Molecular Resolution Imaging and Friction Anisotropy of Highly Oriented Polyethylene and Poly(tetrafluoroethylene) by Scanning Force Microscopy with Chemically Modified Probes

Holger Schönherr and G. Julius Vancso*

Faculty of Chemical Technology, Polymer Materials Science and Technology, University of Twente, P.O. Box 217, NL-7500 AE Enschede, The Netherlands

Received April 1, 1997
Revised Manuscript Received July 10, 1997

Introduction. During the last 10 years scanning force microscopy (SFM) has played an increasingly important role in polymer science because of its ability (a) to characterize surface structure and morphology and (b) to study surface properties (friction, adhesion, elasticity, etc.) from the subnanometer to the millimeter scales.[1] Different techniques, based on different contrast mechanisms, include atomic force (AFM),[2] lateral force (LFM),[3] and force modulation (FMM)[4] microscopy.

Chemical force microscopy (CFM),[5−9] a technique that has been introduced relatively recently, allows one to measure adhesion and friction between the surface and a functionalized probe. This method uses gold-covered force microscopy tips that are modified with self-assembled monolayers (SAMs) (e.g., ω-functionalized thiols). In addition to investigating the topology of the sample surface, modified tips can be simultaneously utilized to measure forces, as well as to image "with chemical sensitivity".[5−9] In CFM, the friction forces between the functionalized tip and the sample surface were reported to be dominated by the chemical species located at the surface of the tip and the surface that was studied, respectively. The application of these tips requires that the imaging forces be minimized in order to avoid damaging the sample or the monolayer on the tip. In addition, nanometer resolution of the method is highly desirable in order to benefit from the potentially high resolution of SFM. Previously, silane-modified silicon tips have been used to study rough surfaces.[10] Another approach to controlling the chemical functionality of the tip is through the physisorption of poly(tetrafluoroethylene) (PTFE). Howald et al.[11] applied this method to nondestructively image the Si(111) 7 × 7 surface reconstruction by AFM.

Our aim is to exploit chemically modified SFM tips for *routine* imaging of surfaces, preferably with (sub)-nanometer resolution. In this context, understanding the interaction between the functionalized tip and the sample surface and knowledge about the friction processes in the nanoscale are of fundamental importance. The use of uniaxially oriented crystalline polymers to explore molecular resolution in AFM applications seems to be particularly beneficial. These model materials can include crystallographically well-defined surfaces (e.g., *ac* or *bc* facets), as polymers can be prepared with the chain axes in the surface imaged. The main objective of this study was to find out whether it is possible to image (by AFM and LFM) oriented polymers with molecular resolution using modified tips. The tips were functionalized by the established method of forming a self-assembled monolayer[12,13] on gold-covered silicon nitride SFM probes.

The first sample investigated in this study—"single crystal-like" HDPE obtained by uniaxial compression—was previously characterized by small angle X-ray scattering, wide angle X-ray scattering, and optical and electron microscopy.[14] The periodicities of the orthorhombic unit cell of PE in the *a*, *b*, and *c* directions were imaged by AFM on microtomed surfaces of "single crystal-like" HDPE specimens, utilizing Si_3N_4 tips.[15] These AFM measurements in air were limited to a maximum scan size of ca. $(15\ nm)^2$ at low forces.[16] The second sample discussed in this communication was a PTFE surface that was unidirectionally oriented by sliding a block of PTFE over a heated (220 °C) glass slide. In our study, the worn surface of the slider[17] (rather than the transferred film[18]) was investigated. Our AFM scans performed on this surface unveiled a microfibrillar morphology with the fibrillar axes oriented predominantly in the sliding direction. For microfibrils, the polymer chain axis is expected to be oriented parallel to the fibril axis. Thus, the crystallographic *c* direction was known for both specimens in this work. This allowed us to adjust the specimen orientation manually in the force microscope such that SFM scans could be performed parallel or perpendicular to the polymer chain axis.

Experimental Section. Triangular-shaped silicon nitride cantilevers and silicon nitride tips (Digital Instruments (DI), Santa Barbara, CA) were covered with 50−70 nm of gold in a Balzers SCD 040 sputtering machine at an argon pressure of 0.1 mbar. The gold-covered tips were then functionalized with 11-carboxy-undecane thiol (−COOH), octadecanethiol ($-CH_3$), or (2-mercaptoethyl)perfluorononanamide ($-CF_3$), following the procedures described in refs 13 and 19. The lattices of, e.g. fluorinated thiols can be imaged routinely on similar gold films deposited onto mica.[19,20]

The SFM measurements were carried out with a NanoScope III AFM (DI) in the contact mode. AFM scans were performed in air or in ethanol (p.a., Merck) utilizing a liquid cell (DI). The LFM data were obtained by scanning the sample under the tip at an angle of 90° to the long axis of the cantilever. The direction of the polymer chains, the crystallographic *c* direction, was adjusted parallel or perpendicular to this scan direction by manually turning the sample. The friction force was measured by recording friction loops for 10−15 nm line scans at a scan rate of 19−36 Hz for different setpoints after correcting the offset. For scans captured perpendicular to the polymer chain direction, the friction loops displayed *in all cases* (for all different tip modifications) the molecularly resolved arrangement of polymer chains; for scans parallel to the chain direction, only for HDPE was the repeat unit recognized.[15] The corresponding normal forces (applied load + pull-off force) were measured prior to and after the collection of the friction data. The torsional spring constant was calibrated as described in ref 8 (double beam approach). It was calculated as 97 N/m for cantilevers with a bending spring constant of 0.12 N/m. Due to variations in the tip/sample contact area, only the results obtained using a single cantilever/tip, or in other words, only scans along and perpendicular to the polymer chain direction that were performed with the *same* tip, could be compared. From a large number of experiments we could nevertheless conclude a clear trend for the differences in friction of tips modified with different ω-functionalized thiols.

Results and Discussion. Using functionalized tips, we imaged the microtomed surfaces of the HDPE sample in air. In addition to collecting scans with

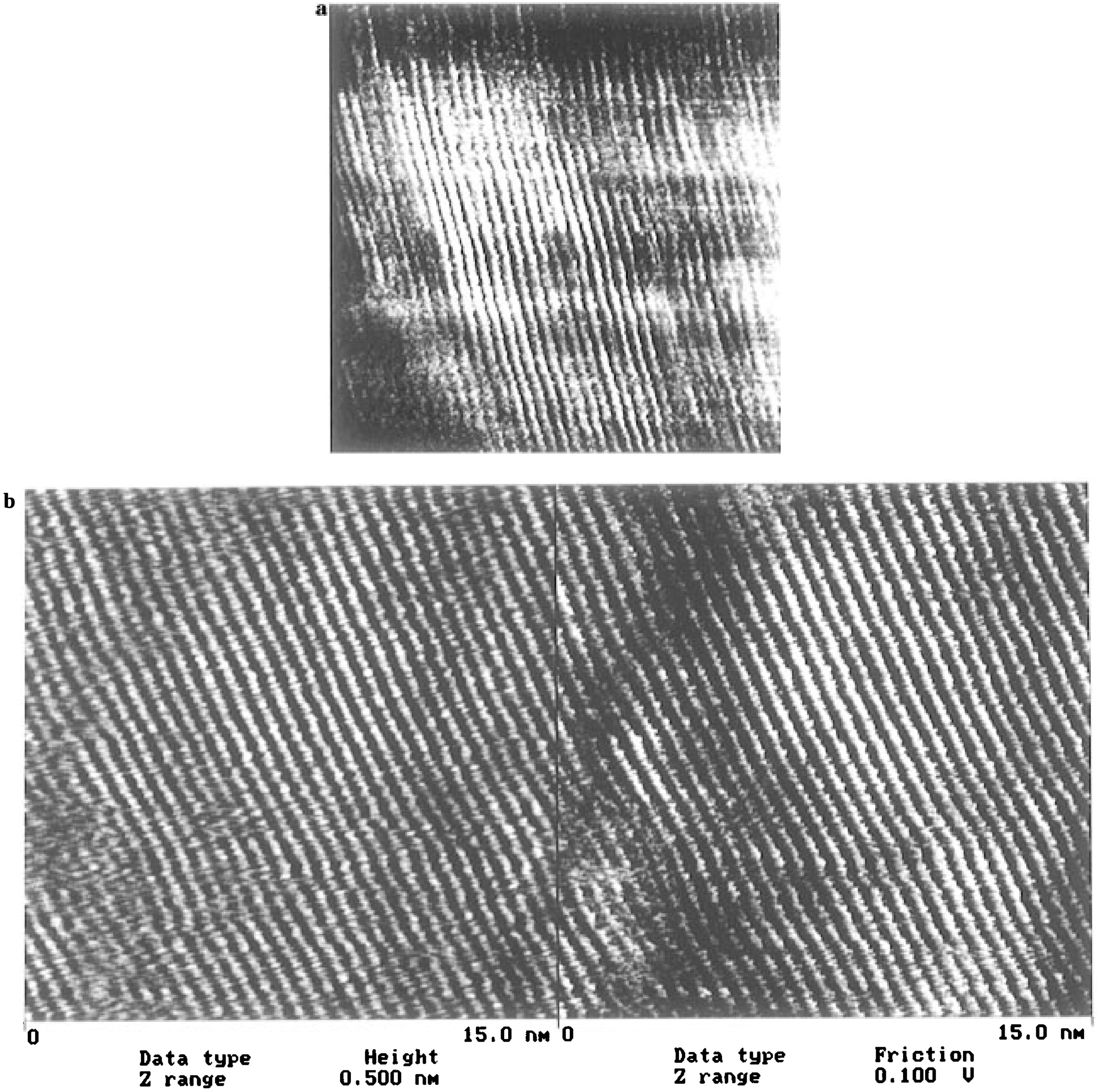

Figure 1. (a) Unfiltered friction force nanograph (17.3 nm × 17.3 nm) of highly oriented HDPE imaged with a $-CF_3$-terminated tip ($k = 0.38$ N/m) in air, showing the close-packed polyethylene chains on the (*bc*) crystal facet of orthorhombic PE. (b) Unfiltered height image of oriented PTFE (left) (15.0 nm × 15.0 nm) and the corresponding friction image (right) obtained with a $-CF_3$-terminated tip ($k = 0.12$ N/m) in ethanol.

molecular resolution, we measured the friction between the sample surface and the different functionalized tips with dependence on the normal force.[21,22] In general, it was possible to image the polyethylene sample with molecular resolution with all tips (silicon nitride as well as the different functionalized tips) in both height and friction modes. An unfiltered friction force nanograph of the (*bc*) facet of the HDPE crystal obtained with a $-CF_3$-terminated tip is shown in Figure 1a. The parallel lines correspond to tightly packed polyethylene chains. The average distance, which was measured to be 4.8 Å, corresponds to the lattice parameter *b* of the orthorhombic unit cell of PE ($b = 4.946$ Å).[23] The image contrast is dominated by the stick−slip process.[24] The quality of the resolution of the image is comparable to images taken with unmodified tips.[15] The surface of the oriented PTFE sample could also be imaged with modified tips with molecular resolution. The interchain distance was measured to be 5.6 Å, which compares well with the literature value of 5.55 Å of the phase IV hexagonal structure of PTFE.[25] A dual AFM/LFM scan of the worn surface of a PTFE slider obtained with a $-CF_3$-terminated tip in ethanol is shown in Figure 1b.

These results clearly prove that although the tip used is modified (which is concomitant with an increase in tip radius),[5] it is still possible to image with subnanometer lattice resolution. Typical force curves of unmodified and fluoroalkanethiol-modified tips measured on HDPE in air are compared in Figure 2a. The pull-off force, and thus the lowest possible minimum imaging force, was significantly less for the modified tip.[26]

In Figure 2b, results of friction force vs normal force measurements obtained on the (*bc*) facet of the PE crystal using tips modified with different SAMs are shown. For different tip modifications different friction forces were measured. The values obtained at a given normal force decreased in the following order: $-CH_3 > -COOH > -CF_3$. It can clearly be seen in Figure 2b that the observed friction signal depends (a) on the orientation of the crystallographic *c* direction of the crystal with respect to the scan direction (perpendicular

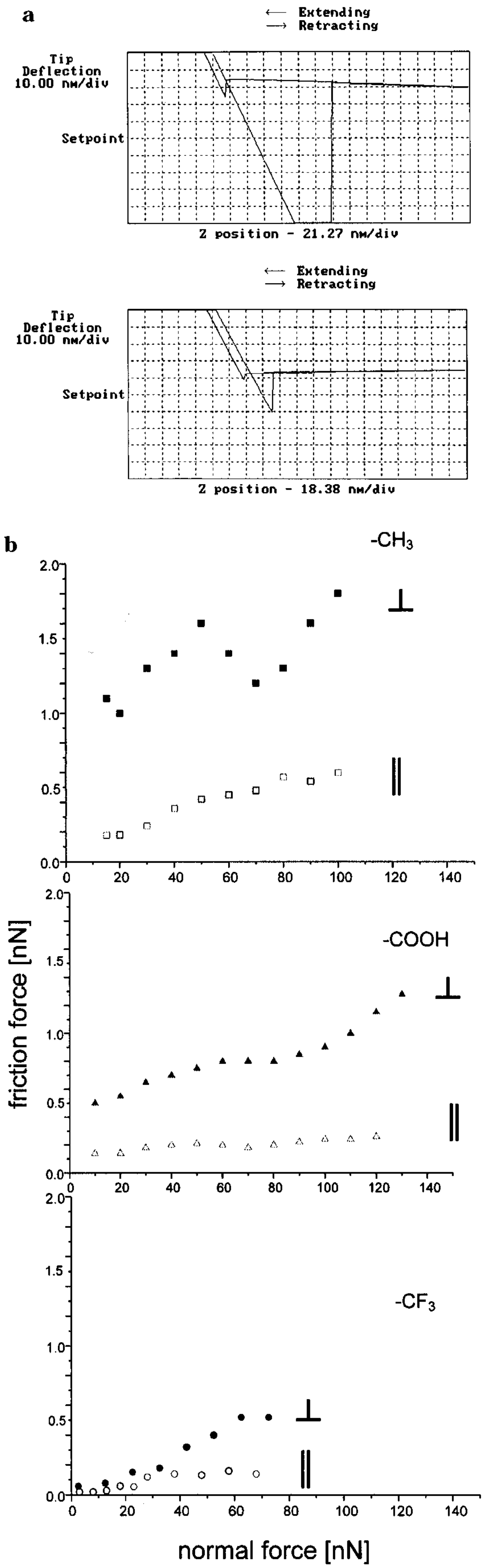

Figure 2. (a) Force curves measured with an unmodified (top) and a $-CF_3$-terminated tip (bottom) on the (*bc*) crystal facet of highly oriented HDPE in air. (b) Friction force for scans parallel and perpendicular to the polymer chain direction with dependence on the normal force for different modified tips ($k = 0.12$ N/m). (Measurements were performed on the (*bc*) crystal facet of highly oriented HDPE in air.) The error in friction force is ca. 15%.

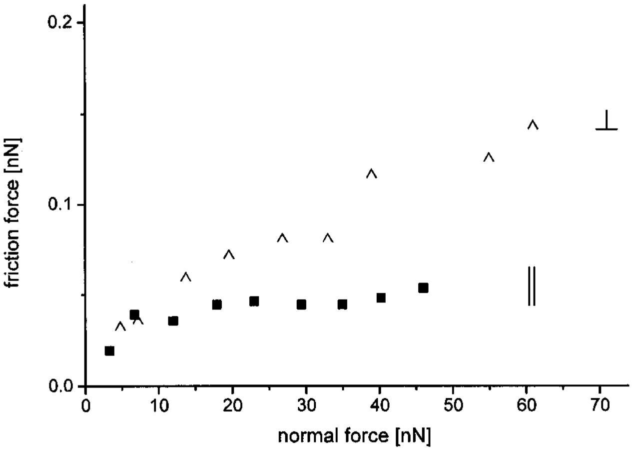

Figure 3. Friction force for scans parallel and perpendicular to the polymer chain direction with dependence on the normal force for a Si_3N_4 tip ($k = 0.12$ N/m). (Measurements were performed on highly oriented PTFE in ethanol.) The error in friction force is ca. 15%.

or parallel) and (b) on the functionality at the surface of the tip. As expected from previous measurements on highly oriented films of PTFE on glass,[27] the friction measured perpendicular to the polymer chains was significantly larger than the friction measured along the chains.

The friction signal that was measured when scanning perpendicular to the polyethylene chains was about 4 times greater than the friction signal that was measured when scanning along the chains. This ratio was independent of both the tip functionality *and* the normal force. This observation indicates that the friction anisotropy is due to the polyethylene surface because all the isotropic contributions to the total friction are canceled by taking the ratio of the friction forces observed for the two scan directions. These isotropic contributions include the surface free energies[5,8] and the (unknown) influence of the capillary forces. The (*bc*) and (*ac*) crystal facets were investigated with unmodified silicon nitride tips in air and exhibited the *same* friction anisotropy. For a discussion of the influence of the acting surface corrugation potentials and cantilever spring instabilities, see ref 24b.

For forces exceeding 20 nN, the friction increased approximately linearly with the applied load. This has been reported for a number of systems studied by LFM with and without functionalized tips.[5,8,28] For very small forces, however, there is a clear deviation from this linearity. The curves for scans parallel and perpendicular to the polymer chain direction for each tip must meet in the origin of the coordinate system, as at zero normal force there cannot be any friction between the tip and the surface. By comparing the slopes of the two different curves for each tip modification, it becomes evident that this requires the curves to be nonlinear (see Figure 2b).

Qualitatively similar observations were made for the friction of a silicon nitride tip on the highly oriented PTFE specimen in ethanol. The friction force observed with a Si_3N_4 tip on PTFE in ethanol was reduced by ca. 25% compared to the friction force measured in air. The friction force versus normal force dependence for scanning parallel and perpendicular to the PTFE chain direction becomes nonlinear for normal forces below approximately 5−8 nN (Figure 3). Thus, the empirical extension of Amonton's law ($f = \mu F_N$), which is often used to describe friction between macroscopic objects, to a linear relation ($f = \mu F_N + \alpha$)[8] does not seem to be valid for very small forces.[29] Here f denotes the friction force, μ the friction coefficient, F_N the normal force, and α the intercept at zero load.

In conclusion, the surface of highly oriented HDPE and PTFE could be imaged with molecular resolution using functionalized tips. Imaging forces of below 10 nN could be achieved at ambient conditions by utilizing perfluoroalkanethiol-modified tips. The use of such tips allowed us to perform AFM/LFM measurements under nondestructive imaging conditions in air (low forces), which are otherwise only possible in fluids. In addition to molecular imaging, the friction anisotropy of HDPE was studied. The ratio of friction for scans perpendicular to and scans parallel to the polyethylene chains was found to be equal to 4 and was found to be independent of the tip functionality and the normal force. Over the range of normal forces studied in this work, the friction coefficient was found to be nonlinear. The results demonstrate the great potential of modified SFM tips for routine measurements in ambient conditions, even in the nanometer size range.

Acknowledgment. We are indebted to Prof. A. S. Argon (Massachusetts Institute of Technology) for the HDPE sample. This work was financially supported by the University of Twente and by the Foundation for Chemical Research in the Netherlands (SON) (Priority Program Materials). The help of Ms. Anne Klemperer in editing the manuscript is appreciated.

References and Notes

(1) Miles, M. J. In *Characterization of Solid Polymers*; Spells, S. J., Ed.; Chapman and Hall: New York, 1994; Chapter 2, pp 17−55. For a recent collection of papers see: *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1996**, *37* (2), 546−625.
(2) For a recent review see: Magonov, S. N.; Wangbo, M. H. *Surf. Anal. with STM and AFM*; VHC: Weinheim, 1996.
(3) Ruan, J. A.; Bhushan, B. *Trans. ASME, J. Tribol.* **1994**, *116*, 378.
(4) Maivald, P.; Butt, H.-J.; Gould, S. A. C.; Prater, C. B.; Drake, B.; Gurley, J. A.; Elings, V. B.; Hansma, P. K. *Nanotechnology* **1991**, *2*, 103.
(5) (a) Frisbie, D.; Rozsnyai, L. F.; Noy, A.; Wrighton, M. S.; Lieber, C. M. *Science* **1994**, *265*, 2071. (b) Noy, A.; Frisbie, D.; Rozsnyai, L. F.; Wrighton, M. S.; Lieber, C. M. *J. Am. Chem. Soc.* **1995**, *117*, 7943.
(6) Akari, S.; Horn, D.; Keller, H.; Schrepp, W. *Adv. Mater.* **1995**, *7*, 549.
(7) For adhesion measurements with silicon nitride tips see: Berger, C. E. H.; van der Werf, K. O.; Kooyman, R. P. H.; de Grooth, B. G.; Greve, J. *Langmuir* **1995**, *11*, 4188.
(8) Green, J.-B. D.; McDermott, M. T.; Porter, M. D.; Siperko, L. M. *J. Phys. Chem.* **1995**, *99*, 10960.
(9) Thomas, R. C.; Tangyunyong, P.; Michalske, T. A.; Crooks, R. M. *J. Phys. Chem.* **1994**, *98*, 4493.
(10) Alley, R. L.; Komvopoulos, K.; Howe, R. T. *J. Appl. Phys.* **1994**, *76*, 5731.
(11) Howald, L.; Lüthi, R.; Meyer, E.; Güthner, P.; Güntherodt, H.-J. *Z. Phys. B* **1994**, *93*, 267.
(12) (a) Ulman, A. *Introduction to Ultrathin Films, From Langmuir-Blodgett Films to Self-Assembly*; Academic Press: Boston, 1991. (b) Dubois, L. H.; Nuzzo, R. G. *Annu. Rev. Phys. Chem.* **1992**, *43*, 437.
(13) Jaschke, M.; Schönherr, H.; Wolf, H.; Butt, H.-J.; Bamberg, E.; Besocke, M.K.; Ringsdorf, H. *J. Phys. Chem.* **1996**, *100*, 2290.
(14) Galeski, A.; Bartczak, Z.; Argon, A. S.; Cohen, R. E. *Macromolecules* **1992**, *25*, 5705.
(15) Schönherr, H.; Vancso, G. J.; Argon, A. S. *Polymer* **1995**, *36*, 2115.
(16) The reduction of the imaging forces for SFM performed in air is limited due to capillary forces. The tip pulls off the surface very easily when measurements are done in the attractive regime. This is pronounced when larger scan sizes are chosen because the overall variation in topography increases.
(17) Schönherr, H.; Vancso, G. J. *Polymer*, in press.
(18) Wittmann, J. C.; Smith, P. *Nature* **1991**, *352*, 414.
(19) Schönherr, H.; Vancso, G. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1996**, *37* (2), 612.
(20) Schönherr, H.; Vancso, G. J. *Langmuir* **1997**, *13*, 3769.
(21) Overney, R. M.; Meyer, E.; Frommer, J.; Güntherodt, H.-J.; Fujihira, M.; Takano, H.; Gotoh, Y. *Langmuir* **1994**, *10*, 1281.
(22) Liu, Y.; Wu, T.; Evans, D. F. *Langmuir* **1994**, *10*, 2241.
(23) *Macromolecular Physics*; Wunderlich, B., Ed.; Academic Press: New York, 1973; Vol. 1, p 97.
(24) (a) Mate, C. M.; McCelland, G. M.; Erlandsson, R.; Chiang, S. *Phys. Rev. Lett.* **1987**, *59*, 1942. (b) Overney, R. M.; Takano, H.; Fujihira, M.; Paulus, W.; Ringsdorf, H. *Phys. Rev. Lett.* **1994**, *72*, 3546.
(25) *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley: New York, 1989; p V/37.
(26) As the observed forces depend on the area of contact and thus the radius of curvature of the tip, the absolute reduction of forces was only observed for sharp tips. Blunt tips result in larger forces, even when they are functionalized with $-CF_3$-terminated thiols. See also ref 5b. The pull-off force measured with the $-CF_3$-modified tip is reduced to ca. 20% of the force measured with an unmodified tip (see Figure 2a).
(27) Vancso, G. J.; Förster, S.; Leist, H. *Macromolecules* **1996**, *29*, 2158.
(28) Xiao, X.; Hu, J.; Charych, D. H.; Salmeron, M. *Langmuir* **1996**, *12*, 235.
(29) There are many indications in the literature that, in general, polymers do not obey Amonton's law to better than a rough approximation; see e.g.: Cherry, B.W. *Polymer Surfaces*; Cambridge University Press: Cambridge, U.K., 1981. For example, in PTFE, the friction coefficient was found to vary with load (load range from 10^{-5} to 10^{6} g). In this range the friction coefficients of many polymers can be described by $\mu = kF_N{}^{n-1}$, where F_N is the normal load and $n - 1$ lies between -0.2 and -0.3. (Pascoe, M. W.; Tabor, D. *Proc. R. Soc. A* **1956**, *235*, 210.)

MA970441B