

Nanoscale Frictional Dissipation into Shear-Stressed Polymer Relaxations

Lars Jansen and André Schirmeisen*

*Physikalisches Institut, Westfälische Wilhelms-Universität Münster, Wilhelm-Klemm-Strasse 10, 48149 Münster, Germany
and Center for Nanotechnology (CeNTech), Heisenbergstrasse 11, 48149 Münster, Germany*

James L. Hedrick

IBM Almaden Research, 650 Harry Road, San Jose, California 95120, USA

Mark A. Lantz, Armin Knoll, Rachel Cannara, and Bernd Gotsmann

*IBM Zurich Research Laboratory, Säumerstrasse 4, CH-8803 Rüschlikon, Switzerland
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Sliding friction between a silicon tip and a highly cross-linked polyaryletherketone film is studied using friction force microscopy. The friction force as a function of temperature between 150 and 500 K shows distinctive maxima corresponding to α and β polymer relaxations in dynamic mechanical analysis (DMA). In contrast to DMA, the nanoscale friction shows comparable coupling of mechanical energy to both relaxation modes. We report a strong shift in the peak temperatures with applied load. This effect is modeled with an Arrhenius activation by incorporating the applied shear stress in the effective activation energy of the two relaxations. The effect of the stress-shifted relaxation on friction-versus-load experiments is discussed.

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Uncovering the basic dissipation processes that give rise to friction is an important motivation for tribology research. Friction force microscopy (FFM) has been used to elucidate numerous processes that contribute to friction on the nanometer scale [1–3]. However, it remains a challenge to identify the individual dissipation channels. Having distinct modes of dissipation, polymers are an ideal model system for tribology. In addition, friction of polymer surfaces is of fundamental importance to established technologies [4] as well as emerging applications, including nanoscale data storage [5] and patterning [6].

Structural relaxations ranging from molecular motion of sidegroup and backbone entities to sliding modes of the polymer chain are fundamental processes that govern energy dissipation in polymers. In the glassy state, only local processes are active. By convention, the symbols α , β , and γ are assigned to these processes, with γ and α used for the transitions active at the lowest and highest temperature, respectively [7,8]. The most prominent mode, the α transition, is responsible for a transition from the glassy to the rubbery state at the so-called glass-transition temperature T_g . The α transition has been identified clearly in FFM and in macroscopic friction experiments [9–11]. Secondary relaxations (β and γ) are local and couple at most weakly to the polymer backbone motion. They have only rarely been observed using FFM [9,11].

Here, we present nanoscale friction data on a polymer over a wide temperature range covering both α and β relaxations. The relaxation temperatures are found to be a strong function of load forces applied.

The polymer used in this study (see Fig. 1) is a highly cross-linked polyaryletherketone (PAEK), as used for ther-

momechanical data storage [5]. A 100-nm film was prepared by spin coating from solution onto a silicon substrate. Subsequent curing at 623 K initiated a cross-link reaction, involving the phenyl-ethynyl groups that are placed both at the ends of the molecule and along the polymer backbone. The cross-link density was chosen to be high enough to suppress the formation of ripples under the influence of the sliding tip [12] (a common observation that may influence friction measurements).

Figure 2(a) shows the macroscale thermomechanical properties of the polymer as measured by dynamic mechanical analysis (DMA). The peak in the loss modulus [$\tan(\delta)$ signal] at around 510 K can be assigned to the α transition, with an onset, i.e., T_g , at 453 K. In comparison, the secondary relaxation modes exhibit a much smaller signal, because these modes couple more weakly to macroscopic deformation. The broad peak is caused by several individual β relaxations. A β transition at around 150 K has been previously observed for a closely related polymer, polyetheretherketone (PEEK) [13–16]. It has been shown that this relaxation is linked to a rotation of aromatic rings around the C-C bonds in the polymer backbone. The corresponding molecular motion involves a cooperative

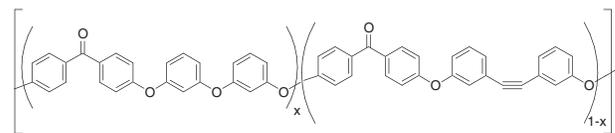


FIG. 1. Chemical structure of the polymer used for the experiments. The triple bonded carbon atoms in the backbone serve as cross-link sites.

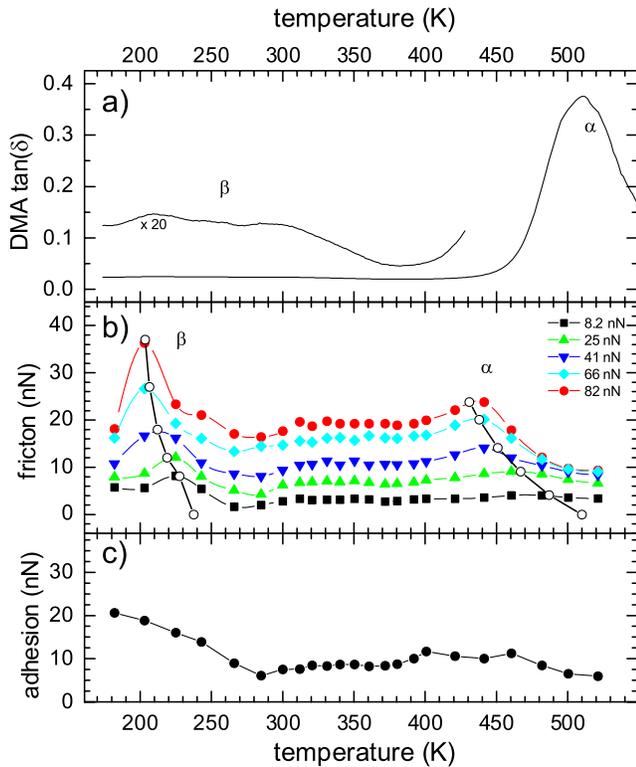


FIG. 2 (color online). (a) Mechanical loss tangent of bulk polymer sample measured by DMA. (b) Average absolute friction force as a function of temperature for different applied load forces using FFM. For clarity only five out of ten measured loads are shown. The open circles show the predicted load-induced temperature shift of the α and β peaks using an Arrhenius-type activation model. (c) Adhesion (pulloff) force between tip and surface.

motion of 5–9 monomer units [13]. With respect to PEEK, the PAEK polymer used in this study (see Fig. 1) was designed to prevent crystallinity, increase mechanical stability, and lower the T_g . These properties were achieved by replacing the two ether linkages around a single aromatic ring from an orthoconfiguration to a metaconfiguration. Further, the ethynyl cross-linking groups are directly attached to aromatic rings, influencing their mobility. These modifications lead to a splitting and shift to higher temperatures of the β relaxation, as observed in the DMA data.

The friction experiments were performed in ultrahigh vacuum with a commercial atomic force microscope (AFM), Omicron VT-AFM, with the ability to vary the sample temperature from 25 to 650 K. The force sensor used in this experiment is a rectangular silicon cantilever (Nanosensors, FM type). The normal and torsional spring constants, k_{\perp} and k_{\parallel} , were calculated from the measured cantilever dimensions and the resonance frequency [17,18], leading to $k_{\perp} = (1.72 \pm 0.35)$ N/m and $k_{\parallel} = (220 \pm 88)$ N/m. Measurement method and calibration procedures were the same as used before to determine nanoscale friction on silicon [19]. Scanning electron microscopy images taken before and after the experiment

revealed no significant change of tip shape through the experiment (tip radius 32 ± 4 nm).

The sample was preheated in UHV to a temperature of 540 K for about 30 min to remove water and solvent traces. The experiment was performed in three consecutive runs over different temperature ranges (182–300 K, 300–400 K, and 300–520 K, in steps of 10 or 20 K with an accuracy of 1 K), over 3 days. Prior to each run of ramping the temperature, a measurement of friction versus load was taken at room temperature in order to get an estimate of the reproducibility. Hence the representative error bar of about 1.5 nN [not shown in Fig. 2(b)] is determined by the standard deviation from the direct comparison of the three reference measurements. At each set temperature, friction was measured as a function of applied load between 8.2 and 82 nN before setting the next temperature. For each temperature-load combination, the friction force was determined as half the difference of the lateral force signals during trace and retrace scans, averaging over 250 scan lines taken over an area of 50×50 nm² at a scan speed of 500 nm/s. A virgin scan area was chosen for each such measurement.

Figure 2(b) shows the FFM measurements of the friction force as a function of applied load and sample temperature. The polymer relaxations can be identified as well-defined peaks in the friction spectra. Further β peaks (as in the DMA) may be present but are not clearly resolved. The adhesion [Fig. 2(c)], however, although showing an increase towards lower temperatures, appears to be unaffected by the relaxation peaks.

A striking difference between the DMA and the FFM results is the relative strength of α - and β transition peaks. While the α transition is about 50 times stronger than the β relaxation in DMA, it is weaker in FFM.

To interpret this, we consider the different length scales and respective interaction volumes which are addressed in the FFM experiments. On a molecular level, both the α and β transitions are related to rotations around C-C bonds in the backbone, but the corresponding rearrangement involves different cooperativity and therefore different volumes: For example, in polyetherketone (PEK), which is similar to our PAEK, the α relaxation involves cooperative motion on a length scale of ≈ 3.2 nm at T_g [20]. The β transition volumes have a diameter of ≈ 1 nm in PEEK [13]. In order to excite mechanical relaxations the respective cooperative volumes should be equal to or less than the volume subject to mechanical stress and deformation by the scanning tip. Using the Johnson-Kendall-Roberts model [21] for the tip sample contact below T_g with a reduced elastic modulus of 5.7 GPa and Fig. 2(c), we estimate that for the applied loads from $F_{\text{appl}} = 8.2$ to 82 nN the contact radius varies from $a = 8.4$ to 11.0 nm. The shear stress underneath the tip is more constrained than the normal pressure, and therefore we estimate the interaction volume is just about equal to the cooperativity volume of the α transition and a few tens of times larger than that of the β

transition. This implies that FFM can dissipate energy into both channels. However, the β transition apparently couples more efficiently to the tip motion than the α transition.

The FFM data in Fig. 2(b) reveal a strong temperature shift of both transition peaks as a function of applied load. In response to a load increase by $\Delta F_{\text{appl}} = 73.8$ nN, the α and β dissipation maxima shift by 30 and 20 K, respectively.

What is the reason for the observed load dependence? We recall that dissipation peaks are observed when there is a match of the time scale of the mechanical interaction of the tip with the polymer and the relaxation of the polymer chains. This was demonstrated by a systematic shift of transition peaks with applied scan velocity [10,11]. However, our results show that this resonance condition is also significantly altered by the applied load. From simple geometric considerations one could argue that the tip-surface contact area becomes larger with increasing load. Accordingly, the interaction time increases for any given relaxation volume within the interaction volume under the sliding tip [11]. For the above calculated values for contact radii at a sliding speed of 500 nm/s, we find that the interaction time varies from 34 to 44 ms. With activation energies for α of $E_a = 11$ eV and β of $E_a = 0.4\text{--}0.7$ eV (typical for various PAEKs [13–16]), we obtain temperature shifts of 1 order of magnitude below the observed effect. Even if we consider the (aforementioned) length scale of cooperativity for the time scale estimation [22], we do not obtain the measured shift.

Alternatively, we relate the shift of peak temperatures T_p to the stresses involved in the interaction with the sliding tip [23]. In the case of purely *compressive* stress (hydrostatic pressure) we expect an *increase* of T_p [8]. Conversely, *shear* stress can cause a *reduction* of T_p . In a tip-surface contact, there always exist sheared and compressed regions simultaneously. Motivated by our observation of a significant T_p reduction, we continue our analysis assuming that the frictional energy dissipation is located predominantly in shear-stressed regions.

To test this hypothesis, we turn to the relaxation kinetics $\tau(T)$ of energy dissipation in the two relaxation modes: The Arrhenius law, $\tau = \tau_0 \exp(E_a/k_B T)$, holds for both the β transition and the α transition, as long as the temperature range is sufficiently small, as assumed in our analysis. Following the Eyring model [24], the activation energy E_a is reduced due to the shear stress σ under the tip by an amount $V_a \sigma$, while the time scale τ_0 is assumed to be constant. The constant V_a is termed activation volume and is not the same as the aforementioned volume of cooperative motion. This leads to $\tau = \tau_0 \exp[(E_a - V_a \sigma)/k_B T]$, and therefore to a shift of the peak temperature of $\Delta T = T_p - T'_p = -T_p V_a \sigma / E_a$.

For the α process the activation volume V_a^α of PAEK [25] is on the order of 4 nm³. The shear stress in the polymer under action of the sliding tip can be estimated by the average shear stress at the interface. Based on the

measured friction forces and the above calculated contact radii we obtain shear stresses ranging from 185 to 630 MPa [26]. Combining these values with an apparent activation energy of 11 eV (see above) allows us to predict ΔT values for the loads applied, F_{appl} [open circles in Figs. 2(b) and 3(a)]. Despite the simplicity of the model the agreement with the experiment is remarkable, corroborating this explanation of the load-induced temperature shift.

The temperature shift of the β peak can be similarly calculated, using literature values for the activation energy (0.4–0.7 eV; see above). The activation volume V_a^β of the β process, however, is unknown and therefore used as a fit parameter. We get good agreement with the experimental temperature shift ΔT for $V_a^\beta = 0.14\text{--}0.25$ nm³ [Figs. 2(b) and 3(b)]. Within the uncertainty given by the uncertainty in E_a the resulting V_a^β is not influenced by the variation of the adhesive force [Fig. 2(c)]. It is remarkable that the ratio V_a^α/V_a^β is about 15–30, and therefore of a similar order of magnitude as the ratio of volumes of cooperative motion for the two processes (≈ 10). This correlation has been postulated from simulations of polymer chain mobility [27].

To estimate the width of the relaxation peaks on the temperature axis, we consider the frequency response of an activated process. In the frequency domain, the width of the imaginary part of a modulus changing due to an activated relaxation can be obtained by calculating the dynamic modulus [7]. A relaxation process described by a single time constant, i.e., a Debye process, has a FWHM of just above 1 order of magnitude [7]. Invoking the Arrhenius equation to translate the given frequency range into a temperature range, we find a width of 20 K for a Debye process with $E_a = 0.55$ eV and $T_p = 220$ K. As most processes in polymers exhibit a distribution of time constants which can be described by a stretched exponential function, the width of the peak also broadens by the stretched exponent. A typical stretching exponent of 0.5 thus leads to a doubling of the peak width to 40 K. The width of the β peak therefore can be estimated to 40 K with 20 K as a lower bound, which agrees with the observed beta peak width of 50 ± 20 K in the FFM data in Fig. 2(b).

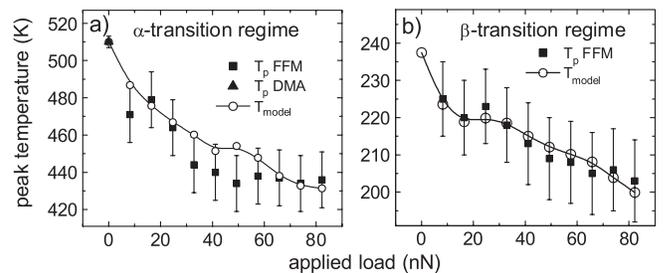


FIG. 3. Peak temperatures T_p as obtained from experiment and model predictions of the α peak (a) or from a model fit to the β peak (b) using V_a^β as a fit parameter. As experimental T_p the maxima of spline interpolations were used, but the error bars are given by half the temperature sampling. The black lines are guides to the eye.

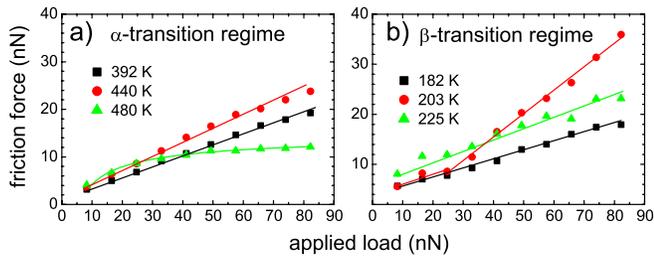


FIG. 4 (color online). Friction force versus applied load curves for different temperatures around (a) the α transition and (b) the β transition. The solid lines are guides to the eye.

The stress-induced shifts of transition peaks in FFM have an interesting consequence for commonly used and fundamentally important measurements of friction versus load (FVL) at a fixed temperature. A change of slope of FVL is observed especially at temperatures around the relaxation peaks, see Fig. 4, because the width of the β peak is comparable to the amount of stress-induced temperature shift. Nonlinear FVL have been previously observed near T_g using FFM [22] and were interpreted in terms of exciting different activation processes at low and high loads. In our case, this behavior is due to the load-induced peak shifting.

A linear relation between friction and load is found at temperatures sufficiently below the peak region [e.g., at 182 K in Fig. 4(a)]. In contrast, a much steeper slope is observed at 203 K (in particular at high loads), since the β peak shifts as we approach 203 K with increasing load and shear. The inverse effect is found at 225 K, where the FVL curve crosses over the 203 K curve. For the α peak [see Fig. 4(b)] we also find an increased slope of the FVL at 440 K with respect to 392 K. However, the effect is less prominent, because the width of the α peak is larger than the stress-induced shift. At temperatures of 480 K and above we observe a very strong decrease in the FVL slopes which cannot be explained by the peak shift alone. This indicates a reduced coupling efficiency to the dissipative (background) channels above T_g . In other words the increasingly active molecular motion below the tip provides lubrication to the tip motion.

In conclusion, we have performed temperature-dependent FFM experiments and clearly identified α and β transitions. We found a strong negative temperature shift of both relaxation peaks with increasing tip load. This stress-induced temperature shift is modeled in terms of Arrhenius kinetics. Our analysis indicates that there is a

strong link between the kinetics of frictional energy dissipation and the applied shear stress.

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*schirmeisen@uni-muenster.de

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