Correlation of Nanowear Patterns to Viscoelastic Response in a Thin Polystyrene Melt

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The response of a thin-film polystyrene melt to a raster-scanned scanning force microscope tip was investigated. At high temperatures the scanning process induced intricate pattern formation whose quantitative characteristics were compared at different temperatures and scan rates. The dependence of the patterns on temperature and scan rate was consistent with time-temperature superposition as described by the Williams–Landel–Ferry (WLF) equation. WLF analysis implies an increased glass transition temperature derived from elevated pressure beneath the tip. The latter provides an estimate of the radius of the affected film region near the tip.

Nanotribology of thin organic films has become a topic of extreme technological and scientific interest. The performance of ultrathin lubricants is critical in magnetic storage media devices, as well as new technologies like microelectromechanical systems. Fortunately the need to understand the tribological behavior of ultrathin organic films has coincided with the development of analytical tools to measure shear forces on the nanometer scale, i.e., the scanning force microscope (SFM) and modified versions of the surfaces forces apparatus. At the scientific frontier these methods have enabled careful studies of confinement effects on molecular dynamics and thermodynamics.

SFM has proven to be a powerful tool for measuring time-dependent mechanical properties of polymer films at ambient temperatures. Because piezoelectric scanners are incompatible with substantial temperature elevation, however, the SFM community has only begun to examine the role of temperature in material response. Clearly temperature is critical in mechanical device applications. Fundamentally, the response of soft material to external forces is often dominated by entropic (i.e., temperature-dependent) effects. The approach to thermodynamic equilibrium for polymeric systems is typically slow, so that the response to mechanical perturbation is a function of both temperature and rate (i.e., is viscoelastic). Rigorous studies of thin-film polymer nanotribology therefore must include methodologies to quantify the interrelated roles of these two parameters.

Several researchers have reported that “bundles” commonly form in a variety of thin polymer films when they are raster scanned by a sharp, slow-moving tip. All previously reported studies were performed at room temperature, and the bundles were observed to align perpendicular to the tip trajectory. Elkaakour et al. found that the velocity dependence of the repeat distance of the scan-induced features correlates with the frequency-dependent shear modulus. In the present report, we examine the temperature and scan-velocity dependence of more complex bundle formation in the melt regime. Analysis of the orientation of the features provides a mathematical correspondence between temperature and rate.

Sample heating or cooling must be accomplished without significantly altering the temperature of the piezoelectric transducer. In the SFM used in this study (Molecular Imaging), an aluminum-coated silicon cantilever with a spring constant of 3.8 N/m and a tip radius of 10 nm was mounted on the scanner and isolated from the sample, except at the point of contact. The sample was placed on top of a resistive heating stage, and the temperature controller was independently calibrated with a thermocouple. A Digital Instruments (DI) NanoScope III controller was interfaced to the SFM in order to drive the scanner and collect data. The sample was prepared by spin coating a 0.5% solution of polystyrene (Mw = 110 000; Mw/Mn = 1.1) in toluene at 2000 rpm onto a dehydrated silicon (100) substrate (with native oxide present), resulting in a 20 nm film. A feedback loop was used during imaging to adjust the height of the cantilever support in order to maintain a constant cantilever deflection (and a constant applied load) when sample tilt or variations in the surface topography were encountered.

The width and height of scan-induced bundles were observed to be strongly dependent upon the temperature

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15(13) The tip’s velocity is calculated from the following equation: v = (f×scan time) / (image size). The fast-scan frequency refers to how many trace–retrace cycles (refer to Figure 2) are performed per second.
16(14) This cantilever was chosen for its tip sharpness, its high reflectivity, and its stiffness. We found that the thermal strain (i.e., bending of the cantilever due to a mismatch in the thermal expansion of silicon and the metal coating) was very small in comparison with other commercially available cantilevers.
and scan velocity, yet the orientation of the features remained constant over a wide temperature range (20 °C to approximately 140 °C). At temperatures above 140 °C the pattern of the scan-induced features changed dramatically. Figure 1A is a topographical image acquired at 151 °C while raster scanning from top-to-bottom, and Figure 1B is the subsequent scan taken while rastering from bottom-to-top. Brighter features correspond to higher surface elevations. The bundles are widest at the center of the image and tend to orient themselves vertically (i.e., perpendicular to the tip trajectory); toward the left and right edges of the scan area, these wide features branch off into narrower ones which orient themselves at an angle less than 90° relative to the tip trajectory. Continued scanning over the same region eventually caused the film to rupture, resulting in the accumulation of polymer at the center of the scanned region and bare silicon at the left and right edges. (Contrast between the polymer melt and the bare substrate can be detected by the change in friction between the polymer-coated regions and the silicon.)

To understand the morphologies seen in Figure 1, we examined the effect that variations in tip trajectory have on the observed morphologies. The SFM tip was raster scanned in a triangular wave pattern (i.e., the standard pattern programmed into the DI control system(16)) over the sample surface as depicted on the left side of Figure 2; the departure from strictly horizontal scans is exaggerated in Figure 2 for clarity. The angle of the tip trajectory relative to the X-axis (i.e., φ in the left of Figure 2) was varied by changing the number of scan lines executed during the acquisition of an image from 128 to 512 fast-scan cycles per image. The topography images in the right side of Figure 2 display the scan-induced patterns corresponding to the three different scan angles. We measured the angles that the bundles form with the X-axis at the left (θl) and right (θr) edges of each image. The values of θl and θr shown in Figure 2 are averages determined from 10 different bundles in each image. The angles φ and θ differ by 2 orders of magnitude, yet they are directly proportional over the range examined.

We present here a model to describe the patterns observed in Figures 1 and 2. Surrounding each scan line is a region of finite width over which the polymer film is perturbed by shear stresses (light gray regions in Figure 2 (left)). Because of slow relaxations, the effects of this tip-induced perturbation are cumulative for successive scans. Whenever portions of successive scans overlap (as represented by the dark gray regions in the left of Figure 2), the first pass is toward the edge of the imaged region, and the second pass is toward the center (i.e., toward the vertical line represented by X = 5 μm). The first pass softens the polymer (perhaps by orienting the polymer coils along the fast-scan axis), and the second pass sweeps the polymer toward the center. The result is a net movement of polymer toward the center of the raster-scanned region. The overlap with the previous scan is greatest near the edges of the imaged region, increasing the efficiency with which polymer is swept inward. This accounts for the more nearly horizontal orientation of polymer bundles near the edges of the scanned area.

To develop a mathematical expression describing the orientation of the bundles with respect to the tip trajectory, we define the location of a particular point on a bundle with the coordinates (X, Y). For brevity, we only discuss the left half of the scanned region. Results presented in Figure 2 indicate that the slope of a bundle with respect to the fast-scan axis at some value of X is

$$\frac{dY}{dX}_{X=0} = a_1 \Delta Y_{t-t}$$

where $a_1$ is a constant and $\Delta Y_{t-t}$ is the vertical distance between successive “trace” (left-to-right) scan lines. Clearly $dY/dX$ is not constant across the entire X axis. A more general expression is:

$$dY/dX = a_1 \Delta Y_{t-t} + f(X), \text{ with } f(0) = 0$$

Whereas $\Delta Y_{t-t}$ is constant across the entire fast-scan axis, $\Delta Y_{r-t}$ (the vertical distance between a retrace and the subsequent trace scan line) varies linearly from zero at the left edge of the imaged region to a maximum equal to $\Delta Y_{t-t}$ at the right edge

$$\Delta Y_{r-t} = \frac{X}{X_{\text{max}}} \Delta Y_{t-t}$$

Assuming that the functional dependence of the bundle slope on $\Delta Y_{r-t}$ at position X is the same as it is for $\Delta Y_{t-t}$
at the image edge (i.e., it is linear), we can write

$$\frac{dY}{dX} = a_1 \Delta Y_{t-t} + a_2 \Delta Y_{r-t} = \Delta Y_{t-t} \left( a_1 + \frac{a_2}{X_{\text{max}}} X \right) \quad (4)$$

Integration yields:

$$Y = \left( \frac{a_2 \Delta Y_{t-t}}{2X_{\text{max}}} \right) X^2 + \left( a_1 \Delta Y_{t-t} \right) X + a_3 \quad (5)$$

We tested eq 5 by tracing three bundles on each side of an image, plotting the data to a common curve (Figure 3, solid and open symbols), and performing a quadratic fit (solid lines) with fitting parameters $a_1$, $a_2$, and $a_3$. The ratio of the second derivatives for the 128-, 256-, and 512-line images is expected to be 4:2:1 (reflecting the ratio of the slopes of the dark triangles in Figure 2). The empirical ratio (from the quadratic fit) is 4.7:2.4:1. Thus, the

Figure 2. (left) Schematic of the tip trajectory for 128 (top), 256 (middle), and 512 (bottom) fast-scan cycles per image. The angle of the tip’s trajectory ($\phi$) relative to the fast-scan axis is greatly exaggerated for clarity. The light gray regions are areas that are perturbed by the tip. Overlap of perturbed regions occurs at the left and right edges of the scan area (dark gray triangles), at which time the tip is moving toward the center of the scan area. Decreasing $\phi$ results in the overlapping perturbed regions extending further from the edges of the scan area. The corresponding topography images are shown on the right. $\theta$, as defined in the figure, is proportional to, but much larger than, $\phi$.

Figure 3. Three bundles on each side of 128-, 256-, and 512-line images were traced and plotted onto common curves (solid and open symbols). The lines represent a quadratic fit to the symbols. The quality of the fit and the dependence of the fitting parameters on the relative distances between scan line perturbations suggest the validity of eq 5.
agreement of the quadratic fits and the experimental results suggest the validity of our model.

The parameters $a_1$ and $a_2$ are related to the width of the perturbed region surrounding a scan line, the strength of the tip–polymer interaction, and the relaxation time of the polymer's (viscoelastic) response to this perturbation. By changing these parameters, one can manipulate the morphology of the scan-induced pattern. One way to modify the viscoelastic response of the polymer is to vary the temperature and fast-scan frequency at which images are acquired. Extrinsic parameters of further importance would be the magnitude of shear (and tensile) forces applied as well as the tip–sample contact area (in turn a function of tip shape). In the collection of the images shown in Figure 4, the extrinsic parameters were held approximately constant by using a single, stable tip at constant load, while the intrinsic parameters of temperature and rate were varied. We must caution, however, that variation of the (experimentally accessible) scanning rate necessarily convolves two distinct elapsed times of importance: (1) the time during which perturbative forces act on a polymer conformer during a single scan (velocity dependence), and (2) the time between repeated applications of perturbative forces (successive trace/retrace scans).

We demonstrate the temperature and frequency dependence of scan-induced patterning in the $10 \times 10 \mu$m topography images of Figure 4. (Images were acquired at five different temperatures and over a greater frequency range than depicted in Figure 4.) At higher fast-scan frequencies for a given temperature—or at lower temperatures for a given frequency—the bundles tend to align nearly perpendicular to the tip trajectory. Decreasing the scanning frequency or increasing the temperature caused the bundles to align more efficiently with the tip trajectory.

The images in Figure 4 were quantified by measuring the slopes of the bundles near the left and right edges of the scan area. Twenty measurements were performed for each image (10 on each side), and the results are plotted in Figure 5A as $|dY/dX|$ vs the fast-scan frequency for five temperatures varying from 142 to 160 °C. Note that a given slope is reached at a higher frequency (shorter relaxation time) as the temperature increases. This observation is consistent with the time–temperature superposition principle which describes viscoelastic behavior.

**Figure 4.** $10 \mu$m images acquired at different temperatures and fast-scan frequencies. Decreasing the fast-scan frequency has a similar effect on the scan-induced pattern as increasing the temperature.
Figure 5. (top) The images in Figure 4 were quantified by measuring the slope of the scan-induced bundles at the left and right edges of the scan area. Each point represents the average of 20 measurements from many more images than shown in Figure 4. Empirical factors were determined which, when applied to the frequency axis, shift the data taken at different temperatures to 142 °C (bottom). The linearity of the plot in the inset suggests that the shift factors are described by the WLF equation.

Recognizing the similarity in the curve shapes for each of the data sets in Figure 5A, we determined an empirical shift factor for each temperature ($a_T$) which, when applied to the frequency scale for each curve in Figure 5A, shift the data to a chosen reference temperature ($T_0 = 142$ °C). The shifted data are shown in Figure 5B.

The linearity of ($T - T_0$)/log $a_T$ vs ($T - T_0$) (where $a_T$ is the empirical shift factor and $T_0$ is the reference temperature to which the data are shifted), shown in the inset, implies that the results are consistent with the Williams–Landel–Ferry (WLF) equation, known to describe viscoelastic behavior in many amorphous polymers.\(^{17}\)

\[
\frac{(T - T_0)}{\log a_T} = \frac{C_2}{C_1} \left( \frac{1}{C_1} (T - T_0) \right)
\]  

(6)

Here $C_1$ and $C_2$ are constants evaluated from the slope and intercept and depend on the value chosen for the reference temperature, $T_0$. If the master curve is referenced to the glass transition temperature ($T_g$), then $(2.303 C_1)^{-1}$ is theoretically understood to be the fractional free volume at the glass transition ($f_g$).\(^{6,7,17}\)

For the glass transition to occur, a critical free volume, $f_g$, must be reached. At $f < f_g$, the polymer is hard and brittle, while $f > f_g$ results in rubbery or fluidlike behavior. As shown in Table 1, $f_g = 0.032$ for PS. Using this value of $f_g$, we fixed the value of $C_1$ in order to estimate an effective glass transition temperature of 113 °C from our measurements. In interpreting this result, we must consider two complications in SFM of ultrathin films: interfacial effects and elevated pressure. Several studies have demonstrated that as the thickness of a polystyrene film approaches the polymer coil dimensions, $T_g$ decreases significantly below the bulk value of 100 °C.\(^{18-20}\) In a system similar to what we investigated (i.e., 20 nm PS film on a Si substrate), Keddie et al. measured a $T_g$ of 87 °C. On the other hand, substantial increases in $T_g$ have been reported in bulk PS when the sample was subjected to elevated hydrostatic pressure.\(^{21}\) Assuming that the 26 °C increase in $T_g$ is exclusively due to pressure effects, we estimate—based on the effect of hydrostatic pressure on the $T_g$ of bulk PS—that the effective tip pressure on the surface is 84 MPa.\(^{21}\) Given the effective pressure and the applied load (110 nN), we can calculate an effective perturbation radius of 20 nm, which is remarkably close to the tip's radius of curvature (approximately 10 nm).

In summary, both temperature and scan frequency affect the patterns created by movement of a nanoscopic tip in contact with a polymer surface. The time–temperature dependence of the patterns is well-described by the WLF equation which is typically used to describe viscoelastic behavior. Analysis of our data further suggests that the $T_g$ of the polymer is elevated in the region confined between the tip and the substrate.

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Table 1. Comparison of WLF Analysis to Literature Values for Bulk Polystyrene

<table>
<thead>
<tr>
<th>$T_0$ (°C)</th>
<th>$(2.303 C_1)^{-1}$</th>
<th>$C_2$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>142</td>
<td>0.10</td>
<td>43</td>
</tr>
<tr>
<td>100 (bulk $T_g^a$)</td>
<td>0.032 = $f_g$</td>
<td>51$^a$</td>
</tr>
<tr>
<td>100</td>
<td>0.014</td>
<td>7.6</td>
</tr>
<tr>
<td>113</td>
<td>0.032</td>
<td>14</td>
</tr>
</tbody>
</table>

$^a$ From ref 17.