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High-Speed, Sub-15 nm Feature Size Thermochemical Nanolithography

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ABSTRACT

We report a nanolithography technique that allows simultaneous direct control of the local chemistry and topography of thin polymer films. Specifically, a heated atomic force microscope (AFM) tip can write sub-15 nm hydrophilic features onto a hydrophobic polymer at the rate of 1.4 mm per s. The thermally activated chemical reactions and topography changes depend on the chemical composition of the polymer, the raster speed, the temperature at the AFM tip/sample interface, and the normal load. This method is conceptually simple, direct, extremely rapid, achievable in a range of environments, and potentially adaptable to other materials systems.

In the past decade, there has been a tremendous increase in the number of techniques for patterning materials on the nanoscale (10−100 nm), driven by numerous potential applications, for example in sensing,[1] data storage,[2] optoelectronic,[3] display,[4] nanofluidic,[5] and biomimetic[6] devices. An ideal nanolithography technique would be able to: (i) write with nm resolution, (ii) write with speeds of multiple cm/s (while preserving nanometer-scale registry) for wafer-scale lithography, (iii) impart different chemical functionality and/or physical properties (with or without topographical changes) as desired, (iv) function in different laboratory environments (for example, under ambient pressure or in solution), (v) be capable of massive parallelization for both writing and metrology, and (vi) write on a variety of materials deposited on a variety of substrates. Specific applications will require one or more of the attributes described above, but the most versatile technique would encompass as many as possible. To our knowledge, no technique currently in practice can simultaneously attain all of these features.

Many nanoscale-patterning techniques can provide *topographical* patterning[2,7−12] through material deformation, removal, oxidation, cross-linking, or degradation, with resolution down to tens of nanometers in certain cases. *Chemical* patterning has been achieved through different strategies including direct assembly of chemically distinct regions by microcontact printing,[13] scanning probe-assisted deposition on the surface,[14] and removal or manipulation of functional groups at the surface via photolithography,[15] catalytic probe lithography,[16,17] or other scanning probe methods.[18,19] Scanning probe-based nanografting and replacement lithography techniques using self-assembled monolayers (SAMs) are able to produce chemical features with sizes of the order of 10 nm at speeds of 50−2000 nm/s.[20,21] Electrochemical lithography with a conductive AFM tip has been used to write conducting polymer lines down to 45 nm wide[22] at speeds of the order of μm/s and has been employed to deprotect amine functional groups on suitable SAMs with similar speed and resolution.[23] Dip-pen nanolithography (DPN) is extremely versatile[24] and can be used to pattern a range of desired chemistries with spatial control by depositing several different kinds of molecules on the same substrate. The intrinsic speed of DPN depends on molecular transport between the probe tip and the surface and is, therefore, limited by mass diffusion; this is discussed in more detail below. Another challenge facing DPN lies in in situ detection and massive parallelization, which requires independent control of the force applied to, and the height of, each cantilever on or above the surface;[24−26] recent work has demonstrated a dense DPN tip array.[27] Other nanoscale patterning strategies lie within the arena of self-assembly;[28,29] however, self-assembly processes cannot currently be tailored to afford any arbitrary structure.

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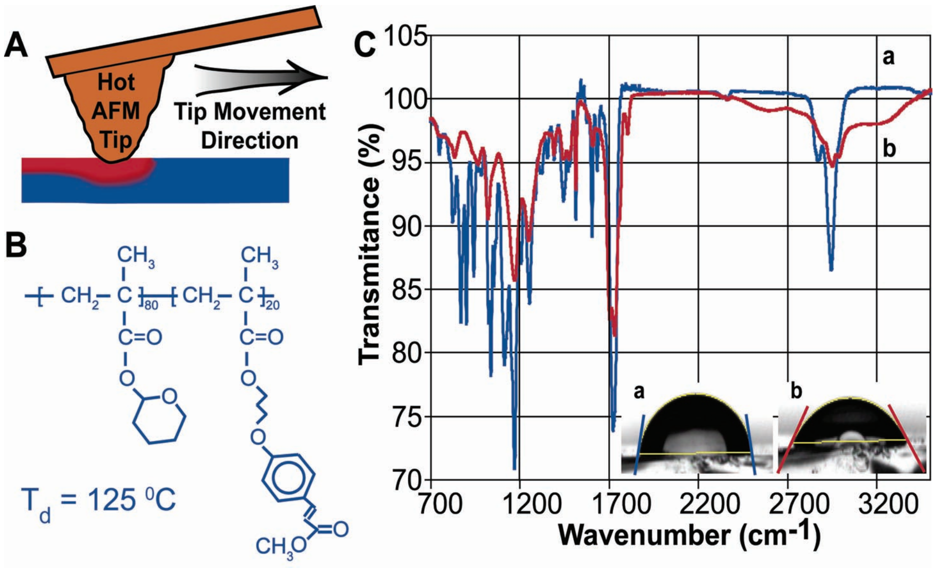

Figure 1. (A) Experimental setup showing a resistively heated silicon cantilever controlled by an AFM (Multimode Nanoscope IVa from VEECO) scanning across a polymer sample. This heated conical silicon tip initiates thermal reactions of the polymer film above certain temperatures. (B) Structure of copolymer p(THP-MA)$_{80}$ p(PMC-MA)$_{20}$. (C) Attenuated total-reflection FT−IR spectra of a bulk sample of cross-linked p(THP-MA)$_{80}$ p(PMC-MA)$_{20}$ film (a) before heating and (b) after heating to 150 ± 5 °C. These show the growth of an −OH stretching band above 3000 cm^{-1} and a new carbonyl peak at 1720 cm^{-1} after heating, consistent with thermal deprotection to give the carboxylic acid. Accordingly, static water contact angles show a change from (a) 79° (b) 60° upon heating. When the film is heated above 180 °C, new peaks start to develop in the range 1780 and 1820 cm^{-1}, characteristic of anhydrides (not shown).

Herein we report a conceptually simple, yet potentially very adaptable scanning-probe method that we call thermochemical nanolithography (TCNL). TCNL employs a resistively heated AFM cantilever (Figure 1A) to induce well-defined chemical reactions in order to change surface functionality of thin polymer films (or, potentially, SAMs). Such an approach is appealing as it is known that the thermal profile in the vicinity of a heated AFM tip can give rise to sharp thermal gradients[30−35] and that chemical reaction rates increase exponentially with temperature; therefore, one can, in principle, achieve a very high degree of spatial resolution. A wealth of thermally activated chemistries can feasibly be employed to change the material's subsequent reactivity, surface energy, solubility, conductivity, or other property of interest as desired. The distance of the tip from the surface and the temperature of the tip can be modulated independently, and the tip does not need to indent the surface. Therefore, it is possible that chemical changes could be written very quickly through rapid scanning of the substrate or the tip, as no mass is transferred from the tip to the surface (writing speed is limited only by the heat transfer rate). In addition, judicious choice of the physical properties of a material (e.g., polymer glass transition temperature, T_g) may afford a system wherein chemical changes can be performed either separately from, or accompanied by, topographical modification as required (for example, above T_g of a polymer, creation of substantial topographical changes (ripples) is exponentially amplified).[36] Furthermore, the use of a material that can undergo multiple chemical reactions at significantly different temperatures renders the possibility of a multistate system wherein different functionalities can be addressed at different temperatures.

Here, we show how TCNL on a polymer substrate can be used to write chemical features with 12 nm line width while controlling the topography of the surface. We demonstrate that TCNL can be performed at rates of millimeters per second. The technique is not limited to "SAM-friendly" surfaces, as the polymer films we use can be deposited on a wide variety of substrates, and TCNL avoids the need for additional chemicals to be present at the surface and/or strong external electrical fields. Furthermore, we show patterning under high humidity conditions, whereby a water film several nanometers thick is present on the surface, suggesting that TCNL may be extended to function in liquid environments. Finally, large-scale parallelization of individually addressable thermal probe tips has already been demonstrated,[2] and it has further been shown that these cantilevers can be used for both nanolithography and metrology.[33]

As a starting point, we examined the thermal deprotection of an ester group to give a carboxylic acid due to the large change in hydrophilicity accompanying such a transformation; this has the potential to be detected on the local scale by lateral force microscopy (see below). Because small molecules and SAMs can desorb at the relatively high temperatures required for thermal deprotection, we attached the ester groups to a polymer backbone. Preliminary studies using films of commercial poly(*tert*-butyl methacrylate) on glass showed that a substantial change in the local hydrophilicity of the film may be achieved by heating with the AFM tip, as imaged by lateral force microscopy. However this is accompanied by a large topographical deformation (features with depth >100 nm) because the deprotection temperature, T_d, of the acid is significantly above the polymer T_g. Inspection of the lithographic resist literature suggested

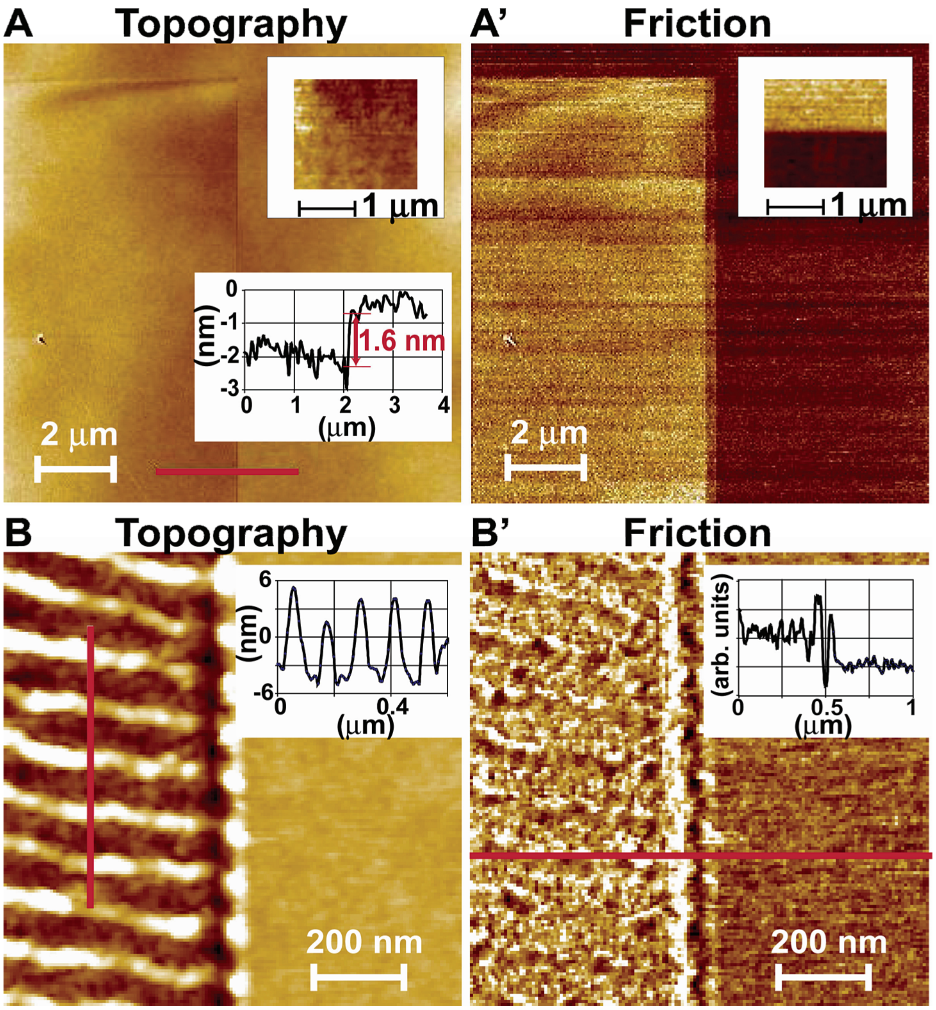

Figure 2. (A) 10 μm × 10 μm AFM topography image and (A′) corresponding friction image of a cross-linked p(THP-MA)$_{80}$ p(PMC-MA)$_{20}$ film. The zone showing much higher friction (about 30% more on the left side in A′ compared to the right side) was modified by local heating to 160 ± 30 °C at a scanning speed of 85 μm/s. Insets show analogous comparison of topography and friction changes between modified (upper part) and unmodified (lower part) regions of a p(THP-MA)$_{80}$ p(PMC-MA)$_{20}$ film patterned at 1420 μm/s. (B) 1 μm × 1 μm AFM topography image and (B′) corresponding friction image of a cross-linked p(THP-MA)$_{80}$ p(PMC-MA)$_{20}$ film recorded with a sharp-contact AFM cantilever. Ripples shown in (B) (10 ± 3 nm) result from thermal modification by local heating at 180 ± 30 °C while scanning at 85 μm/s. The friction measured in the modified zone is noticeably larger than in the unmodified zone (inset); the changes in friction observable along the edges of ripples are presumably due to artifacts arising from the greater local contact area between the AFM tip and the sample while scanning across a sharp edge.

that a tetrahydropyranyl (THP) analogue would undergo deprotection at a lower temperature.[37] Characterization of a p(THP-MA) homopolymer in the bulk by IR and thermogravimetric analysis (TGA, see Supporting Information) suggested the removal of THP around 120 °C and formation of anhydrides above 180 °C, with the expected concomitant changes in polymer hydrophilicity as determined by water contact angle measurement. Use of an AFM tip to locally heat a thin film of p(THP-MA) on glass to 140 ± 20 °C gave a patterned structure with the desired local changes in hydrophilicity detected by lateral force imaging. However, these changes were accompanied by significant rippling of the film, as the polymer T_g is comparable to its T_d. While such simultaneous chemical and topographical changes may be advantageous for certain applications, we were interested in probing the limits of resolution possible solely by introduction of a chemical change in these systems. Therefore, we synthesized a photocross-linkable copolymer analogue, poly(tetrahydro-2*H*-pyran-2-yl methacrylate)$_{80}$ poly(3-{4-[(*E*)-3-methoxy-3-oxoprop-1-enyl]phenoxy}propyl 2-methacrylate)$_{20}$ (p(THP-MA)$_{80}$ p(PMC-MA)$_{20}$, Figure 1B), which, after spin-coating and photocross-linking of the cinnamate groups,[38] exhibited no glass transition at or below the T_d. Bulk thermal properties of p(THP-MA)$_{80}$ p(PMC-MA)$_{20}$ were essentially identical to those of p(THP-MA) (Figure 1C).

We modified a pristine p(THP-MA)$_{80}$ p(PMC-MA)$_{20}$ film on glass by heating it locally with a silicon thermal cantilever to 160 ± 30 °C, at which we expect a transformation from hydrophobic to hydrophilic to occur. In ambient conditions, the Si tip is covered by a thin layer of native silicon dioxide, which makes the tip somewhat hydrophilic. The magnitude of the friction force between the tip and the sample surface is a sensitive relative measurement of the sample hydrophilicity, e.g., larger the friction force, the more hydrophilic the sample.[39−41] Figure 2A′ shows a 12 μm × 12 μm frictional force image of a copolymer sample where we have

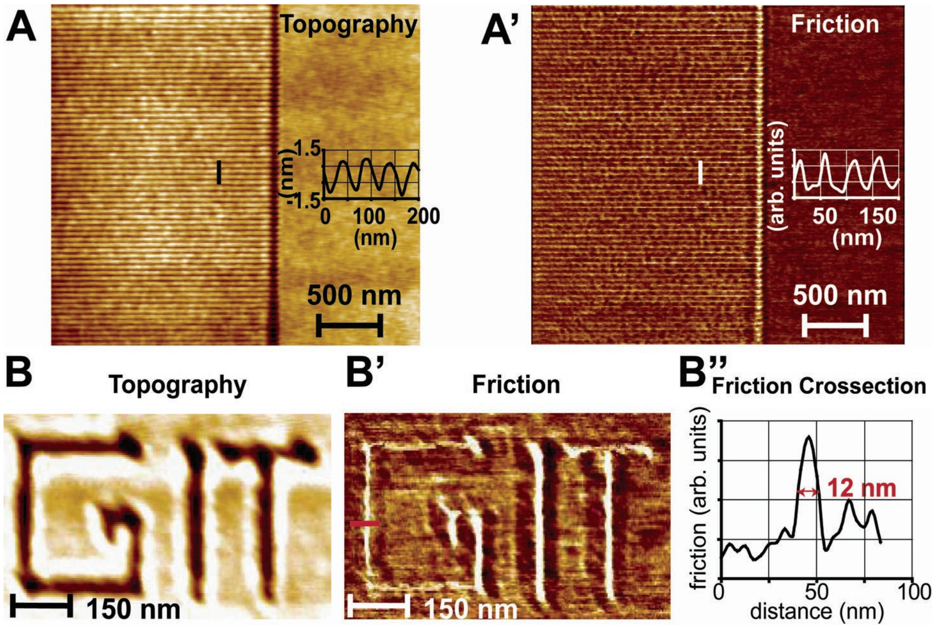

Figure 3. (A) 3 μm × 3 μm AFM topography image and (A′) corresponding friction image of a cross-linked p(THP-MA)$_{80}$ p(PMC-MA)$_{20}$ film showing a high-density line pattern written chemically on the left side. This pattern was produced by modifying alternate lines at a speed of 9.6 μm/s. (B) AFM topography and corresponding friction image (B′) of a modified copolymer film written at a speed of 0.5 μm/s, with the indentation depth kept within 3 nm. The resulting friction cross-section (B″) shows about 12 nm half-width within the modified zone (in the letter G); topographical changes are minimal, similar to those shown in Figure 2A. Interestingly, the modified zone appears wider in the topography image than in the friction image; this is under further investigation but potentially has its origin in the convolution of the true topography with the tip profile.

chemically modified the left-hand side by means of local heating. The frictional force is clearly higher in the modified region, supporting the occurrence of a chemical change in this area. The AFM topography image taken over the same 12 μm × 12 μm area (Figure 2A) shows no significant induced topographical differences, as desired. The slight difference in height (~1.6 nm) between the modified and unmodified areas is consistent with removal and vaporization of dihydropyran (bp = 84 °C) upon heating. The insets of parts A and A′ of Figure 2 show a similar TCNL experiment, this time performed at a scanning velocity of 1.4 mm/s (i.e., 16 times faster, but with similar results).

If topographical changes are desired, this can be achieved by varying the normal load, tip temperature, and scanning velocity used during the TCNL process. Parts B and B′ of Figure 2 show topography and frictional force images, respectively, of a 1 μm × 1 μm copolymer area modified on the left side by heating. Because of the higher tip temperature and loads (see figure caption), regular ripples appear in the topography. Figure 2B′ shows that the friction force in the modified area is higher than in the unmodified area, consistent with a chemical change as described above (Figure 2A′) and is essentially constant in this area. Thus both the local topography and chemistry of the polymer film can be modified by simultaneously activating a chemical reaction and exploiting the mechanism of ripple formation, as required. Ripples of different sizes (ranging from 2 to 8 nm in height) can be created in a controlled manner on this substrate; however, use of a p(THP-MA) homopolymer film enables the formation of even larger ripples, up to 300 nm in height (see Supporting Information). We note that scanning with varying speeds offers a means to create high-resolution hydrophilicity/hydrophobicity gradients, which could have important impact in the area of nanofluidic devices.[42]

Our TCNL technique can be employed to write a controlled chemical pattern on a polymer surface with high density and at high resolution. Parts A and A′ of Figure 3 show use of TCNL to write a chemical change on the copolymer (via deprotection of the carboxylic acid functionality) as a series of lines with a linear density of about 2 × 10^7 lines/m (corresponding to 260 Gbit/in.^{2}) in the absence of significant topographical changes (the differences visible in the topographical image arise from desorption of dihydropyran as before). Parts B and B′ of Figure 3 show topography and friction images of “GIT” written chemically on a copolymer sample. Figure 3B″ gives the cross-section of a friction line, demonstrating that chemically modified lines can be created reproducibly with width at half-maximum as small as 12 nm. The very small feature size achievable is attributed to the large temperature gradients in the polymer in the vicinity of the tip.[30]

The fundamental limit to writing speed in TCNL is the thermal diffusivity of the substrate material as opposed to mass diffusivity which limits deposition-based approaches. For example, the mass diffusivity of small molecules typically used in DPN is ~10^{-10} m^2/s,[43] while the thermal diffusivity of the organic substrates used in the present work is ~10^{-7} m^2/s.[44] Thus, the speed of our TCNL technique is currently limited by accessible AFM scanning velocity. However, modeling (see Supporting Information) suggests that the maximum patterning speed can be estimated as about 30 mm/s and is, therefore, much faster than any comparable

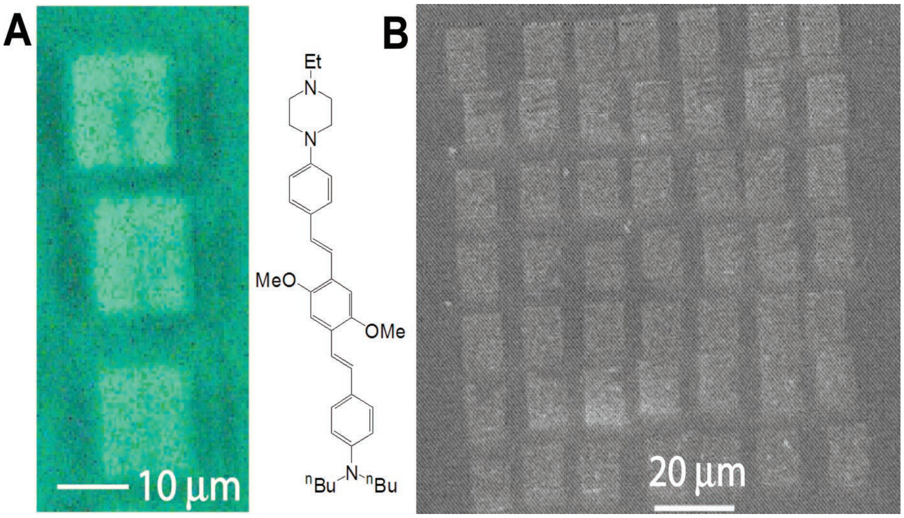

Figure 4. (A) Epifluorescence microscopy image of a cross-linked p(THP-MA)$_{80}$ p(PMC-MA)$_{20}$ film stained using a tertiary amine fluorescent dye in THF/EtOH after modification. The areas of highest fluorescence intensity correspond to the thermally modified regions, consistent with an acid−base reaction between thermally generated carboxylate groups and the dye. The excitation wavelength was 480 nm and the bright regions show emission at 520 nm. (B) SEM image of a cross-linked p(THP-MA)$_{80}$ p(PMC-MA)$_{20}$ film stained with Pb(acac)$_2$ in MeOH after thermal modification. The areas of brightest contrast show assimilation of Pb^{2+} in registry with the pattern drawn (a 7 × 7 grid of approximately 12 μm × 12 μm squares), arising from concomitant local deprotonation of thermally generated carboxylate groups by acetylacetonate ion.

chemical nanopatterning technology. In addition, the single-tip actuation time for our resistively heated AFM cantilevers approaches 1 μs,[32] while thermomechanical actuation of similar tips requires closer to 1 ms.[26]

To show that the modified areas can be further functionalized, we have performed a range of different experiments that provide further evidence that the thermally modified zones correspond to *chemically*-modified areas. First, a fluorescent dye in tetrahydrofuran/ethanol (THF/EtOH) was reacted with a modified copolymer film. Figure 4A shows an epifluorescence microscope image obtained from this sample after reaction; three squares, each 12 μm × 12 μm, are clearly distinguishable as the areas of highest fluorescence intensity, corresponding to the thermally modified regions. This is consistent with the occurrence of an acid−base reaction between thermally generated carboxylate groups and tertiary alkylamine groups of the dye, staining the locally modified regions of the polymer film. Second, reaction of lead(II) acetylacetonate (Pb(acac)$_2$) in methanol with a modified copolymer film (consisting of 47 squares, each 12 μm × 12 μm) resulted in incorporation of lead into the modified areas, consistent with deprotonation of the carboxylic acid groups by acetylacetonate ion and concomitant immobilization of Pb^{2+} ions. A scanning electron microscope (SEM) image of the resulting surface shows significant contrast, corresponding to increased brightness in regions where lead has been assimilated, in registry with the initial modified pattern. X-ray photoelectron spectroscopy of a similar patterned copolymer film confirms local enrichment of lead in the modified regions (see Supporting Information).

In conclusion, we have demonstrated a new and versatile chemical patterning technique, TCNL, which can write and read in situ chemical patterns at speeds faster than 1 mm/s, with sub-15 nm feature size and line density of 2×10^7 lines/m. TCNL works under high humidity conditions in ambient pressure and lends itself to massive parallelization through use of dense arrays of thermal tips. These features offer some advantages relative to other nanolithography techniques and, as such, TCNL could have the ability to complement some of these techniques (specifically if high resolution over large surface areas is required), for example in biological and nanoelectronics applications, and may also be a robust technique for the study of thermally-induced chemical reactions at the molecular scale.

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Supporting Information Available: Materials, synthesis, and characterization; thermal cantilever fabrication and calibration; modeling of maximum speed achievable by TCNL; control friction AFM experiments on hydrophobic and hydrophilic polymers; control friction AFM experiments with high loads; control over formation of ripples; details of AFM experiments shown in main text figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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