# Compositional Mapping of Polymer Surfaces by Chemical Force Microscopy Down to the Nanometer Scale: Reactions in Block Copolymer Microdomains

*Holger Schönherr,* Chuan Liang Feng, Nikodem Tomczak, G. Julius Vancso**

**Summary:** The laterally resolved analysis of the chemical surface composition of surface-treated block copolymers by atomic force microscopy (AFM) pull-off force mapping in the force volume (FV) mode and the automated analysis of the FV data is discussed. Poly(*tert*-butyl acrylate) (PtBA) microdomains residing in a polystyrene (PS) matrix at the surface of cyclohexane-treated polystyrene-*block*-poly(*tert*-butyl acrylate) (PtBA-b-PS) block copolymer thin films were domain-selectively deprotected, activated and chemically modified, as also shown by fluorescence microscopy. AFM pull-off force mapping in conjunction with an automated analysis of the data provided real space evidence for the successful conversion of reactive esters located in the PtBA domains and showed that AFM and related approaches, such as chemical force microscopy (CFM), can indeed contribute to assess changes in heterogeneous surface chemical composition of polymers down to sub-50 nm length scales.

**Keywords:** block copolymers; chemical force microscopy (CFM); local chemical analysis; nanoheterogeneity; surface chemistry

## Introduction

The laterally resolved analysis of the chemical surface composition of polymers and surface-treated polymers remains an experimental challenge.[1] Spectroscopic and spectrometric approaches have been refined in recent years to address successfully the surface chemical analysis of polymer films prior to and after reactions. These improvements enable one to assess, for instance, the kinetics of surface reactions *ex situ* and also *in situ* via advanced compositional analyses.[1,2] To combine quantitative chemical analysis with high lateral resolution for soft condensed matter, however, has so far remained a challenge. This is particularly true for polymer systems that are at the interface of sensors, implants etc. and biological media and species, where aqueous media are a prerequisite and vacuum-incompatibility is often observed.

In these polymer systems, as well as for a broad range of other surfaces comprising soft condensed matter, chemical heterogeneity is known, or expected to play an important role.[1] Work by Spatz and coworkers, for instance, showed how clustering of individual proteins or polypeptide sequences affects cell adhesion.[4] Similarly, meso and nanoscale chemical heterogeneities are important for surface treatments for adhesion improvement, as well as for biosensors and array platforms.[5] Finally, recent advances in nanoscale chemistry (for instance nanopatterning via soft lithographic,[6,7] scanning probe lithographic[8–10] and other approaches) clearly require and would benefit from advanced chemically sensitive surface characterization techniques that operate on sub-50 nm length scales.

MESA$^+$ Institute for Nanotechnology and Faculty of Science and Technology, Department of Materials Science and Technology of Polymers, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands
Fax: (+31) 53 489 3823
E-mail: h.schonherr@utwente.nl; g.j.vancso@utwente.nl

Until recently, there were few, if any, solutions available to tackle the mentioned laterally resolved compositional analysis on non-conducting, vacuum-incompatible substrates. Among others, the scanning probe microscopy method called ''chemical force microscopy'' (CFM) has begun to contribute to solving relevant problems in this area. The extension of pioneering research conducted by Lieber and co-workers led to the development of chemically sensitive imaging down to the sub-100 nanometer scale by CFM, mostly demonstrated for self-assembled monolayers (SAMs),[11–17] but also for polymers.[18,19] In recent years we have successfully applied CFM to study polymer surface chemical composition, in particular on surface-treated polymers.[20–24]

It is instructive to have a closer look at how forces can be measured to eventually assess surface composition. Friction force microscopy (FFM) measurements using atomic force microscopy (AFM), for instance, have been frequently ''applied'' to perform sub-micrometer lateral compositional mapping.[25] However, it must be noted that owing to problems of performing quantitative and reproducible FFM measurements on the one hand, and the unsolved question how friction coefficients (and not only relative differences in friction contrast/forces) and surface coverages are related on the other hand, only qualitative information is in many instances obtained at best.[26]

For chemical imaging by CFM it is typically more straightforward to record a mesh of laterally resolved force-displacement (f-d) curves.[22,23,27] In these measurements, a central aspect is the controlled chemical modification of AFM probe tips (Figure 1).[11] By controlling the surface chemistry at the tip apex, as well as the imaging medium, the intermolecular interactions (between the functional groups exposed on the tip and on the sample surface) can be systematically varied and controlled. These spatially different interactions can be measured in normal (or lateral) force detection schemes, providing access to variations in, e.g., surface chemistry averaged over the tip – sample contact area.

It is clear that this methodology provides indirect information about the chemical composition via the measured interaction forces. For apolar systems, in which only van der Waals interactions operate, work by Feldmann and co-workers established a quantitative approach based on the theoretical framework of the Lifshitz theory.[29] For polar groups interacting in such experiments, contact mechanics provide a theoretical framework to rationalize the data.[30,31] In so far the quality of the data is not (yet) comparable to various

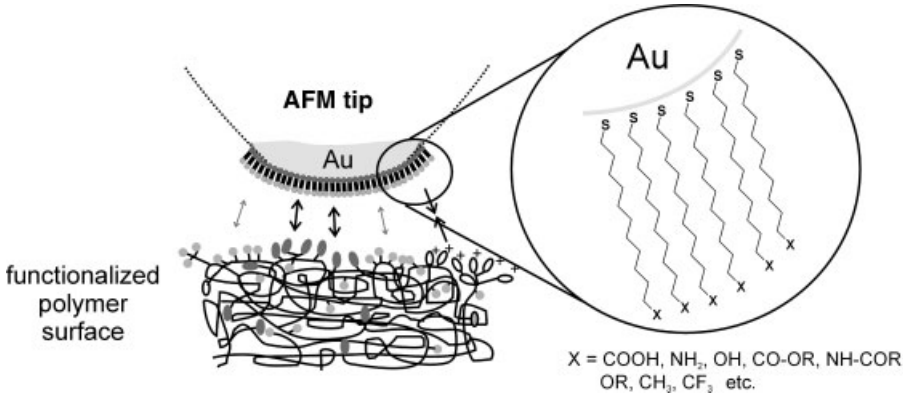


***Figure 1.***
Schematic of gold-coated AFM tip modified with a SAM of $\omega$-functionalized organothiols used in CFM studies of surface-treated polymers. Reproduced with permission from reference [28].

 

spectroscopic and spectrometric approaches, however, combined with quantitative spectroscopies laterally resolved information can be acquired down to the sub-50 nm level.

As we demonstrate in this paper, a commercially available AFM (operated in the force volume (FV) mode)[1] can be used in conjunction with a custom-made analysis software to unravel fine details of surface chemical reactions carried out in PtBA microdomains exposed in polystyrene-*block*-poly(*tert*-butyl acrylate) $PS_{690}$-*b*-$PtBA_{1210}$ block copolymer thin films. The extension of this work to include modified tips and controlled liquid media will broaden the scope of the methodology and will enable us to determine surface chemistry locally in a quantitative manner.

## Experimental

### Materials

The $PS_{690}$-*b*-$PtBA_{1210}$ diblock copolymer (polydispersity: 1.03) was purchased from Polymer Source Company (Dorval, Canada) and used as received. Fluoresceinamine, 1-ethyl-3-(dimethylamino)-propylcarbodiimide (EDC), *N*-hydroxysuccinimide (NHS) and cyclohexane were purchased from Aldrich and were used as received.

### Preparation of Thin Films

Thin polymer films were prepared by spin-coating polymer solutions in toluene (typical concentration between 10 and 20 mg/ml) onto clean silicon wafers, as reported previously.[35]

### Solvent Treatment of Thin Films

Cyclohexane was used to enrich the surface in PS as reported previously.[35]

### Chemical Modification

A drop of trifluoacetic acid (50 μL) was applied to the solvent-treated films. Subsequently, the films were activated by immersion into an aqueous solution of EDC (1 M) and NHS (0.2 M) for 30 min. The films were immersed inside fluoresceinamine solution (100 μM, PB buffer, pH = 7.4). Then the samples were taken out, rinsed with PB buffer and Milli-Q water, and dried in a steam of nitrogen. Finally, the samples were dried inside a vacuum oven for 1 day.

### Atomic Force Microscopy (AFM)

The AFM measurements were carried out with a NanoScope IIIa multimode AFM (Digital Instruments/Veeco, Santa Barbara, CA). Tapping mode AFM data were acquired using a 100 μm scanner and microfabricated tapping mode silicon tips/cantilevers ($k \sim 30$ N/m, Nanosensors, Wetzlar, Germany) in ambient atmosphere (ca. 30% relative humidity, 24 °C temperature) as described previously.[35] For laterally resolved pull-off force measurements V-shaped $Si_3N_4$ cantilevers ($k \sim 0.06$ N/m, Model NP, Veeco Nano Probe, Santa Barbara, CA) were used; the AFM was operated in the FV mode using a 10 μm scanner, as reported previously.[24]

### Fluorescence Microscopy

The fluorescence microscopy data was obtained using a Zeiss LSM 510 confocal fluorescence microscope with a BP 500-550 IR filter for fluoresceinamine, as described elsewhere.[37]

## Results and Discussion

In the work described below, nanometer scale chemical information was acquired by capturing force-volume images[32] using AFM tips with known surface chemistry in ambient atmosphere. The data sets acquired consisted of $64 \times 64$ force displacement curves (Figure 2a and b) and complementary topological information. Using a custom-made software written in Labview (National Instruments), these individual f-d curves are analyzed off-line, as reported previously.[24]

From these f-d curves the desired information on the underlying surface mechanical (elastic) and adhesive properties of the nanometer scale tip-sample

 

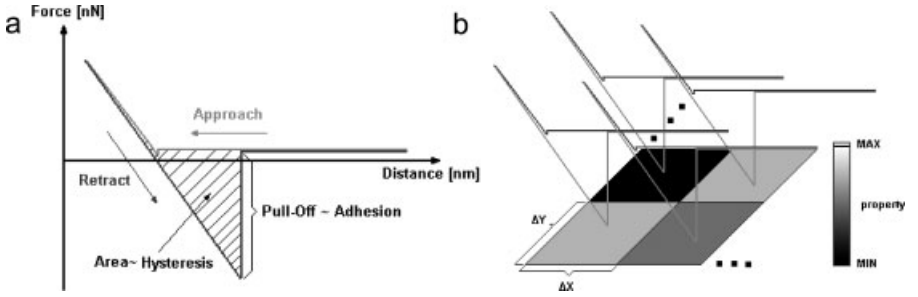


***Figure 2.***
a) Schematic f-d curve showing the data evaluated by the software routine; b) Illustration of the mesh of f-d curves acquired in the FV mode.

contact can be obtained from the approach (indentation) and retracing parts of the curves, respectively.[24] From the displacement (distance) a height image is calculated, while the approaching and retracing curve yield an estimate of the modulus and the pull-off force (and adhesion hysteresis), respectively. These data will then be analyzed statistically (1 file contains $64 \times 64 = 4096$ data points for each quantity estimated) or the corresponding properties can be localized in a 2D analysis. Finally, if parameters, such as time or temperature, are being varied, more demanding correlation analyses are possible. In principle, one could also perform the analysis on-line, similar to an earlier report on inverted chemical force microscopy (iCFM), which is a useful methodology to assess surface reactions in SAMs on the nanometer scale in real time.[33]

The pull-off force data obtained contain useful information on the tip-sample interactions, which can be rationalized on the basis of continuum contact mechanics theories, such as the Johnson-Kendall-Roberts (JKR) or the Derjaguin-Muller-Toporov (DMT) theory.[30,31] The lower limitation of the lateral resolution is given by the size of the probe tip, the mechanical properties of the substrate, and thermal/instrumental drift of the set-up.

As shown below, surface chemical reactions confined to the area of PtBA microdomains of PS-*b*-PtBA block copolymers exposed in these thin films can be mapped with sub-50 nm resolution. Following the hydrolysis of the *tert*-butyl ester groups at and near the surface of $PS_{690}$-*b*-$PtBA_{1210}$ films under acidic conditions (using aqueous HCl, $CF_3$–COOH, or gaseous HCl), these groups were converted to reactive NHS ester groups by reaction with 1-ethyl-3-(dimethylamino)-propylcarbodiimide (EDC) and N-hydroxysuccinimide (NHS).[34] Nucleophiles, such as primary amino groups, react efficiently with these active esters (also in aqueous media) and yield robust derivatized layers owing to covalent coupling. The corresponding surface derivatization reactions have been previously analyzed on neat films in detail using, among other techniques, contact angle, FT-IR spectroscopy, X-ray photoelectron spectroscopy (XPS) measurements (not shown here).[34]

In spin-coated films of $PS_{690}$-*b*-$PtBA_{1210}$ on oxidized silicon, tapping mode AFM phase images revealed the microphase separation.[35] The minority phase was recognized as cylindrical features. In such films, angle dependent XPS, among other techniques, proved that there is a skin layer of acid sensitive PtBA present (owing to the lower surface tension of PtBA compared to PS).[35]

Using a cyclohexane treatment analogously to work by Stadler and co-workers,[36] both blocks were exposed at the surface of the films in a poorly ordered, yet microphase separated structure (Figure 3). The analysis of the surface composition by XPS (surface coverage $\chi(\mathrm{PtBA}) \sim 0.60$) showed a clear correspondence of the

 

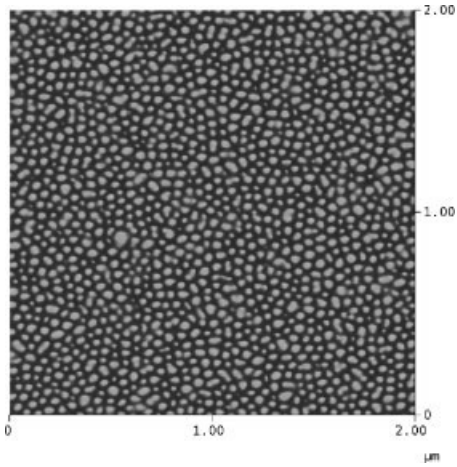


***Figure 3.***
Tapping mode AFM phase image of cyclohexane-treated film of $PS_{690}$-*b*-$PtBA_{1210}$ on oxidized silicon. The areas with bright phase contrast are PtBA microdomains with an average diameter of 60 nm.

surface area covered by the phase with bright phase contrast in the AFM image ($\chi \sim 0.55$). Similarly, the hydrolysis kinetics were in favorable agreement with the interpretation that in the cyclohexane-treated films *both* blocks are exposed at the surface and that PtBA is located inside the islands seen in Figure 3.

After the reaction of NHS ester-activated, previously solvent treated films with fluoresceinamine, the fluorescence emission intensity was lower by a factor of ~0.5 compared to neat $PS_{690}$-*b*-$PtBA_{1210}$ films that were treated similarly (Figure 4). Neat PS films showed no fluorescence emission (no data shown). This significantly decreased fluorescence emission intensity suggests that the reaction took place inside the PtBA domains.

In Figure 5 we show the height and FV images of a spin coated, a hydrolyzed and a hydrolyzed $PS_{690}$-*b*-$PtBA_{1210}$ film after EDC/NHS reactivation and coupling of fluoresceinamine.

The experiments were performed using a silicon nitride tip in ambient conditions. The image contrast is related to differences in capillary forces that vary systematically with surface composition. It can be clearly seen that the protruding features (which are identified as PtBA islands by comparison with TM-AFM height, not shown, and phase images, see Figure 3) changed in their adhesive properties from initially low pull-off force (PtBA) to high pull-off force (poly(acrylic acid)), and finally to low pull-off force (fluoresceinamine) vs. PS. The same trend was observed in the pull-off force images and distributions (see below).

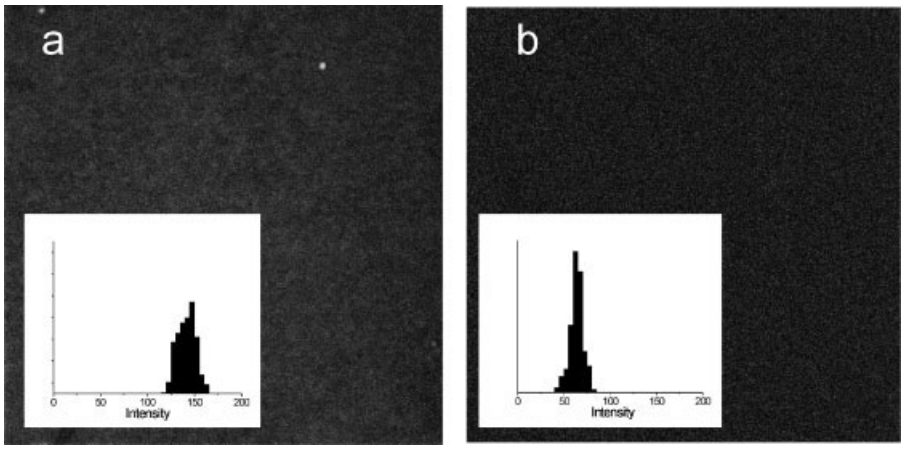


***Figure 4.***
Fluorescence microscopy images (146 μm × 146 μm; insets: intensity histograms) of a) neat $PS_{690}$-*b*-$PtBA_{1210}$ film and b) cyclohexane-treated $PS_{690}$-*b*-$PtBA_{1210}$ film, both after hydrolysis, reactivation by EDC/NHS, and coupling with fluoresceinamine under identical conditions.

 

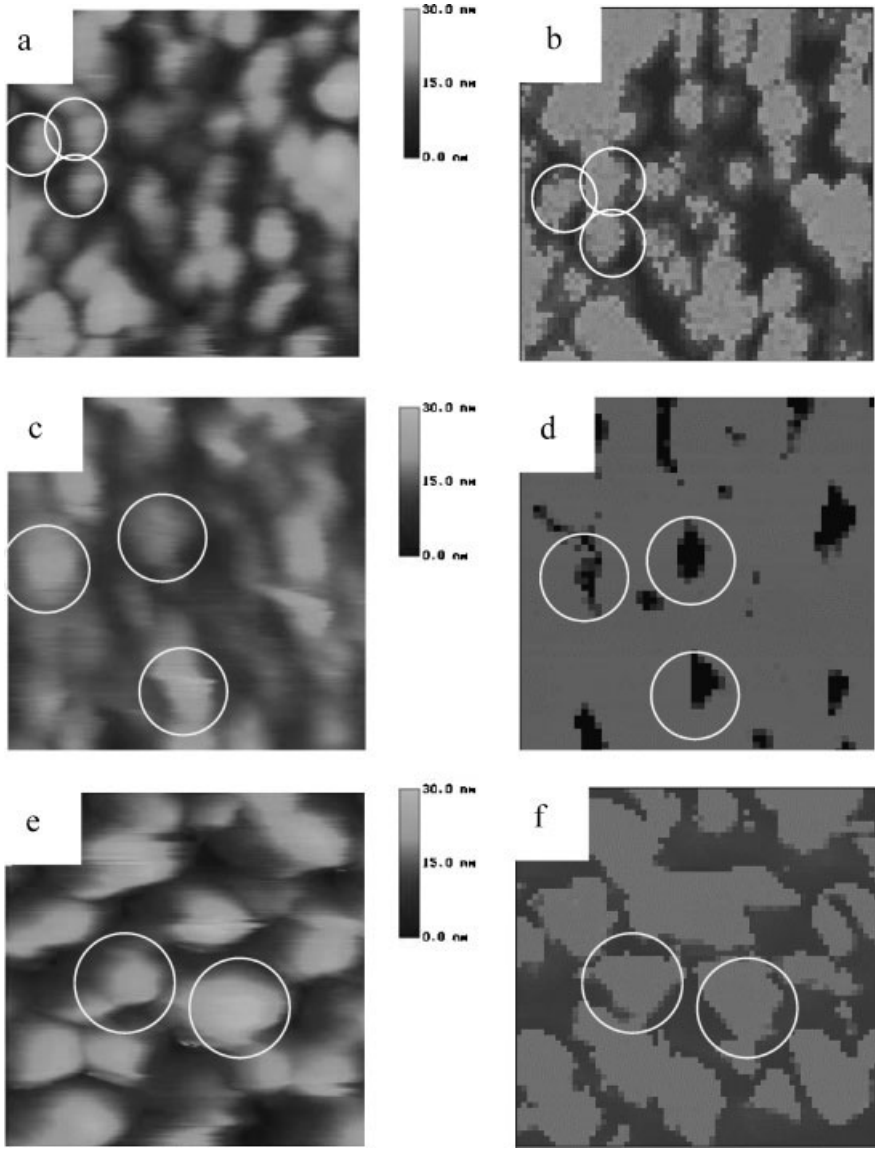


***Figure 5.***
a) AFM height and b) FV images (500 nm × 500 nm) of the cyclohexane-treated $PS_{690}$-*b*-$PtBA_{1210}$ polymer films; c) AFM height and d) FV images of the cyclohexane-treated PS-*b*-PtBA polymer films after hydrolysis; e) AFM height and f) FV images of the cyclohexane-treated PS-*b*-PtBA polymer films after hydrolysis, reactivation by NHS/EDC and grafting of fluoresceinamine. By convention, the bright areas in the FV images correspond to low pull-off forces (several protruding circular areas have been marked with circles to guide the eyes).

A more detailed insight into the surface derivatization in this heterogeneous system was obtained by a quantitative analysis of the FV images using the mentioned custom-made software. As shown in Figures 6 and 7, the pull-off force maps were locally not homogeneous.

While we observed a multimodal pull-off force distribution (and a qualitatively very similar distribution of the adhesion hysteresis, data not shown) with pull-off forces around 40 nN for the hydrolyzed films, the derivatization with fluoresceine-amine inside the PtBA microdomains led to

 

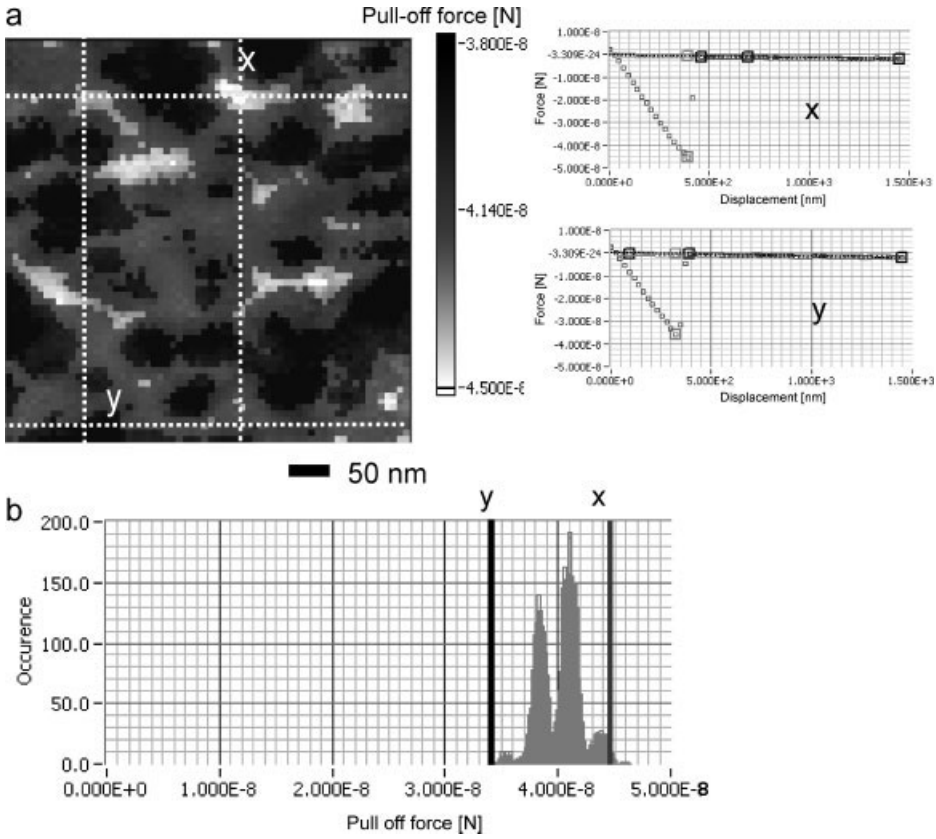


***Figure 6.***
a) Pull-off force map (500 nm × 500 nm, forces increase from dark to bright contrast) and two representative f-d curves (the position of these curves labeled x and y is located at the crossing of the corresponding dotted lines) of cyclohexane-treated $PS_{690}$-*b*-$PtBA_{1210}$ polymer films calculated from the FV data, such as shown in Figure 5. b) Pull-off force distribution (again the data points x and y refer to the ones schematically indicated in (a)).

a broadening of the distribution. In this case the maximum of the distribution was shifted at ~7 nN and a long tail was observed towards higher pull-off force values. Also for the fluoresceinamine-derivatized films, the distribution of the adhesion hysteresis looked qualitatively very similar to the pull-off force distribution.

These pull-off force distributions reflect on the one hand the surface chemistry, i.e. the different relative coverages of the functionalized polymer film surface (PtBA phase vs. PS phase and fluoresceinamine-derivatized areas vs. PS phase, respectively), on the other hand they show the lateral heterogeneity of the different surface chemistries. The differences between PtBA and PS are small, although the highest pull-off force values were observed for the PS matrix (e.g. point x in Figure 6), consistent with the higher surface energy of PS compared to PtBA leading to a higher work of adhesion.[11,21,30,31] The covalently attached fluoresceinamine rendered the PtBA microdomains hydrophobic, thus the low pull-off forces are associated with the fluoresceinamine-rich microdomains (e.g. point w in Figure 7).

All data have been acquired in air using an unmodified, yet chemically distinct, silicon nitride tip. In order to map and evaluate the lateral chemical composition

 

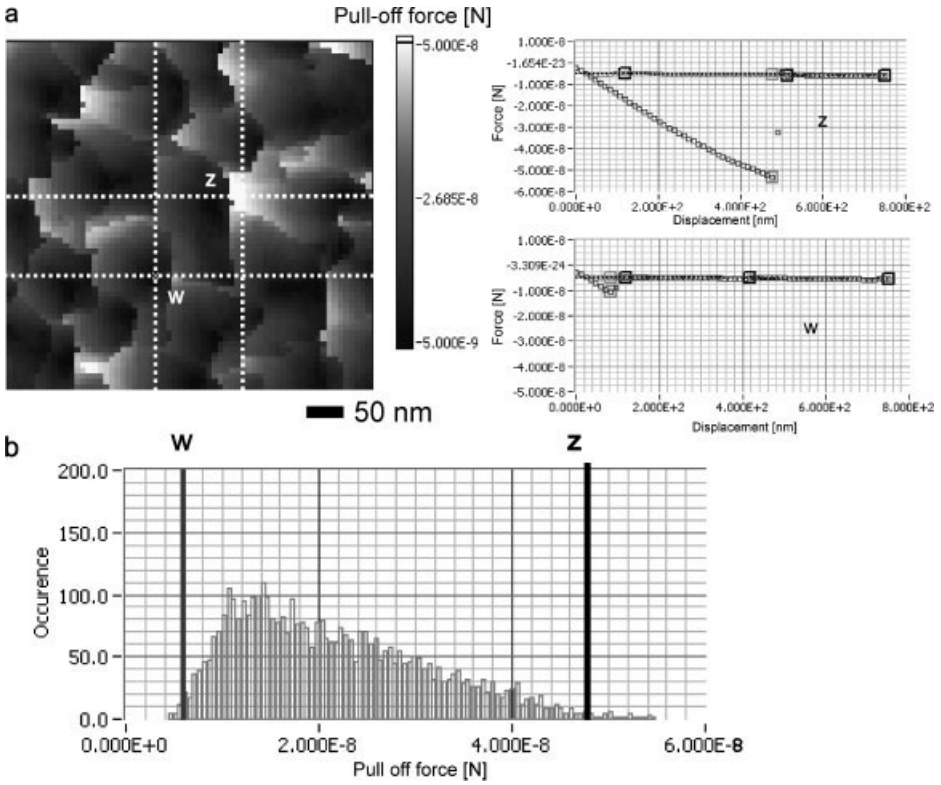


***Figure 7.***
a) Pull-off force map (500 nm × 500 nm, forces increase from dark to bright contrast) and two representative f-d curves (the position of these curves labeled z and w is located at the crossing of the corresponding dotted lines) of cyclohexane-treated PS-*b*-PtBA polymer films after hydrolysis, reactivation by NHS/EDC and grafting of fluoresceinamine calculated from the FV data, such as shown in Figure 5. b) Pull-off force distribution (again the data points z and w refer to the ones schematically indicated in (a)).

of these films quantitatively, CFM experiments under carefully controlled conditions (incl. drift control) with an increased number of data points averaged in time (for each position) and in plane are required.

Additional work in different media using SAM-modified tips is currently underway to help to quantify the coverages *locally* for $PS_{690}$-*b*-$PtBA_{1210}$ films derivatized also with poly(ethylene glycol), DNA and proteins. This work will contribute to obtain a better understanding of confined reactivity at surfaces of organic and polymeric thin films and the development of local chemical heterogeneities in surface modification reactions.

## Conclusion

Atomic force microscopy pull-off force mapping in the force volume mode showed that poly(*tert*-butyl acrylate) microdomains at the surface of cyclohexane-treated polystyrene-*block*-poly(*tert*-butyl acrylate) block copolymer thin films were domain-selectively deprotected, activated and chemically modified. The results obtained clearly show that CFM mapping of surface-treated polymers is feasible also on sub-50 nm length scales and that the custom-made software allows one to conveniently and rapidly evaluate AFM adhesion and CFM force mapping experiments. In contrast to the FV data,[32] *quantitative*

 

pull-off force maps are directly obtained, along with force distributions with more than 4000 data points per FV image. With further improved experimental routines and in particular sharper CFM tips, resolutions on the order of 10 nm appear ultimately feasible.

*Acknowledgements:* The authors gratefully acknowledge the assistance of M.Sc. J. Song in converting some of the FV data and Dr. H. Hillborg for stimulating discussions. This work has been financially supported by the MESA$^+$ Institute for Nanotechnology of the University of Twente and the Council for Chemical Sciences of the Netherlands Organization for Scientific Research (CW-NWO) in the framework of the *vernieuwingsimpuls* program.

[1] G. J. Vancso, H. Hillborg, H. Schönherr, *Adv. Polym. Sci.* **2005**, *182*, *in press*.
[2] See e.g. M. Herrero, R. Navarro, N. Garcia, C. Mijangos, H. Reinecke, *Langmuir* **2005**, *21*, 4425 and references herein.
[3] H. Schönherr, C. L. Feng, A. Shovsky, *Langmuir* **2003**, *19*, 10843.
[4] M. Arnold, E. A. Cavalcanti-Adam, R. Glass, J. Blummel, W. Eck, M. Kantlehner, H. Kessler, J. P. Spatz, *Chem Phys Chem* **2004**, *5*, 383.
[5] P. Gong, D. W. Grainger, *Surf. Sci.* **2004**, *570*, 67 and references herein.
[6] Y. N. Xia, G. M. Whitesides, *Annu. Rev. Mater. Sci.* **1998**, *28*, 153.
[7] H. W. Li, W. T. S. Huck, *Current Op. Solid State Mater. Sci.* **2002**, *6*, 3.
[8] S. Kramer, R. R. Fuierer, C. B. Gorman, *Chem. Rev.* **2003**, *103*, 4367.
[9] D. Wouters, U. S. Schubert, *Angew. Chem. Int. Ed.* **2004**, *43*, 2480.
[10] G. Y. Liu, S. Xu, Y. L. Qian, *Acc. Chem. Res.* **2000**, *33*, 457.
[11] C. D. Frisbie, L. F. Rozsnyai, A. Noy, M. S. Wrighton, C. M. Lieber, *Science* **1994**, *265*, 2071.
[12] A. Noy, D. V. Vezenov, C. M. Lieber, *Annu. Rev. Mater. Sci.* **1997**, *27*, 381.
[13] R. C. Thomas, P. Tangyunyong, J. E. Houston, T. A. Michalske, R. M. Crooks, *J. Phys. Chem.* **1994**, *98*, 4493.
[14] J. B. D. Green, M. T. McDermott, M. D. Porter, L. M. Siperko, *J. Phys. Chem.* **1995**, *99*, 10960.
[15] R. C. Thomas, J. E. Houston, R. M. Crooks, T. Kim, T. A. Michalske, *J. Am. Chem. Soc.* **1995**, *117*, 3830.
[16] S. Akari, D. Horn, H. Keller, W. Schrepp, *Adv. Mater.* **1995**, *7*, 549.
[17] E. W. van der Vegte, G. Hadziioannou, *Langmuir* **1997**, *13*, 4357.
[18] S. K. Sinniah, A. B. Steel, C. J. Miller, J. E. ReuttRobey, *J. Am. Chem. Soc.* **1996**, *118*, 8925.
[19] M. P. L. Werts, E. W. van der Vegte, V. Grayer, E. Esselink, C. Tsitsilianis, G. Hadziioannou, *Adv. Mater.* **1998**, *10*, 452.
[20] H. Schönherr, G. J. Vancso, *J. Polym. Sci. B Polym. Phys.* **1998**, *36*, 2483.
[21] H. Schönherr, Z. Hruska, G. J. Vancso, *Macromolecules* **1998**, *31*, 3679.
[22] H. Schönherr, M. T. van Os, R. Förch, R. B. Timmons, W. Knoll, G. J. Vancso, *Chem. Mater.* **2000**, *12*, 3689.
[23] H. Schönherr, Z. Hruska, G. J. Vancso, *Macromolecules* **2000**, *33*, 4532.
[24] H. Hillborg, N. Tomczak, A. Olah, H. Schönherr, G. J. Vancso, *Langmuir* **2004**, *20*, 785.
[25] D. S. Ginger, H. Zhang, C. A. Mirkin, *Angew. Chem. Int. Ed.* **2004**, *43*, 30.
[26] H. Schönherr, P. J. A. Kenis, J. F. J. Engbersen, S. Harkema, R. Hulst, D. N. Reinhoudt, G. J. Vancso, *Langmuir* **1998**, *14*, 2801 and references herein.
[27] C. E. H. Berger, K. O. van der Werf, R. P. H. Kooyman, B. G. de Grooth, J. Greve, *Langmuir* **1995**, *11*, 4188.
[28] H. Schönherr, Ph.D. thesis, University of Twente, Enschede, The Netherlands, **1999**.
[29] K. Feldman, T. Tervoort, P. Smith, N. D. Spencer, *Langmuir* **1998**, *14*, 372.
[30] K. L. Johnson, K. Kendall, A. D. Roberts, *Proc. R. Soc. London A* **1971**, *324*, 301.
[31] B. V. Derjaguin, V. K. Muller, Y. P. Toporov, *J. Coll. Interf. Sci.* **1975**, *53*, 314.
[32] In the so-called force-volume images the pull-off forces can be graphically displayed in a layered image. Pull-off forces larger than a certain value are displayed in a gray scale. As an attractive force has per definition a negative sign, the scaling ranges from dark tones (high pull-off force) to bright tones (low pull-off force).
[33] B. Dordi, J. P. Pickering, H. Schönherr, G. J. Vancso, *Surf. Sci.* **2004**, *570*, 57.
[34] C. L. Feng, G. J. Vancso, H. Schönherr, *in preparation*.
[35] C. L. Feng, G. J. Vancso, H. Schönherr, *Langmuir* **2005**, *21*, 2356.
[36] H. Elbs, K. Fukunaga, R. Stadler, G. Sauer, R. Magerle, G. Krausch, *Macromolecules* **1999**, *32*, 1204.
[37] C. L. Feng, Z. Zhang, R. Förch, W. Knoll, G. J. Vancso, H. Schönherr, *Biomacromolecules* **2005**, *submitted*.

 