 ± 0.05 respectively.¹²⁻¹⁴ The amplitude and phase variation showed that, at $r_{sp} > 0.85$, we scanned at attractive interaction regime. The repulsive mode was in place at $r_{sp} = 0.65$. SPM scanning was done for each sample after rinsing prior to measuring static contact angle. Static contact angle measurements were made using a contact angle goniometer (Kruss, Model DSA10). Calculation of contact angle was made using the tangent method. Contact angle measurements were made with water (pH 7.0), and a static time of 30 seconds before angle measurement. Ellipsometry measurements were made at an angle of incidence of 70° on a Compel (InOmTech, Inc.).

RESULTS AND DISCUSSION

In this study we vary the percent composition of the hybrid polymer brushes by varying the grafted ratios of PS-COOH and PVP-COOH at constant molecular weights for each polymer. The composition of each polymer brush is shown in Table 1. The composition of grafted layers was calculated from the ellipsometric measurements performed after every step of grafting. The chemical composition of the coatings was proved with FTIR ATR spectroscopy. It is noteworthy that the binary brush can be synthesized if PVP-COOH is grafted after PS-COOH. For the inverse case we did not detect grafting of PS-COOH after PVP-COOH. It is evidence that high affinity of polar polymers is a driving force to overcome the repealing of PS brush and reach the Si-substrate surface.

Table 1. Composition of Hybrid PS/PVP Brushes

% PS	dGPS (Å)	dPS grafted (Å)	dPS-PVP grafted (Å)	Contact angle, deg	
				After THF	After ethanol
40	16	22	55	69	51
43	16	25	58	79	54
48	16	29	60	79	58
63	17	38	60	67	60
72	17	41	57	70	61
79	16	56	71	83	68
87	18	54	62	80	68
93	18	63	68	84	72
95	18	62	65	87	77

The switching capability of the polymer brushes can be seen in Figure 1 by the change in contact angle after the ethanol rinse. There is a marked decrease in contact angle after the ethanol rinse. There is a marked decrease in contact angle upon exposure of the polymer brush to a more energetically favorable solvent for PVP. The ethanol acts to swell the PVP chains that can then extend to the polymer solvent interface. The PS polymer chains contract the unfavorable solvent and contract from the polymer solvent interface. Upon drying this new morphology is locked in place.

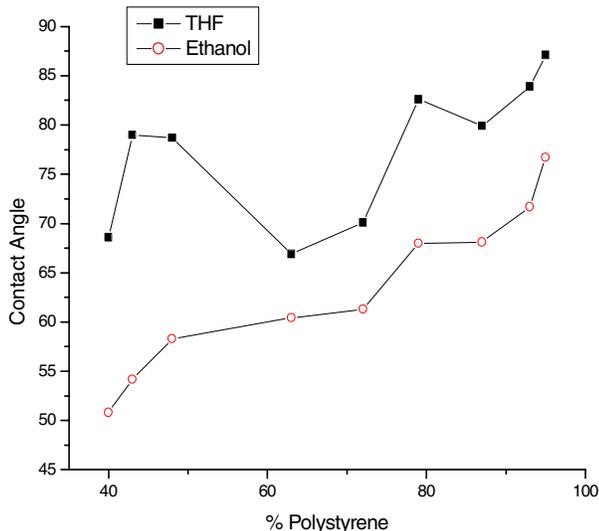


Figure 1. Contact angle versus PS content in the polymer brushes rinsed first in THF, and then in ethanol.

SPM images confirm that a change in the surface morphology as the percent composition of the polymer brush changes. We can also see a difference in the morphology using “light tapping” versus “moderate tapping”.

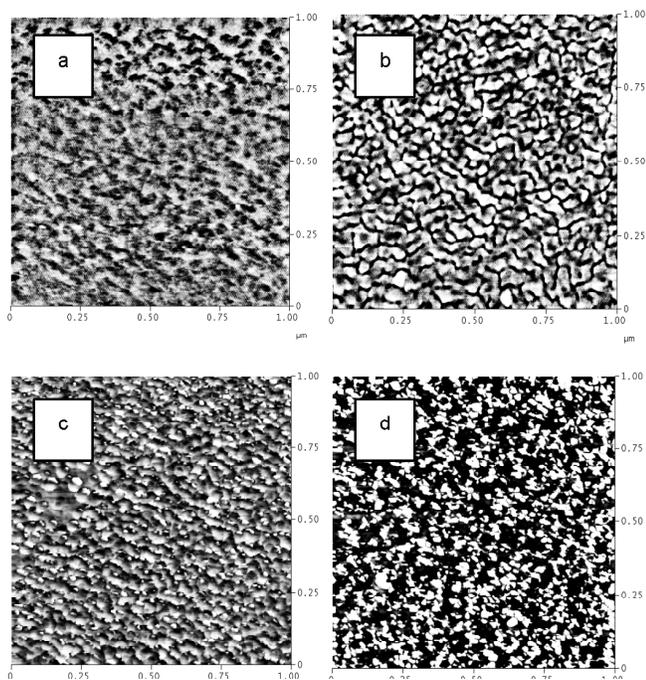


Figure 2. SPM images (1x1 μm) of polymer brushes after rinsing with ethanol: (a) light tapping image of 40% PS; (b) light tapping image of 79% PS; (c) moderate tapping image of the same 40% PS; (d) moderate tapping image of the same 79% PS.

We can surmise from the SPM images that the polymer brush is composed of two distinct regions and that a binary system is present. This is more evident in the moderate tapping images. This binary phase data was used to determine the percent of each component from the SPM image. The light areas are representative of the PS chains, while

the dark areas represent the PVP phase. Using the Cassie equation to predict the contact angle for the hybrid polymer brushes supports the assignment of the phase areas to PVP and PS in this way. The Cassie equation has been shown to adequately predict the contact angle for thin polymer films.¹⁵ Figure 3 illustrates the predicted contact angles from the equation using the phase fraction from the SPM images and the contact angles for the pure polymers. The predicted contact angles are based on the light phase areas of the SPM images representing the PS phase.

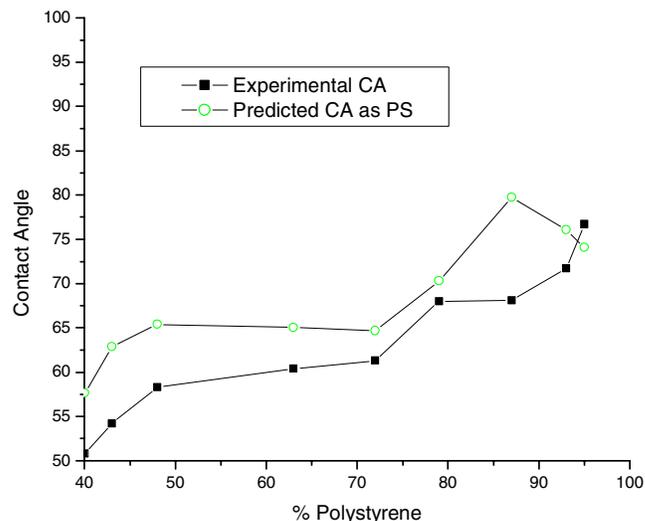


Figure 3. Experimentally measured contact angles for the brushes compared to the predicted contact angles (Cassie equation).

ACKNOWLEDGEMENT

This work was supported by Department of Commerce through National Textile Center, M01-C03 Grant. The financial support of DFG, AIF and BMBF is also gratefully acknowledged.

REFERENCES

1. Marko, J.F.; Witten, T.A. *Phys. Rev. Lett.* **1991**, *66*, 1541.
2. Lai, P.-Y.; Binder, K. *J. Chem. Phys.* **1992**, *97*, 586.
3. Brown, G.; Chakrabarti, A.; Marko, J. F. *Europhys. Lett.* **1994**, *25*, 239.
4. Soga, K. G.; Zuckermann, M. J.; Guo, H. *Macromolecules* **1996**, *29*, 1998.
5. Minko, S.; Müller, M.; Usov, D.; Scholl, A.; Froeck, C.; Stamm, M. *Phys. Rev. Lett.* **2002**, *88*, 3, 035502-1 -035502-4.
6. Sidorenko, A.; Minko, S.; Schenk-Meuser, K.; Duschner, H.; Stamm, M. *Langmuir* **1999**, *15*, 8349.
7. Minko, S.; Sidorenko, A.; Goreshnik, E.; Usov, D.; Stamm, M. *Proceedings PMSE ACS* **2000**, *83*, 533.
8. Minko, S.; Usov, D.; Goreshnik, E.; Stamm, M. *Macromol. Rapid Commun.* **2001**, *22*, 206.
9. Minko, S.; Patil, S.; Pionteck, J.; Stamm, M. *Proceedings of the Amer. Chem. Soc. Div. Polym. Mater.: Science and Engineering*, **2001**, *84*, 877.
10. Minko, S.; Datsyuk, V.; Simon, F.; K.-J. Eichhorn, Motornov, M.; Usov, D.; Tokarev, I.; Stamm, M. Synthesis of adaptive polymer brushes via grafting to approach from melt. *Langmuir*, **2002**, *18*, 289-296.
11. Luzinov, I.; Julthongpiput, D.; Malz, H.; Pionteck, J.; Tsukruk, V.V. *Macromolecules* **2000**, *33*, 1043.
12. Magonov, S.N.; Cleveland, J.; Elings, V.; Denley, D.; Whangbo, M.-H. *Surface Science* **1997**, *389*, 201.
13. Bar, G.; Thomann, Y.; Brandsch, R.; Cantow, H.-J.; Whangbo, M.-H. *Langmuir* **1997**, *13*, 3807.
14. Pickering, J. P.; Vancso, G. J. *Polymer Bull.* **1998**, *40*, 549.
15. Luzinov, I.; Minko, S.; Senkovsky, V.; Voronov, A.; Hild, S.; Marti, O.; Wilke, W. *Macromolecules* **1998**, *31*, 3945.