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High-Resolution Imaging of Polymer Surfaces with Chemical Sensitivity

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ABSTRACT: We have studied the potential of friction and stiffness measurements with high spatial resolution for the surface characterization of glassy polymers. We present experimental evidence for quasi-chemical sensitivity on a heterogeneous surface consisting of polystyrene islands on a poly(methyl methacrylate) base layer. Although similar in their bulk mechanical properties, the two polymers are easily distinguished by their different nanomechanical behavior. As an example, we characterize the domain pattern formed after spinodal decomposition of a symmetric blend of the two polymers.

In recent years, the investigation of thin and ultrathin polymer films has become an area of intensive research.[1–4] While the microstructure perpendicular to the plane of the films can be probed by a variety of different real-space[5] and k-space[6] profiling techniques with high spatial resolution, the number of suitable lateral profiling techniques with sufficient spatial resolution is rather limited. With the invention of scanning tunneling microscopy and the large number of its descendants,[7] a new class of techniques has evolved which, in principle, allows surface imaging with subnanometer spatial resolution. For nonconducting samples, atomic force microscopy (AFM) has proven quite successful, and with the commercial availability of atomic force microscopes, the number of AFM studies on thin films of various polymer samples has been rapidly increasing over the last few years.[8] However, in spite of the beauty of the images obtained, the bare topography information recorded in conventional AFM experiments is rather limited and an unambiguous interpretation of the images often proves difficult.

In the present paper, we shall show that the simultaneous measurement of the local mechanical properties of the polymer sample, i.e., the local friction between the AFM tip and the polymer as well as the local stiffness of the polymer, can be used to operate an AFM with quasi-chemical sensitivity. While a similar experimental scheme has been used to gain contrast between nonpolymeric materials with rather different bulk properties,[9–11] we shall explore its potential for the imaging of two rather similar, amorphous polymers. We demonstrate that glassy polymers such as polystyrene (PS) and poly(methyl methacrylate) (PMMA), which exhibit almost identical bulk mechanical properties, can be easily distinguished through their nanomechanical surface properties. We shall first present experimental evidence for material-specific contrast on dewet PS films on a PMMA base layer with known morphology to establish the contrast mechanism. In a second step, we investigate the (a priori unknown) domain structure in a phase-separated blend of the two materials to demonstrate the capabilities of the nanomechanical imaging technique.

For our experiments we used a home-built standalone atomic force and friction microscope.[12] All experiments were performed in contact mode with a rectangular Si_3N_4 tip (compliance: 0.015 N/m) with a typical load of 10 nN. For local stiffness measurements, the cantilever is driven at 6 kHz with a peak-to-peak amplitude of about 0.8 nm perpendicular to the sample surface. The normal force signal was additionally fed into a lock-in amplifier locked to the exciting frequency. Thereby, the derivative of the force–distance curve is monitored, which can be understood as a measure of the local stiffness of the sample.

PMMA films ($M_{w,PMMA} = 109\,000$) of various thickness were spun cast from toluene solution onto polished silicon wafers and used as a base layer. PS films ($M_{w,PS} = 902\,000$) thinner than their radius of gyration R_g ($R_g \approx 30$ nm) were spun cast onto glass slides and floated onto deionized water where they picked up from above onto the PMMA base layer. The thickness of the individual films was determined by ellipsometry. After drying in air, the samples were vacuum annealed at 443 K ($p < 10^{-5}$ mbar) for several days. On annealing above the glass transition temperature, PS films thinner than R_g dewet the PMMA substrate; i.e., they break up into isolated islands, leaving portions of the PMMA base layer exposed to air.

In parts a–c of Figure 1, we show topography, friction, and stiffness measurements on a 20-nm-thick PS film floated onto a 50-nm-thick PMMA base layer after vacuum annealing at 443 K for 4 days. The topography image (Figure 1a) shows quite large islands extending over areas up to about 500 × 500 nm^2. We anticipate this topography to be due to a dewet PS film covering only part of the underlying PMMA base layer; it should, however, be pointed out that the topography information alone does not justify this conclusion. The situation becomes a little clearer though when we inspect the friction and stiffness signals shown in parts b and c of Figure 1, respectively. In the friction signal, a clear contrast is observed between the islands and the surrounding areas. The islands appear darker and represent regions of smaller friction. A similar contrast is observed in the stiffness image shown in Figure 1c. The islands therefore represent areas of smaller friction and stiffness, suggesting a chemical difference between the islands and their surrounding areas.

In order to rule out any topography-induced artifacts in the nanomechanical images, some of the specimens prepared and imaged as described above were subsequently covered with a 20-nm-thick PMMA top layer. After drying in air, these samples were then imaged again (Figure 1d–f). We find that the topography of the sample (Figure 1d) is similar to the uncovered one (thereby pointing to the shortcomings of "conventional"

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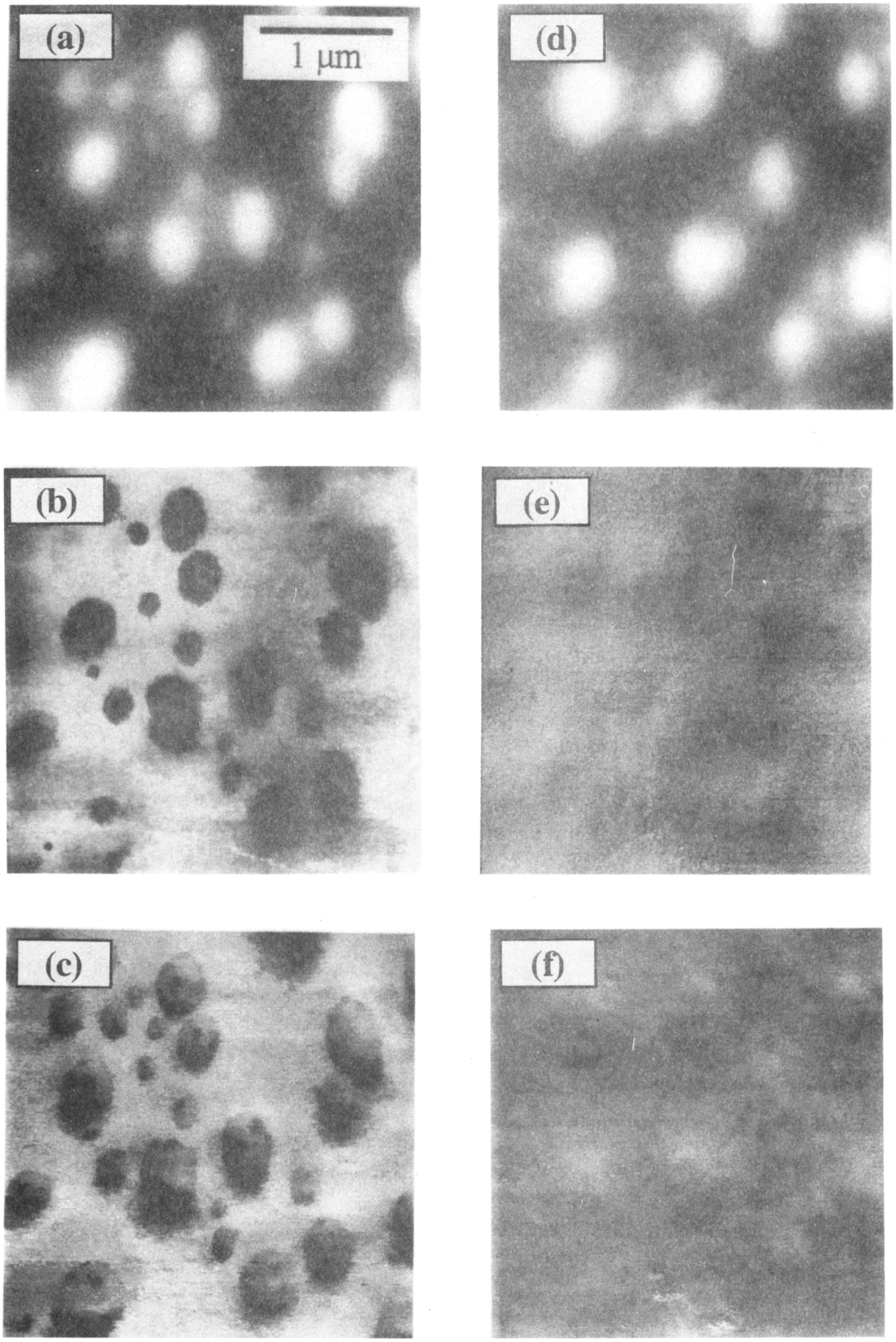

Figure 1. (a) Topography, (b) friction, and (c) local stiffness images of a 20-nm-thick PS layer on PMMA after annealing at 160 °C for 4 days. The right part of the figure (d–f) shows the respective images of the same sample after additional coverage with a 20-nm-thick top layer of PMMA. The gray scales are chosen such that brighter areas correspond to an increased frictional force and a stiffer region, whereas darker areas correspond to a smaller frictional force and a softer region of the specimen. The scales have been chosen identical for the two topography, friction, and stiffness plots. The vertical scales for (a) and (d) ranges up to 50 nm. The differences in the frictional force and the local stiffness on top and next to the islands amount to about 5% and 8%, respectively.

AFM imaging); i.e., the PMMA top layer smoothly follows the underlying island structure. In the friction and stiffness image shown in parts e and f of Figure 1, however, the contrast is strongly reduced and only some edge-induced artifacts are observed. In addition, one could argue that the differences in the mechanical properties of the polymer film on top and next to the islands may at least in part be due to a change in the overall film thickness.[13] We therefore prepared a series of bilayers where the PMMA and PS thicknesses were varied between 10 and 300 nm and 10 and 50 nm, respectively. No influence of the film thickness on the contrast in the friction and stiffness images was observed. These findings strongly suggest that the nanomechanical images do indeed exhibit material-specific, i.e., chemical, contrast.

We have used the contrast mechanisms discussed above to image samples of unknown surface composition. A symmetric mixture of PS and PMMA was prepared in a toluene solution, and 60-nm-thick films were spun cast onto silicon wafers. After drying in air, the samples have been investigated both by optical microscopy and by AFM. The films are found to undergo spinodal decomposition as the solvent is removed during the spinning process. This can be seen in Figure 2a, where we show a detail of the topography of the films as imaged by AFM. Similar to the situation after dewetting (Figure 1), the formation of islands is observed. While the bare topography signal does not allow one to distinguish between the two coexisting phases, the friction and stiffness measurements shown in parts b and c of Figure 2 give a clear hint on the nature of the domain structure of the films. Resembling the situation shown in Figure 1a–c, on top of the islands both friction and stiffness are found to be smaller than those in the surrounding area. Comparing to the situation discussed above, we may therefore identify the islands as PS-rich domains located on a PMMA-rich base layer. This PMMA-rich layer wets the entire silicon substrate, as can be seen by the fact that even the holes observed within the area of the islands exhibit the mechanical properties of the regions surrounding the islands. As a matter of fact, we were able to scratch a hole into the PMMA-rich layer by repeatedly scanning a small area with a high normal load applied to the AFM tip. After a while, any polymer is removed in this region and the bare silicon substrate is exposed to air. A subsequent large area scan under the conditions specified above (not shown here) reveals a distinct contrast in both friction and stiffness between the polymer surface and the silicon substrate. The contrast observed between silicon and polymer is roughly an order of magnitude larger than the one between the two polymers, thereby allowing an unambiguous test whether or not the substrate is covered with a polymer layer entirely.

A domain pattern of the above type is in agreement with earlier investigations of the surface effects on the ordering in thin films of symmetric P(S-*b*-MMA) block copolymers,[3] indicating a higher affinity of PMMA to silicon and a lower surface energy of PS, respectively. The inherent high mobility in the phase-separating solution obviously enables an almost one-dimensional demixing process to take place, with the PMMA-rich domains wetting the substrate surface. A detailed discussion of the phase separation is beyond the scope of the present paper and shall be addressed in a separate publication.

We shall now return to the unexpectedly large contrast obtained between the two polymers. From their bulk properties, PS and PMMA exhibit rather similar characteristics; e.g., both the bulk moduli and the glass transition temperatures of the two materials are about

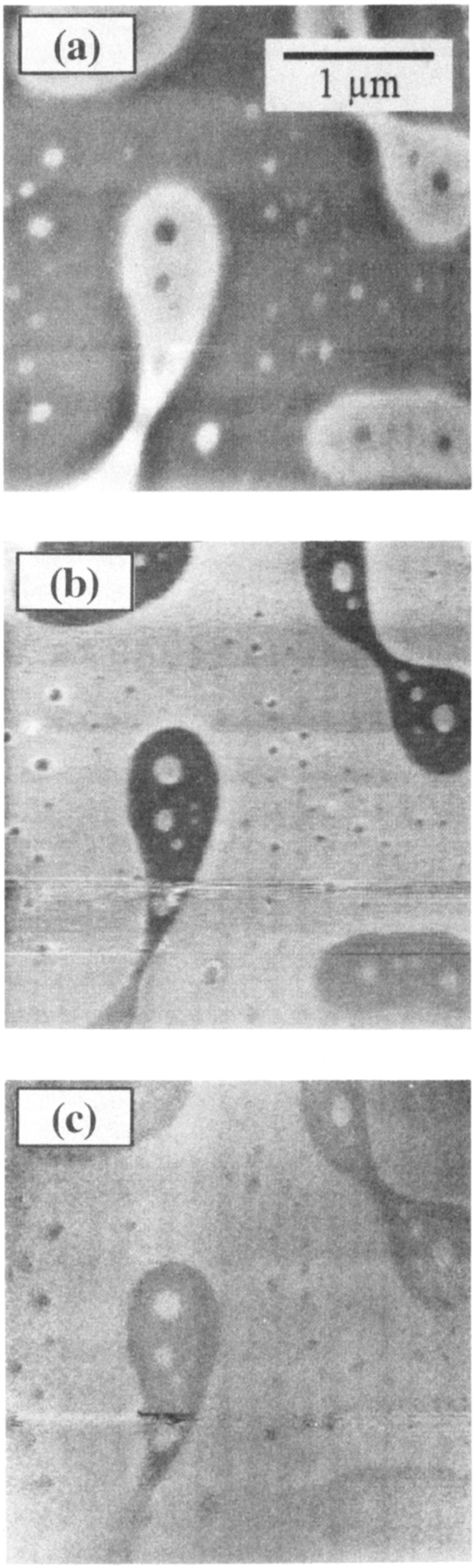

Figure 2. (a) Topography, (b) friction, and (c) local stiffness images for a 50/50 blend of PS and PMMA after spin casting from a toluene solution onto a polished Si wafer. The vertical scale ranges up to 50 nm.

equal. As far as macroscopic friction measurements are concerned, somewhat contradictory results are reported in the literature.[14,15] Recent tracer diffusion experiments involving the two polymers revealed a large disparity between the PS and PMMA monomeric friction coefficients;[16] it is not clear, however, whether this difference influences the relative friction between the respective polymers and the AFM tip. In any case, a quantitative comparison of the microscopic results and the macroscopic data proves difficult, since (to the best of our knowledge) no friction data between the polymers and Si_3N_4 are reported and the exact shape of the tip and thereby the size of the contact area are only roughly known. The situation is even more complex as we observe a strong dependence of the friction coefficient on the normal load applied to the cantilever. It turns out that the friction contrast between the two polymers can be eliminated and even reversed as the normal load is decreased. This result points to a nonlinear dependence of the frictional force on the load.

We may take the difference in the interfacial energies between the two polymers and the oxidized silicon substrate surface discussed above as a hint that there exists a stronger affinity between PMMA and the Si_3N_4 tip as well; this assumption would lead to a larger adhesive contribution to the friction between one of the polymers and the tip and could thereby explain the observed differences in the lateral force. Alternatively, a different dynamic behavior of the two materials at the characteristic time scales (defined by the scan speed and the vibration frequency) may be a possible reason for the observed contrast. First, preliminary experiments using an AFM with in situ heating indicate a complex dependence of the observed contrast on temperature and strongly suggest that differences in the dynamic properties of the two materials are at least in part responsible for the observed contrast. Finally, we shall mention that, as far as the stiffness contrast is concerned, our experiment resembles macroscopic hardness (indentation) tests, where PMMA is indeed found to be the harder material.[17]

In summary, we have shown that rather similar glassy polymers can be distinguished in AFM measurements through their nanomechanical properties. This additional feature may be helpful in obtaining AFM images of various heterogeneous polymer surfaces with chemical sensitivity and thereby improving the potential of this technique for the investigation of more complex polymer systems like polymer blends and microphase-separated block copolymers. The origin of the distinct contrast remains somewhat unclear; a systematic variation of both the normal load on the AFM tip and the sample temperature shall be necessary to provide deeper insight.

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References and Notes

(1) Reiter, G. *Phys. Rev. Lett.* **1992**, *68*, 75.
(2) Zhao, W.; Rafailovich, M. H.; Sokolov, J.; Fetters, L. J.; Plano, R.; Sanyal, M. K.; Sinha, S. K.; Sauer, B. B. *Phys. Rev. Lett.* **1993**, *70*, 1453.
(3) Anastasiadis, S. H.; Russell, T. P.; Satija, S. K.; Majkrzak, C. F. *Phys. Rev. Lett.* **1989**, *62*, 1852.
(4) Jones, R. A. L.; Norton, L. J.; Kramer, E. J.; Bates, F. S.; Wiltzius, P. *Phys. Rev. Lett.* **1991**, *66*, 1326.
(5) See, e.g.: Kramer, E. J. *Physica B* **1991**, *173*, 189.
(6) See, e.g.: Russell, T. P. *Mater. Sci. Rep.* **1990**, *5*, 171.
(7) For a recent review on scanning probe microscopy, see: *Scanning Tunneling Microscopy and Related Methods*; Behm, R. J., Garcia, N., Rohrer, H., Eds.; NATO Advanced Study Institute Series E 184; Plenum: New York, 1990.
(8) See, e.g.: *Bull. Am. Phys. Soc.* **1993**, 38.
(9) Marti, O.; Colchero, J.; Mlynek, J. *Nanotechnology* **1990**, *1*, 141.
(10) 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.
(11) Overney, R. M.; Meyer, E.; Frommer, D. J.; Brodbeck, D.; Lüthl, R.; Hohwald, L.; Günterodt, H.-J.; Fujihira, M.; Takano, H.; Gotoh, Y. *Nature* **1992**, *359*, 133.
(12) Hipp, M.; Bielefeldt, H.; Colchero, J.; Marti, O.; Mlynek, J. *Ultramicroscopy* **1992**, *42–44*, 1498.
(13) It was found recently that various properties of ultrathin polymer films can change as a function of film thickness. Jones et al. observed a thickness-dependent glass transition temperature (Keddie, J.; Jones, R. A. L.; Cory, R. A., preprint), and Reiter reported on a thickness-dependent density in PS films thinner than R_g (Reiter, G. *Europhys. Lett.* **1993**, *23*, 579).
(14) See, e.g.: Bowden, F. P.; Tabor, D. In *The friction and lubrication of solids*; Oxford University Press: London, 1968.
(15) See, e.g.: Briscoe, B. J.; Tabor, D. Friction and Wear in Polymers. In *Polymer Surfaces*; Clark, D. T., Feast, W. J., Eds.; John Wiley & Sons: New York, 1978.
(16) Green, P. F.; Russell, T. P.; Jerome, R.; Granville, M. *Macromolecules* **1989**, *22*, 908.
(17) The Rockwell hardness of the two materials is reported as M65–M85 (PS) and M80–M105 (PMMA). See: *Handbook of Chemistry and Physics*; West, R. C., Ed.; RCR Press: New York, 1980.

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