

Tunable Microstructure and Nanomechanical Properties in a Binary Polymer Brush

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INTRODUCTION

The next generation of sophisticated nanomachines is being designed with integrated mechanical, optical, chemical gating, and biological devices to perform complex sensing functions.¹ Such systems require "adaptive surfaces", or surfaces that have the ability to respond to external stimulus and have their surface properties tuned for necessary functionality. Polymer brushes are prospective materials for such applications because as a result of the high grafting density and uniformity in composition and chain height throughout the brush, the layer responds communally to very subtle changes in the surrounding environment such as pH or solvent quality.^{2,3}

For a binary polymer brush layer, we investigate the morphological state, the structure reordering, and the nanomechanical properties as a function of treatment with a wide range of solvents. Two incompatible polymers, polymethylacrylate (PMA) and poly(styrene-co-2,3,4,5,6-pentafluorostyrene) (PSF), were randomly grafted one after another onto a silicon wafer via the "grafting from" method producing thick (20 – 150 nm) dense mixed brush layers. The resulting layers possessed a nanostructured surface exhibiting either lateral, or vertical microphase segregation of the two components.

EXPERIMENTAL

Materials. *Monomers:* Styrene (S, Aldrich), 2,3,4,5,6-pentafluorostyrene (FS, Fluka), and methacrylate (MA, Aldrich) were purified with an aluminum oxide type 507C, neutral, 100-125 mesh (Fluka) chromatographic column. Solvents of analytical grade toluene, tetrahydrofuran (THF), and hexane were distilled after drying with sodium. Dichloromethane was dried over molecular sieves overnight, and methanol and ethanol were used as received.

Initiators: 4,4'-azobis(4-cyanopentanoic acid) (ABCPA, Aldrich) and 4,4'-azobis(isobutyronitrile) (AIBN, Fluka) were purified by recrystallization from methanol. All reagents were used immediately after purification. Water was cleaned with Milli-Q[®] ultrapure purification system, $\Omega > 18.0$ M Ω x cm. Silicon wafers (Wacker-Chemitronics GmbH, Burghausen, Germany) were cleaned with dichloromethane, then in an ultrasonic bath mixture of NH₃ (25%), H₂O₂ (30%), and water in ratio 1:1:10 at 60° C, and rinsed several times with water. 3-glycidoxypropyl-trimethoxysilane (GPS, Aldrich), ethylenediamine (ACROS Organics), and phosphorus pentachloride (Merck) were used as received. Triethylamine (Riedel-deHaën) was dried on calcium hydride.

Introduction of azo-initiator. Si-wafers were treated under Ar atmosphere by 1% GPS in dry toluene for 16 h and afterwards washed two times with dry toluene under Ar and 3 times with ethanol in ultrasonic bath. In the second step, the Si-wafers were treated with 2% ethylenediamine in ethanol for 1 h and washed 3 times with ethanol. Separately, a chloroanhydride derivative of ABCPA (Cl-ABCPA) was prepared. A suspension of 5 g ABCPA in 50 ml CHCl₃ and a slurry of 40 g PCl₅ in 100 ml CHCl₃ were mixed at 0°C under Ar atmosphere. The mixture was stirred overnight under Ar atmosphere while it warmed up to room temperature. CH₂Cl₂ was evaporated out under reduced pressure to precipitate the major part of the dissolved PCl₅. The yellow solid of PCl₅ was filtered off. Cl-ABCPA was precipitated at 0°C as a white powder in 300 ml dry cold hexane, filtered and washed with dry cold hexane and dried in vacuum, giving 84% yield. In the

next step, Cl-ABCPA was introduced on the surface of the Si-wafers from 1% solution in dichloromethane with catalytic amount of triethylamine at room temperature under Ar atmosphere for 2 h. The resulting samples of Si-wafers with chemically attached initiating groups were rinsed with dichloromethane under Ar and then with ethanol in an ultrasonic bath. Every step of the modification of the Si-wafers was controlled by ellipsometry measurement of the layer thickness.

Graft polymerization. We grafted PMA at the first polymerization step and PSF at the second step using the residual amount of the azo-initiator on the Si substrates. Oxygen was removed from the monomer solution (MA in toluene, 5 mol/L, or a mixture of S and FS in ratio 4:1 wt. in THF, 5 mol/L, and AIBN, 4.4×10⁻⁴ mol/L) using five freeze-pump-thaw-cycles. The Si-wafers with the chemically attached azo-initiator were placed into a reactor with the monomer solution under Ar atmosphere. The reactor was immersed in a water bath (60±0.1°C) for 12 h. The Si-wafers were rinsed several times with toluene. The non-grafted polymer was removed by cold Soxhlet extraction in THF for 1 h. The same procedure was used to graft the second polymer. The non-grafted amount of the second polymer was removed by a hot Soxhlet extraction in THF for 12 hours. Grafted amount of the polymers was controlled after each polymerization step with ellipsometry.

RESULTS AND DISCUSSION

PMA and PSF homobrush layers were found to possess very different surface and nanomechanical properties, and thus combined into one mixed brush layer.⁴ In the most extreme case, upon exposure to selective solvents, the binary system of PSF-PMA had surface roughness and wettability (as measured by contact angle) ranging from 1 to 30 nm RMS and 95° to 120°, respectively. The switch in morphology is shown in Figure 1. Surface nanomechanical mapping results indicated a corresponding switch between a glassy state (high modulus, low adhesion) and a rubbery state (low modulus, high adhesion) associated with this change in morphology. Resulting physical properties of the binary brush are summarized in Table 1.

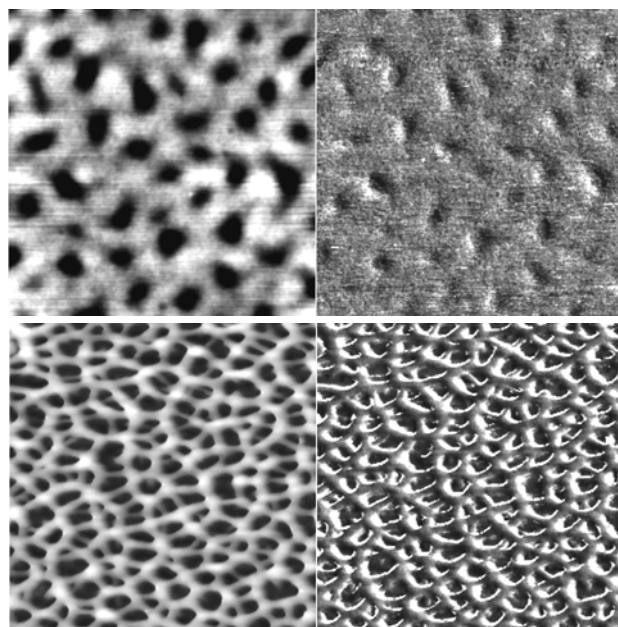


Figure 1. AFM tapping mode image of the binary brush in the glassy state (top, Z scale is 20 nm), and the rubbery state (bottom, Z scale is 150 nm). 2x2 μ m images.

The chain reorganization in the binary brush was determined with high-resolution phase imaging in the dry state combined with depth profiling of the elastic modulus in the dry state and under fluid conditions with selective and non-selective solvents. The model proposed is in agreement with recent theoretical and experimental

calculations in which for the case of both non – selective and selective conditions, varying degrees of vertical and lateral segregation take place depending upon the nature of solvent interaction with each chain in the mixed brush.^{5,6}

Table 1. Physical Properties of Binary Brush and for the Corresponding Homobrush Layers.

Polymer	T _g (°C)	Contact Angle (°)	Elastic Modulus (MPa)
PMA homopolymer	108	95	50 – 60
PSF homopolymer	5	79	700 – 1100
PMA + PSF Rubbery State	NA	80 – 117	50
PMA + PSF Glassy State	NA	95 – 100	600 – 1000

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REFERENCES

1. Tsukruk, V.V. in: *Nanotribology*, Hsu, S.M.; Ying, C. Z.; Eds.; Kluwer Academic Press: Boston, **2002**, p 347.
2. de Gennes, P.G. *Macromolecules* **1980**, 13, 1069.
3. Milner, S.T. *Science* **1991**, 251, 905.
4. Lemieux, M.; Usov, D.; Minko, S.; Stamm, M.; Tsukruk, V.V. *Langmuir*, submitted.
5. Müller, M. *Phys. Rev. E* **2002**, 65, 30802.
6. Minko, S.; Müller, M.; Usov, D.; Scholl, A.; Froeck, C.; Stamm, M. *Phys. Rev. Letters* **2002**, 88, 3, 035502.