Scan-Induced Patterning in Glassy Polymer Films: Using Scanning Force Microscopy To Study Plastic Deformation at the Nanometer Length Scale

Ronald H. Schmidt,† Greg Haugstad,*‡ and Wayne L. Gladfelter*†

Department of Chemistry, University of Minnesota, 207 Pleasant Street SE, and IT Characterization Facility, University of Minnesota, 100 Union Street SE, Minneapolis, Minnesota 55455

Received December 27, 2001. In Final Form: October 17, 2002

The response of thin glassy films of polystyrene and poly(vinyl acetate) to a raster-scanned, sliding SFM tip was investigated. Several of the previously proposed mechanisms of the familiar scan-induced patterns are discussed. Increases in film volume and frictional response are quantified, and suggest that the observed tip-induced plastic deformation may relate to a second-order phase transition (glass-to-rubber) beneath the sliding tip. Analysis of the scan-induced patterns suggests a crazing mechanism for the observed plastic deformation. The susceptibility of the film to plastic deformation was examined as a function of scan geometry, applied load, and the gain of the feedback loop that maintains a constant applied load. An empirical quantity called the roughening susceptibility is defined and shown to be linear with respect to variations in the scan conditions. This roughening susceptibility is highly robust in quantifying the dependences on scan history and load. This finding will be further exploited in the second paper of the series, analyzing rate and temperature dependences and their relationship to the glass transition.

Introduction

This paper is concerned with the damage done to thin, supported, glassy polymer films when they are scanned by a nanometer-scale tip sliding across the sample surface. Qualitatively similar images have been reported in the literature for a wide variety of polymer/substrate systems: polystyrene on mica,1 Si,2 glass,3 and metal,4 self-supported injection molded polycarbonate5 (methyl methacrylate)6 surfaces; a polystyrene/poly-coated glass;13 PEO on mica;10 poly(ethylene terephthalate) on mica;11 polyacetylene on mica and WSe2;12 polyimide on ITO-coated glass;13 PEO on mica;14 nylon on ITO-coated glass.15

While scan-induced patterning appears to be ubiquitous with respect to the variety of polymer/substrate systems for which the phenomenon has been observed, a critical review of the literature reveals that relatively few, and in some cases contradictory, quantitative studies have been published in the field. In the current paper we attempt to address this problem by quantifying several aspects of the patterning process under a wide variety of experimental conditions. The methodology and phenomenological approach presented herein will be applied to the analysis of temperature- and rate-dependent patterning in a subsequent paper, where we will also discuss the issue of temperature-assisted plastic deformation using more fundamental concepts. The scan-induced patterns considered in this work are to be differentiated from the more intricate patterns reported for a tip scanning in contact with a polymer melt at temperatures higher than the glass transition.16,17

Results are presented that characterize the scan-induced morphology as a function of sample loading and raster scan geometry. Within the region of parameter space investigated, the response of the film is highly linear with respect to the loading conditions and the number of successive visits of the sliding tip to the same region of the sample surface. Although the exact mechanism of deformation within the polymer film remains unknown, evidence is presented that refutes several proposed mechanisms. We present frictional data that show that the response of the patterned region is consistent with a “generalized” stick–slip mechanism related to a second-order phase transition in the polymer beneath the sliding tip. It is also shown that the scanning process induces damage in polystyrene films analogous to the familiar phenomenon of crazing in brittle bulk polymer systems.

Experimental Section

Solutions of monodisperse atactic polystyrene (PS; Aldrich) and high-dispersity atactic poly(vinyl acetate) (PVAc; Aldrich) were prepared by dissolving the polymer in toluene. The solutions were prepared by dissolving the polymer in toluene. The solutions

---

* To whom correspondence should be addressed.
† Department of Chemistry.
‡ IT Characterization Facility.

---

were filtered twice through 0.2 μm porosity syringe filters into clean scintillation vials. Silicon(100) wafers (4 in. diameter) were used as substrates. Other than using a nitrogen jet to remove dust from the wafers, no special procedure was used to treat the substrates prior to spin coating the films. As a result, the silicon substrate is covered by a thin (0.6–2 nm) amorphous layer of SiO₂. The films were prepared by spin coating the solutions onto the wafers. By varying the solution concentration in the range of 0.25–2% w/v and the spin rate from 1000 to 5000 rpm, films could be prepared whose thickness ranged from ~3 to 150 nm. Films thinner than 2–3 nm were discontinuous, while films much thicker than 150 nm generally contained fairly long scale (~1 nm) lateral variations in thickness that were visible to the naked eye as optical fringes. Many of the films investigated were unannealed, so that although they were several days to several weeks old at the time that the measurements were made, they may possess anisotropy related to spin coating and/or contain trace amounts of plasticizing solvent.

Data were collected at ambient conditions using a Digital Instruments Multimode SPM with a 150 μm scanner and a Molecular Imaging PicoSPM with scanners ranging from 30 to 50 μm. A Nanoscope III controller and Nanoscope system software were used to control both SPMs and to acquire all data. Except where otherwise stated, all imaging was performed using a feedback loop to maintain a constant vertical deflection of the cantilever (and hence a constant applied load) as the tip was scanned across the sample surface. Gold-coated Si₃N₄ cantilevers, supplied by Digital Instruments, (k<sub>eff</sub> = 0.58 N/m) were used for imaging. The trajectory of the sliding tip is described in detail elsewhere. Briefly, the tip is scanned in a sawtooth pattern at an angle slightly offset from the horizontal (“fast-scan”) axis of the images. A total of 128, 256, or 512 fast-scan cycles (i.e., a left-to-right scan followed by a right-to-left scan) can be acquired along the vertical (“slow-scan”) axis of the imaging window. The fast-scan frequency refers to the number of fast-scan cycles performed per second.

Measuring Film Thickness with AFM. Various techniques (X-ray reflectivity, ellipsometry, RBS/FREES) were employed to determine film thickness. All of these methods yield thickness measurements averaged over macroscopic lateral dimensions. A more convenient method of determining film thickness, and one that measures the thickness at relatively small lateral length scales, is described below. A small region of the film (typically 0.1 × 0.1 to 1 × 1 μm) was scanned at a high load (~25–100 nN) to sweep the polymer out of the scanned region. Multiple raster scans were usually performed, and the scan angle was switched periodically from 0° to 90°, until the scanned region was observed to have a flat topography. The applied load was then reduced to a much smaller value (typically 2.5 nN), and a larger region of the film was imaged, as shown in Figure 1. (In some cases friction images were collected at high temperature and/or low scan velocity, producing material contrast between the undisplaced film and the bared substrate.) The thickness of the film was determined from a horizontal cross section of the image. In the cross section shown, the film thickness was taken to be the depth approached asymptotically as the tip scanned from left to right. The discrepancy between this steady-state value of the depth and the maximum apparent depth (at the left edge of the hole) is attributed to the piezo creep effect. Holes with smaller lateral dimensions therefore require slower scan velocities to ensure that the steady-state depth is reached before the tip encounters the far edge of the hole, thereby minimizing the errors associated with piezo creep.

For lower molar mass (13 kg/mol) ultrathin PS films (i.e., films thinner than ~15 nm), holes that reach the substrate can be produced at ambient temperature. The film shown in Figure 1 had a molar mass of 212 kg/mol and was presumably tougher due to the presence of entanglements; consequently, a slightly higher temperature (50 °C) was required to excavate the polymer. Thicker films (~50 nm) generally require temperatures near the bulk glass transition to produce a hole that reaches the substrate. Sample heating was accomplished using a copper resistive heating stage attached to the Molecular Imaging PicoSPM.

Results

Qualitative Description of Scan-Induced Deformations. Figure 2 shows several series of 1 × 1 μm images of an 8.5 nm, 212 kg/mol PS film acquired at room temperature. Each column represents a single series of images, and the applied load is higher moving from left to right. During the acquisition of a given series of images, the tip was allowed to raster repeatedly over the same region, with 256 fast-scan cycles performed per raster scan. To eliminate sample tilt and the curvature associated with the pendulum arc described by the sweeping piezo tube, a third-order polynomial was fit to each scan line of data, and the fit was then subtracted from the raw data to give the flattened images shown in the figure. (For the sake of consistency and simplicity, we used the same procedure for flattening all images, regardless of image size or the microscope used for acquisition.) The gray scale represents topography, with the darkest colors associated with the lowest features and the brightest colors corresponding to the highest features. The difference in height between the brightest and darkest features is 5 nm.

Initially relatively small, isotropic height fluctuations are present, as in all amorphous polymer surfaces. As
more scans are performed over the same region, the surface morphology changes. Bundles and trenches that are oriented perpendicular to the tip trajectory begin to form. The height and depth of the bundles and trenches, respectively, grow with the number of raster scans performed. At higher applied loads, fewer scans are generally required to produce a given amplitude of these surface waves. Close inspection (compare scans 4 and 16 taken under 30 nN applied load) also reveals that, with repeated scanning, the height fluctuations are more in phase, or better correlated, along the vertical axis.

Quantifying the Frictional Response in the Patterned Region. In Figure 3, we consider the simultaneously acquired lateral force and topography images corresponding to scan 16 at 12 nN applied load from Figure 2. Topography and lateral force data (which have been offset in the figure by an amount equal to the mean height and mean lateral force, respectively) are shown for the same scan line in the image. Waves of similar repeat distance are apparent in both the topography and lateral force traces. It is known that the lateral force between a scanning tip and a sample surface consists of two terms: a friction (dissipative) force as well as a component that is proportional to the topographical gradient along the fast-scan axis (dZ/dX, provided that dZ/dX is not substantially larger than 0.3). To determine whether the observed fluctuations in the lateral force image are related to the topographical gradient, the lateral force data are plotted as a function of both Z and dZ/dX in Figure 4. While there appears to be little correlation between Z and lateral force, a fairly strong correlation is evident between dZ/dX and lateral force. It has been shown that the contribution of dZ/dX to the lateral force can be removed approximately by subtracting the lateral force data acquired during the right-to-left (retrace) scan from the data acquired during the left-to-right (trace) scan. One also must be careful to account for the hysteresis in the piezo scanner. For the features acquired during the trace and retrace scans to properly line up, it was necessary to shift the retrace friction data 6 pixels to the right (a distance equal to 58 nm for the 512 pixel, 5 μm scan lines). When the shifted retrace image is subtracted from the trace image, we are left with an image in which the

Figure 2. Topography images of 1 × 1 μm acquired with an 8.5 nm film for several applied loads. Continuing to scan over the same region roughens the surface, and the effect is stronger for higher loads.

---


(22) An additional term that is proportional to (dZ/dX)² becomes significant for dZ/dX > 0.3. If the pattern shown in Figure 3 is approximated as a sinusoidal wave of amplitude 2.5 nm and repeat distance 70 nm, |dZ/dX| has a maximum value of 0.2. Thus, for this case the quadratic term can be neglected.
contribution of $dZ/dX$ to the lateral force has been effectively removed, so that remaining variations in the image correspond instead to intrinsic variations in the tip-sample friction force. Evidence of a residual alteration in the intrinsic frictional response of the polymer surface is presented in Figure 5. The data were taken with a Si$_3$N$_4$ tip sliding on a 10 nm thick PVAc film cast on a silicon wafer at ambient temperature. The central region underwent 10 512-line raster scans with a 23 nN applied load and a fast-scan frequency of 11 Hz. The scan size was then increased to 5 $\mu$m and the scan frequency was decreased to 3 Hz to image the friction response of the patterned region. Eight images were acquired with different applied loads, ranging from 23 nN during the first scan to 3 nN, and the scan size was increased again to 10 $\mu$m. In the 10 $\times$ 10 $\mu$m scan shown in the figure, very little modification is visible in the topographical data, which may be attributed to the 5 $\times$ 5 $\mu$m scans, and no "friction box" is visible within the central 5 $\times$ 5 $\mu$m region. The central, patterned region (region B) clearly exhibits fluctuations in tip-sample frictional force; these fluctuations are presumably not random, but they could not be clearly correlated with either Z or $dZ/dX$. We turn our attention now to the distribution of friction response in the image. The histograms shown in Figure 6 reveal a single Gaussian peak in region A and two partially overlapping peaks in the friction response of region B. The histogram corresponding to region B was fit to a double-Gaussian distribution function using a nonlinear least-squares curve-fitting routine, and the resulting fit is shown in the figure (the solid line corresponds to the double-Gaussian fit; the two dashed lines correspond to the individual Gaussian curves which comprise that fit). The mean values derived from the Gaussian fits are plotted in Figure 6 as a function of the applied load.

The friction response within region B is interpreted as being partitioned between two states, which tentatively will be termed typel friction and type 2 friction. (Later we will argue that these can be assigned to less/more rubbery domains, respectively.) Inspection of the friction vs load plot (Figure 6) reveals that the coefficient of friction for the less dissipative component (type I) closely matches the coefficient of friction observed in the unperturbed region A, with the remaining pixels exhibiting a larger coefficient of friction (type II). Two islands of high friction are apparent in the 5 $\times$ 5 $\mu$m scan in Figure 5. Analysis of their friction distributions was difficult due to their small size and the presence of noisy scan lines, but it was clear that, with repeated scanning, these regions gradually returned to exhibiting solely type I friction. The high-friction islands are no longer visible in the 10 $\times$ 10 $\mu$m friction image.

The first study of alterations in the frictional response of polymer films caused by a sliding tip was reported by Haugstad et al. for gelatin films cast on mica. When a small region of the film was scanned and a larger image was subsequently taken, the initially scanned region exhibited higher friction than the surrounding, unperturbed region. Unlike the phenomenon presented in this study, no change was apparent in the topographical image. Eventually, with repeated scanning, the frictional response of the inner region returned to its initial state (i.e., to the state of the surrounding region). The tendency to

---

create these friction boxes, and the tendency for them to relax back to the original state during subsequent imaging, exhibited a strong dependence on the applied load and the velocity of the scanning tip. Haugstad et al. postulated that the effect of the tip-sample interaction was to place the region initially scanned into a more dissipative state, effectively moving that subsystem toward the glass transition and hence toward the maximum in the viscoelastic loss tangent. The gradual return of the gelatin to its initial state corresponds to a relaxation of the more highly dissipative conformers present within the subsystem to the equilibrium conditions set by $kT$.

To examine whether a relaxation of the type II friction component occurred within region B, we consider the fraction of the pixels that are present in the two states as defined by the following relationships:

$$x_I = \frac{A_I}{A_I + A_{II}} \quad \text{and} \quad x_{II} = 1 - x_I$$

where $A_I$ and $A_{II}$ are the areas under the single Gaussian curves as exemplified in Figure 6. The friction force was distributed approximately evenly between type I and type II friction (i.e., $x_I = x_{II} = 0.5$) for the 5 μm image shown in Figure 5, and this distribution remained unchanged with repeated scanning of the polymer within region B. This suggests that the high-friction moieties in region B are fundamentally different from the friction boxes seen by Haugstad et al. or from the high-friction islands visible in region A of the 5 × 5 μm scan, which relaxed to type I friction with repeated scanning.

**Volume Change in Patterned Regions.** Hamada and Kaneko have suggested that scan-induced deformations are accompanied by a volume increase which they attributed to the formation of voids within the film. The evidence supporting this conclusion is based on an analysis of a single scan line in a scan-scratched injection-molded polycarbonate surface. A more extensive and quantitative analysis of the volume increase that accompanies bundle formation is described below. After a series of scans were performed over the same region with a relatively high applied load, the contact force was reduced and a larger region was scanned, as shown in Figure 7. Region A corresponds to the pattern shown in Figure 2 acquired with a 30 nN applied load. The scan size was increased to a 3 × 3 μm region after the original 1 × 1 μm scans were...
Figure 7. Left: 5 × 5 μm topography and friction images. After sixteen 1 μm scans were performed in the center of the image, the scan size was increased to 3 μm for several scans prior to the acquisition of the images shown. The previously scanned regions exhibit higher topography and friction. Right: Cross sections of the topography image are used to quantify the mean height difference between the patterned region and the surroundings. The best results are obtained from the average of many vertical lines.

performed. Several scans were performed at various applied loads (ranging from 1.5 to 23 nN), and the scan size was increased again to 5 × 5 μm with an applied load of 9 nN used to acquire the image shown. This process generated topographical "boxes", in which the regions altered by the scanning tip are clearly visible as well-defined regions of brighter color compared to the less perturbed surroundings. It is expected that the scan conditions used to acquire the final image that is shown will also eventually alter the sample surface. Because the applied load was greatly diminished and the distance between successive visits by the tip along the slow-scan axis is much larger than what was used to generate the original surface modification, this is expected to be a gradual process requiring many raster scans. (Evidence will be presented later that justifies this statement.) Thus, we assume that the outer region of the image is unaltered by the scanning tip. Topographical cross sections of the image are shown in the figure. The top section corresponds to a single horizontal scan line drawn through the middle of the image. As is evident in the image, the height fluctuations are largest in the center, smallest in the outer region, and intermediate in the intervening region. These height fluctuations, which were also seen in the topographical cross sections reported by Hamada and Kaneko, make it difficult to compare the mean height of the patterned region to that of the surrounding unperturbed region. We found that these height fluctuations are easily removed by examining the arithmetic mean of many cross sections. In the middle graph, the mean of approximately 50 horizontal cross sections that intersected the center 1 × 1 μm region is plotted. While the height fluctuations in the outer region and the central 3 × 3 μm region are largely removed by averaging, the central 1 × 1 μm region still shows large-scale fluctuations in the height. These fluctuations are largest at the left and right edges of the region and tend to decay in amplitude toward the center of the region. The ability of the scan-induced height fluctuations to cancel out depends on a relatively weak correlation (or poor alignment) of the bundles and trenches between adjacent scan lines. Thus, the middle graph demonstrates that the surface waves are relatively poorly correlated in region B and better correlated at the edges of region A than they are toward the center of that region.

A more useful way to examine the mean height is to average the cross sections along the vertical axis, as shown in the bottom graph in Figure 7. The height fluctuations corresponding to region A are nearly eliminated, and we now can clearly recognize that the mean topography is greater in region B than it is in region C, and that the highest mean topography is present in region A. Thus, we have demonstrated that the tip-induced modifications so far considered have a tendency to raise the average height of the sample surface.

Repeat Distance between Bundles. Figure 8 (top) shows the mean one-dimensional (i.e., measured along the X-axis, or perpendicular to the bundle orientation) power spectra of the images in the rightmost column of Figure 2. The spectra are offset along the vertical axis for clarity. The peaks in the spectra correspond to fundamental and higher harmonics of the "wavelength" or repeat distance of the scan-induced pattern. A plot of the number of raster scans vs the repeat distance of the scan-induced pattern. A plot of the number of raster scans reveals that, under the scan conditions considered, the repeat distance reaches a nearly steady state value after only four raster scans (bottom of Figure 8).

Discussion

Roughening Susceptibility. The RMS roughness of the images shown in Figure 2 are plotted as a function of the number of raster scans in Figure 9. The roughness, or equivalently the wave amplitude, grows linearly for all of the scan conditions shown. The slope of the plots of roughness vs the number of scan lines will hereafter be called the roughening susceptibility. The roughening susceptibility was observed to increase monotonically with

(24) Because the peaks observed in the power spectra are broad and therefore yield a determination of lacking precision, the values plotted in the bottom of Figure 8 were instead determined in real space.
the applied load. The data in Figures 2 and 9 correspond to images acquired with 256 fast-scan cycles per image; similar measurements were also performed on images collected with 128 and 512 fast-scan cycles per raster scan. The results from all of these runs are compiled in Figure 10. To compare roughening susceptibilities collected with different numbers of fast-scan cycles, we divide the roughening susceptibilities plotted in Figure 10 (top) by the number of scan cycles per image and replot all of the results in Figure 10 (bottom). We see reasonable agreement between these normalized roughening susceptibilities acquired with different scan line densities. Thus, we conclude that the roughening susceptibility depends linearly on the scan line density, as well as the applied load. This is to our knowledge the first quantitative report of these fundamental phenomenological relationships.

Figure 11 demonstrates the reproducibility of this rescaling result. In two trials, thirty raster scans were performed over the same region, but the scan line density was changed after scan 10 and returned to the initial value after scan 20. The roughness plotted against the number of raster scans is continuous, but the slope of the data clearly changes abruptly when the scan line density is changed (top of the figure). By plotting the roughness against the total number of scan lines (i.e., the number of raster scans times the scan line density), all of the data collapse onto a single straight line (bottom of the figure). This is further confirmation that, for a given set of loading conditions, the roughening susceptibility appears to depend only on the number of visits by the scanning tip. It further suggests the robustness of this parameter for cross-study comparison.

**Figure 8.** Top: power spectral densities for the images corresponding to the right-most column of Figure 2. The spectra are offset along the vertical axis for brevity. Bottom: repeat distance vs the number of scans for the same set of images.

**Figure 9.** RMS roughness vs the number of scans for the various loads shown in Figure 2. The solid lines represent linear fits to the data. The slopes of such fits define a parameter called the roughening susceptibility. Note the monotonic increase in roughening susceptibility with applied load.

**Figure 10.** Top: roughening susceptibilities plotted as a function of applied load for three different scan line densities. Note that the roughening susceptibility tends to increase with both the applied load and the scan line density. The solid lines represent linear fits forced through the origin. Bottom: The same data are rescaled by the scan line density. All of the data collapse onto a single line.
Another parameter that was investigated was the gain setting of the feedback loop, which controls how effectively the feedback circuit responds to changes in the sample topography and sample tilt. At high gain settings, the feedback circuit is fully engaged, and the applied load is approximately constant across the entire scanned area. At lower gain settings, the tip remains in contact and overall sample tilt is accommodated, but regions of steeply increasing height (which occur at the leading edge of the bundles) experience larger cantilever deflections and hence higher applied loads, while regions of steeply decreasing height (at the trailing edge of the bundles) experience smaller applied loads. The average applied load across the imaged region, however, remains nearly constant. The effect of varying the feedback gain setting during the acquisition of a series of images is shown in Figure 12.

Images 1–10 were acquired with the feedback loop fully engaged (integral gain 2), scans 11–20 were performed with the feedback loop nearly disabled (integral gain 0.25), and scans 21–30 were collected with the feedback fully reengaged. The apparent drop in the RMS roughness during scans 11–20 is an artifact since the signal used to generate the topography image is based on the voltage to the Z-piezo, which in turn is dependent on the output of the feedback circuit. When the feedback circuit is reengaged (scans 21–30), we see that the RMS roughness is precisely as large as expected from a linear extrapolation of the first 10 scan cycles. This result is remarkable in light of the fact that, during the intermediate scans for which the feedback loop was nearly disabled, the applied load was not uniform across a given peak or trough. Thus, we have further confirmation of the linear relationship between surface roughening and the average applied load across the scanned area, as well as the cross-study robustness of the bundle formation phenomenon.

Mechanisms of Tip-Induced Deformations. Schallamach Waves. Meyers noted a similarity in the appearance of the scan-induced morphology in thick (~2 μm) PS films to the buckling phenomenon that occurs at the surface of an elastomer when it is slid across a second, hard surface under a compressive load (i.e., “Schallamach waves”). At the macroscopic scale, Schallamach waves have been observed for both a hard sphere sliding on a rubber track and a rubber sphere sliding on a hard track. The buckling is attributed to “waves of detachment” driven by a tangential stress gradient along the contact zone of the sliding interface. Energy loss occurs during the propagation of the waves of detachment, which Schallamach attributed to the breaking of adhesive bonds between the two surfaces. The buckling of the rubber surface, however, is reversible; when the shear forces are removed from the rubber slider, the surface springs back to its original, smooth state.

Meyers concluded that the surface of a PS film was not glassy, but rather that it behaved as an elastomer. However, contrary to what would be expected for an elastically deformed surface, the bundles were not observed to relax to the initial unperturbed state when the tip was withdrawn and the sample was left unperturbed for up to several hours. Furthermore, it should be recognized that the spacing of Schallamach’s waves of detachment is an order of magnitude smaller than the size of the diameter of contact between the sphere and track, whereas the repeat distance of scan-induced patterns is typically much larger than the radius of curvature of an AFM tip. Meyers attempted to compare the load dependence of wave spacing for his data to those of Schallamach waves. However, Schallamach’s data were...
Mechanisms of Tip-Induced Deformations. Stick–Slip Behavior. Several authors have postulated some form of stick–slip behavior at the tip–polymer interface to explain the repeating nature of the patterns. It is assumed that a mound of polymer accumulates in advance of the scanning tip as it slides across the surface. The presence of this mound results in an increased lateral force on the tip whose vector points in opposition to the sliding direction, and as the mound grows larger, so does the lateral force. Eventually, this lateral force overcomes the tip–sample adhesive interaction, and the tip slips over the mound and begins to form a new one. The extent of the mound along the slow-scan axis is finite, and therefore, the positions of the mounds along adjacent scan lines are correlated; the net result is that the observed mounds appear to be fairly continuous and in-phase along the slow-scan axis.

The phase transition’s model is one of two known mechanisms for intrinsic stick–slip behavior. It was developed to account for the stick–slip friction observed when simple isotropic fluids are confined between two crystalline surfaces. Simulations have suggested that when the sliding plates are very closely spaced so that the thickness of the interfacial film approaches the dimensions of the molecular length scale, the film undergoes a first-order phase transition between crystalline and liquidlike morphologies of the molecular length scale, and the film undergoes a first-order phase transition between crystalline and liquidlike states as the plates shear. While the interfacial film is solidlike, the two crystalline plates cannot slide past one another. Eventually, as shear energy is accumulated within the interfacial region, the film melts, allowing the plates to slip. The film then freezes again, and the plates remain stuck until the next melting event. As the sliding velocity of the plates is increased, the time between successive stick–slip events decreases, and the magnitude of the stick–slip spikes decreases as well. Thompson and Robbins explained this common observation of decreasing coefficient of friction with velocity by postulating that various moieties within the interfacial region can possess one of two values: a “static value” whose coefficient of friction is given by $F_s$, and a “kinetic value” with a coefficient of friction given by $F_k$, where $F_k < F_s$. As the sliding velocity is increased, the number of kinetic events increases at the expense of the number of static events. Because the overall observed friction is the sum of all frictional events (some of which stimulate the static states and some of which stimulate the kinetic ones), the overall observed friction decreases with velocity. Eventually a critical velocity is reached, above which no stick–slip occurs. A semiempirical relationship that describes this critical velocity has been given by Yoshizawa and Israelachvili.

$$V_c = \frac{F_s - F_k}{5kr}$$

where $F_s$ and $F_k$ are the static and kinetic coefficients of friction, respectively, $k$ is the cantilever spring constant, and $r$ is the characteristic time for molecular rearrangements.

We turn our attention now to the measured friction between the sliding AFM tip and the polymer bundles to determine whether evidence of stick–slip behavior can be found.

The strong correlation between lateral force and $dZ/dX$ (Figure 4) implies that tip–sample slippage, at least at length scales corresponding to the pattern’s repeat distance, does not appear to play a role in the observed morphology of the scan-induced pattern. Before stick–slip behavior at the tip–polymer interface is dismissed, however, it must be recognized that the mechanism of stick–slip proposed by Thompson and Robbins depends on the ability of the interfacial region to undergo a first-order phase transition (i.e., melting–freezing). Amorphous polymers do not undergo first-order phase transitions, but instead, experience more gradual changes in their thermodynamic state functions (i.e., second-order phase transitions). For example, rather than experiencing a latent heat or an abrupt volume change (both of which represent discontinuities in the first derivative of the chemical potential) as a polymer is heated or cooled through the glass transition, changes in the heat capacity and changes in the thermal expansivity (i.e., discontinuities in the second derivative of the chemical potential) are observed. Continuing with this theme, we postulate an analogous gradual change in the population of conformational states with varying degrees of energy dissipation within the interfacial region. Rather than experiencing an instantaneous jump from stick to slip behavior, one might instead expect a continuous change (temporal or spatial) of the frictional response as the polymer beneath the tip moves between domains of glassy, rubbery, or transitional dynamics. Thus, one might assign the dissimilar bundle and trough friction states in Figure 6 to more rubbery or glassy dynamics. A detailed examination of the temperature and/or rate dependence of friction would be required to locate precisely the different friction states along the transition from glassy to rubbery.

Mechanisms of Tip-Induced Deformations. A Fracture Mechanics Description. Perhaps the most well-developed proposed mechanism to date of scan-induced patterns in glassy polymer films comes from Elkaakour et al., who studied the formation of bundles while continually scanning the tip back and forth over the same line (i.e., in slow-scan-disabled mode) on a thick (~14 μm) film of polyacetylene on mica. The process was described in terms of a crack propagating within the polymer film in the region directly in front of the tip. Growth of the crack is controlled by an energy balance similar to Griffith’s criterion, in which the release rate of the strain energy accumulated in advance of the scanning tip is balanced by the increased surface energy associated with the walls.

$$F_{s} - F_{k} = 5kr$$

of the crack. Elkaakour invoked the notion of slippage to explain the periodic nature of the patterning process. To our knowledge, no one has published direct evidence of slippage between the scanning tip and the polymer surface. However, as discussed earlier, analysis of the height of the patterned regions suggests that the scanning process induces voids in the polymer film. Using a technique called ultrasonic force microscopy (the tip was driven at a frequency of 2 MHz with an amplitude less than 1 nm), Iwata et al. compared the elastic contact stiffness of scan-induced bundles in an injection-molded polycarbonate surface to that of the unperturbed surroundings.\(^7\) Iwata and coworkers found that the bundles were less stiff than the undamaged surface, which they also interpreted as evidence of the presence of microvoids or cracks in the damaged region. The higher degree of energy dissipation in the patterned regions of the present study (i.e., the type II friction seen in Figures 5 and 6) may be attributed to the greater mobility of the polymer molecules in the vicinity of such voids.

Our findings are consistent with the mechanism of Elkaakour et al.,\(^12\) in that the formation of cracks within a film is expected to increase the measured volume of the perturbed region, which with the assumption of incompressibility of the film is a consequence of mass conservation. (Another possibility is delamination by some mechanism other than delamination.)

A series of measurements similar to those shown in Figure 7 were performed for two different PS film thicknesses. The solid line represents a linear fit forced through the origin.

Of the waves, or equivalently to \(\sqrt{2}\) times the RMS roughness of the flattened image:

\[
R_{\text{RMS}} = \frac{1}{m} \int_{0}^{m} A^2 \sin^2\left(\frac{2\pi X}{\lambda}\right) \, dX = \frac{\sqrt{2}}{2} A
\]  

Thus, assuming that the scan-induced height variations are much larger than intrinsic height fluctuations (which are presumably still present in the scan-induced patterns), the amplitude of the scan-induced waves is equal to \(\sqrt{2}\) times the RMS roughness of the flattened image.

We will consider now several hypothetical models for the cross-sectional morphology of the bundles. Model A in Figure 14 describes the perturbed region as a sinusoidal fluctuation in the film thickness which, in the absence of voids, results in a mean thickness equal to that of the original unperturbed film. In this model, the scanning process simply moves material around the surface, with no rupture within the film or at the film–substrate interface; no increase in average surface height occurs. On the basis of the preceding findings, this model can be dismissed. Model B in Figure 14 explains the scanning process as the delamination of the film from the substrate. Assuming that the thickness of the buckled film in the perturbed region is not altered and that the buckles can be described as a sinusoidal wave, the height discrepancy between the mean topography of the perturbed and unperturbed regions should correspond to the amplitude of the waves, or equivalently to \(\sqrt{2}\) times the RMS roughness of the perturbed region. In other words, if this model was correct, the linear fit shown in Figure 13 would have a slope of unity. Instead, the line has a slope of 0.51. This leaves us with two possibilities: (1) the bundles deviate from sinusoidal waves and/or the film’s thickness is smaller at the peaks and troughs (i.e., regions of high curvature), or (2) the volume increases within the perturbed regions by some mechanism other than delamination.

It must be noted that other authors have seen similar scan-induced patterns in much thicker samples than what we consider here. Elkaakour et al. performed measurements on 14 \(\mu\)m films of polycarbonate cast onto mica and WS\(_2\) substrates.\(^12\) Other authors saw qualitatively similar patterns on bulk samples (injection-molded surfaces) of polycarbonate and poly(methyl methacrylate).\(^5\)-\(^8\) For these
cases, delamination is not a realistic explanation of the observed patterns. Therefore, we return to the idea that the scanning tip produces defects within the polymer in the vicinity of the sample surface. We suggest that the defects are not completely vacant, however, but contain fibrils of polymer that occupy approximately half of the volume within a void matrix, which explains the slope of the graph in Figure 13. This volume discrepancy is consistent with the formation of crazes. Long thought to occur only in amorphous polymer glasses such as polystyrene, poly(methyl methacrylate), and polycarbonate, crazing also has been found in semicrystalline polymers during the past 20 years (though not reported for polyacrylate). Investigations of crazes in bulk samples reveal that the fibrils have diameters on the order of 10 nm, and that these fibrils stretch as the craze grows wider. This results in the storage of an elastic stress within the craze that tends to prevent further opening of the defect. Model C in Figure 14 shows a craze within each of the mounds generated by the scanning tip, and the fibrils are shown perpendicular to the craze within the film, as would be expected on the basis of scanning electron micrographs of crazes in bulk samples. Measurements similar to those described in Figures 7 and 13 were also performed on a 10 nm thick unannealed PVAc film. Given the low bulk glass transition temperature of PVAc (32°C) and the fact that the sample was unannealed, this film was perhaps somewhat rubbery in its unperturbed state. Nevertheless, the mean height of the patterned region was again raised compared to that of the surrounding region.

It is generally accepted that the presence of a free surface (i.e., a polymer-air or polymer-vacuum interface) tends to increase polymer mobility and decrease the glass transition temperature. A detailed discussion of the various models that have been developed to describe the effect of film thickness on the glass transition temperature and polymer mobility can be found in a review by Forrest and Dalnoki-Veress. At a simple level, one may intuitively ascribe a depressed $T_g$, or enhanced polymer mobility, at the polymer-air interface to a larger free volume than what is encountered in bulk samples at the same temperature. More precisely, it has been suggested that polymer molecules near an interface adopt conformational patterns different from those predicted by self-avoiding random walk statistics that govern the behavior in bulk systems. The effect of an altered conformational state near the polymer-air interface may be to reduce the number of entanglements, or to reduce the local density (although differences from the bulk value have not been observed), thereby resulting in an enhanced polymer mobility. Other models describe the $T_g$ behavior in thin films in terms of a characteristic length scale for dynamics in glassy systems, suggesting that a layer near the surface exhibits faster dynamics, and hence a $T_g$ lower than the bulk value. While several studies have shown an increased glass transition temperature for different thin film/substrate systems than what have been considered in this paper, this has been attributed to attractive interactions between the film and substrate and to an increased polymer density in the vicinity of the substrate. In studies of the glass transition in thin, self-supporting polymer films (i.e., films without a substrate and with two polymer-air interfaces), the $T_g$ of the film has always been observed to be less than the bulk value.

Because the generation of voids in the bundles is expected to increase the effective polymer-air interfacial area, it is reasonable to postulate that the bundles will exhibit a lower effective glass transition temperature than the trenches or the surrounding, unperturbed regions of the film. One may therefore expect the more rubbery moieties to exhibit a greater tendency to dissipate mechanical energy compared to the more glassy domains of the film. In fact, this is exactly what was observed in the friction data presented in Figures 5-7, where the mean friction in the patterned region is elevated relative to that of the surrounding film and two discreet domains of friction force were encountered within the pattern itself. We therefore may assign the type I friction to more glassy/less rubbery domains, and type II friction to more rubbery/less glassy domains. The broad distribution of the friction force in the patterned region (Figure 6) is consistent with the continuous transition from glassy to rubbery behavior proposed earlier in this paper. Scan velocity is of course important in locating the system precisely along this transition. In this study no attempt was made to quantify how far along the viscoelastic spectrum the more rubbery domains were translated relative to less rubbery domains.

Nonperturbative scanning-probe friction measurements of semicrystalline poly(vinyl alcohol) and gelatin films have revealed that highly crystalline domains do not exhibit the glass-to-rubber transitional behavior (elevated friction) seen in more amorphous domains. Therefore, it would be illuminating to compare the patterning behavior of predominantly crystalline and amorphous domains of the same polymer film, i.e., examine both volume and dissipative changes. By applying the methodologies presented in this paper to a wider variety of
polymers, the potential universality of our proposed mechanism of scan-induced pattern formation may be explored.

Summary

We have characterized the susceptibility of PS and PVAc films to damage when a sharp tip is scanned in contact with the surface in a raster pattern. The damage caused by the tip can be approximated as a sinusoidal wave oriented perpendicular to the tip trajectory. An analysis of the mean height within patterned regions showed an increased volume that is consistent with the formation of crazes within the polymer film. The volume that is gained while forcing plastic deformation is interpreted to contribute toward a second-order phase transition in the film, including more/less rubbery domains within the patterned regions as contrasted by friction force imaging. Aiding these findings was a newly defined parameter, roughening susceptibility, the slope of the observed linear increase of roughness under repeated raster scanning. This parameter, as well as the wavelength of the scan-induced patterns, was characterized as a function of the number of raster scans performed over the same region, the applied load, the scan line density, and the gain of the feedback circuit used to maintain a constant applied load, generally demonstrating the robustness of our methodology and removing a curtain of mystery regarding the impact of these parameter settings. Moreover, the similarity between the patterns we characterized and those reported by other investigators for a wide variety of polymer/substrate systems suggests that the methodologies we developed can be applied to the analysis of many glassy and semicrystalline polymers. In a subsequent paper, we will address the temperature and rate dependence of these scan-induced patterns and further exploit the methodology reported herein.

Acknowledgment. We thank the Center for Interfacial Engineering and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for supporting this work.

LA015769J

(56) Several authors have examined patterning in nominally semicrystalline polymers. The crystalline nature of the PET films investigated by Jing et al. and the PEO films studied by Nie and co-workers was confirmed by the initial AFM scan of the surfaces (i.e., before the onset of significant damage by the scanning tip). Nie et al. found that crystalline films of PET were much more difficult to pattern than amorphous PET films. For the case of the polyacetylene film investigated by Elkaakour et al., however, the degree of crystallinity is unknown.