

## Orientation of Poly(styrene-*b*-methylmethacrylate) thin films deposited on Self-Assembled Monolayers of phenylsilanes

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### Introduction

When deposited on a substrate, block copolymer thin films spontaneously form a morphology composed of lamellae oriented in a direction parallel to the substrate because of specific affinity for one block with the substrate [1]. For applications in electronics or biomedicine however, a perpendicular orientation is required. In order to obtain this specific orientation, a variety of external fields were applied, such as electric fields [2], evaporation fields [3] or a treatment of substrates with polymer brushes [4] or Self-Assembled Monolayers (SAM) [5]. For the latest two cases, the substrate after treatment should be *neutral* to each block in order to avoid any preferential affinity with the surface. In this study, we tested SAM of phenylsilanes as an efficient route to control the morphology of Poly(styrene-*b*-methylmethacrylate) (P(S-*b*-MMA)) deposited on silicon wafers. SAMs were prepared without any additional irradiation in order to increase the straightforwardness of this technique.

### Experimental

**Preparation and characterization of SAM of phenylsilanes.** Phenyltrichlorosilane (PETS) and Phenylundecyltrichlorosilane (PUTS) with respectively 2 and 11 methylenes in their alkyl chains were used for surface treatment of silicon wafers. Treatment was carried out in toluene solution (0.1% v/v) under Argon atmosphere. The roughness of treated samples was measured by Atomic Force Microscopy (AFM) in tapping mode, the degree of ordering of SAM by Near Edge X-Ray Absorption Fine Structure spectroscopy (NEXAFS) and finally the surface energy by contact angle measurements.

**Preparation of PS-*b*-PMMA block copolymer thin films** P(S-*b*-MMA) with a molecular weight of 50 kg/mol and 100 kg/mol were deposited on SAM treated samples by spin coating. The samples were annealed at 180°C. Resulting morphology was observed by AFM in tapping mode.

### Results and discussion

**Characterization of SAM.** AFM revealed that samples treated with SAMs of PETS and PUTS were both flat at molecular level with a few aggregates only. NEXAFS spectra of both SAMs are shown in Figure 1. The degree of ordering of SAM molecules, evaluated by  $\sigma^*$  transitions, was higher for PUTS because of interactions between long alkyl chains. In both cases phenyl groups were oriented toward the free surface as revealed by  $\pi^*$  transitions. This particular structure of SAMs led to drastic changes in surface energy of substrates, as revealed by contact angle measurements. Indeed, bare silicon oxide substrates are characterized by a high surface energy due to high polarity. After treatment with both types of SAMs, surface energy significantly decreased and was mainly of dispersive character.

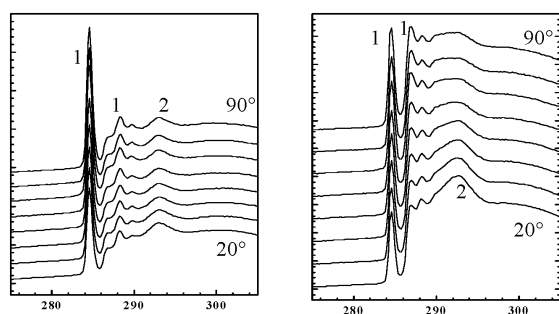


Figure 2. NEXAFS spectra of SAMs of PETS (left) and PUTS (right): angle dependency of (1)  $\pi^*$  transitions and (2)  $\sigma^*$  transitions

### Orientation of P(S-*b*-MMA) on SAM treated substrates.

Figure 2 shows AFM height images of the 50k P(S-*b*-MMA) deposited on the substrates treated with PETS and PUTS respectively. In both cases, morphology was composed of islands, which is the hallmark of lamellae oriented in a direction parallel to the surface. By comparing the thickness of these samples with the interlamellar spacing it was deduced that the morphology was asymmetric, i.e. lamellae of PS present both at the free surface exposed to air and at the interface with the substrate. It should be noted that on bare substrates, the morphology is asymmetric because of specific affinity of polar PMMA with high energy silicon oxide. An increase in molecular weight led to different conclusions. In that case, the lamellae were oriented in a direction perpendicular to the substrates, as shown in Figure 3, which represents AFM phase images of the 100k P(S-*b*-MMA) deposited on both types of SAMs. The morphology was of "fingerprint" type for both samples. The observed morphologies in the study could be correlated to the difference in interfacial energy between each block and the substrates, calculated on the basis of previously measured surface energy values of treated samples. This difference should be zero to satisfy the criteria of neutrality. In our case, this condition was not exactly fulfilled but could nonetheless permit us to give an explanation for the different morphologies observed in the study, as well as for the dependence on molecular weight.

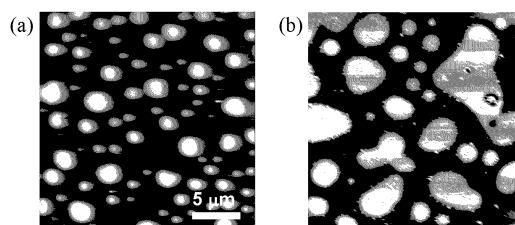


Figure 2. AFM height images of P(S-*b*-MMA) thin films with a molecular weight of 50 kg/mol on (a) PETS and (b) PUTS.

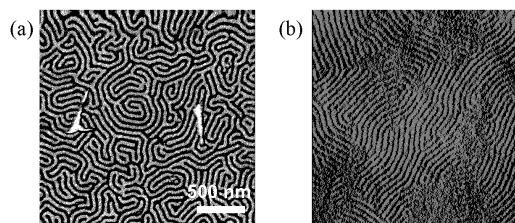


Figure 3. AFM height images of P(S-*b*-MMA) thin films with a molecular weight of 100 kg/mol on (a) PETS and (b) PUTS.

### Conclusions

The treatment of substrates with a SAM of phenylsilane was a straightforward technique to control the morphology of block copolymer thin films. By additionally changing the molecular weight of block copolymer it was possible to obtain various thin film morphologies. The SAM structure could be further adjusted to optimize the surface character of treated samples in order to fully satisfy the condition for surface neutrality. This should guaranty a perpendicular orientation of lamellae over a wider range of experimental parameters.

### References

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