Voltage-assisted asperity formation in styrene butadiene at the order of 10

10^9 V m^{-1}, which is sufficiently large to initiate cross-linking in the rubber. Peaklike surface features, surrounded by a circular trough and a raised ring, are created by careful and controlled retraction of the biased tip. The features' aspect ratios can be controlled by modifying the tip retraction protocol, tip geometry, and bias voltage. Typical feature dimensions reported here vary from approximately (0.5–10)-nm high and up to several hundreds of nanometer in diameter. Although the temperature of the rubber is above the glass transition and the rubber is in a viscous state, the features are stable over a period of several days once created—which is believed to be due to cross-linking of the rubber during feature formation. Modeling of the electric field distribution in the vicinity of the tip is presented, which strongly supports the assertion that the resulting nonuniform electric field induces nanostructure formation and initiates cross-linking. A mechanism is proposed whereby source material is redistributed in the proximity of the tip/surface region to form the observed features.

I. INTRODUCTION

The ubiquity of polymers and polymer-based materials in everyday life arises from important commercial applications at the macroscale. For example, the tire industry utilizes synthetic rubber made from polymerization of different monomers—to their versatility in diverse applications at the nanos1 (hc/F41Tf2.05490TDTj/F21Tf6.9846006.984676.6386332.0645Tm001rg5Tj9.978009.97885.7496328.5723Tm0001k(nd)563(surface

-cyclohexyl benzothiazole sulfenamide (CBS). An antioxidant was added in order to protect the SBR from degradation. Stearic acid and oil are processing aids that facilitate better dispersion of the ingredients in the rubber and sulfur. DPG and CBS are curatives that afford a better degree of control over cross-linking.[12] Mixing was performed using a 65 g Brabender mixer at mixing speed of 60 rpm and the mixing temperature was maintained at 100 °C. Approximately 5 g of

$$\underline{\partial^2 \varphi}$$

$\varepsilon = 2.5$, SBR film thickness $l = 4$ or 100 nm, tip-surface distance $= 1$ nm, tip bias voltage $= 20$ V, and tip radius $= 20$ (normal) or 5 nm (sharp). The calculated electric field [Eq. (2)] and pressure gradient [Eq. (3)] applied to a polymer film in the proximity of the film surface are presented in Fig. 5 as a function of the radial coordinate. A comparison of thin (4 nm) and thick (100 nm) polymer films indicates larger magnitudes and a longer radial extent of the pressure gradient components (ponderomotive forces) in the case of a thin film. In particular, the $/_{\cdot}/$ component of the pressure gradient [Eq. (3)] is stronger and is acting over a larger area in thin films. These observations are not affected by variations in the AFM tip radius between 5 (sharp) and 20 nm (normal).

To compare the results of modeling with experiment, the sets of features were formed in SBR films at various field strengths using AFM tips of two different sharpnesses. The tips used have the following characteristics: Standard silicon tips, covered with gold, and tip radius $= 20$ nm; and sharp tungsten tips—manufacturer's product code DP14/

HI'RES-W with resonant frequency 160 KHz—force constant 5 N m^{-1}, and tip radius $= 5$ nm. A comparison of the features formed using the standard versus sharp tips, for different magnitudes of electric field (as determined by bias voltage and tip-surface separation), is presented in Fig. 6. As can be seen, a trend is observed for the magnitude and structure of the features with increasing bias voltage for a given tip-surface separation. One can see that the features form initially as single dots [Figs. 6(a)–6(c), corresponding to bias voltages of −8, −15, and −20 V, respectively] and their shape gradually changes from dots to protrusions directly under the AFM tip as the bias increases. One also observes that the features' dimensions grow in height and width with increasing bias. At some threshold tip bias, typically −24–−25 V for a standard tip and −13–−15 V for a sharp tip, a ring of elevated material forms around the central peak. Figure 6(d) shows features formed at a bias of −25 V for a normal tip, while Figs. 6(e)–6(h) corresponds to features formed at voltages of −15, −20, −25, and −30 V, respectively, for a sharp tip. Nanostructure dimension may exceed the tip size and the lateral extent of the electric field, which was observed earlier,[8,11] and is most likely related to viscoelastic response of polymeric media.[12,17]

Our calculations indicate that in the case of thin polymer
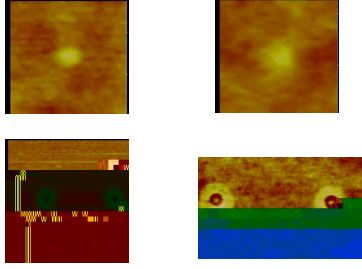
flows toward the tip position (=0), can be induced at a lower bias (−13−−15 V) for the sharp tip (R=5 nm) than for the standard tip (R=20 nm), which requires a bias voltage of −25 V.

It was established that no features are formed when the tip bias was less than −5 V for either the sharp or standard tip and for tip-sample separations between 1 and 100 nm. This suggests that nanostructures are not stable when a small bias is used, and they disappear as molecular relaxation minimizes the surface tension. As the voltage was increased in magnitude above −8 V, the observed stable features were formed on SBR surface, which suggests a field threshold for nanostructure stabilization due to a field induced chemical cross-linking. An order of magnitude estimate of the electric field sufficient to initiate SBR cross-linking can be obtained assuming that the polarization energy stored in a molecular volume has to be as high as the π-bond strength ~ 282 kJ/mol. Such an estimate results in the following threshold field:

$$E_{th} = \sqrt{\frac{2 \rho}{\varepsilon_0(\varepsilon - 1)}},\qquad (4)$$

where ρ and are the mass density and molecular weight, respectively. The threshold field evaluated using material parameters of SBR described in the experimental section is about 0.5 V/nm, which, according to our calculations (Fig. 5), is attained under typical experimental conditions. While polymer surface tension may play an important role in the initial stage of nanostructure formation, it does not result in any significant topographical changes once the cross-linking was induced, and the nanostructures remain very stable as presented in Fig. 3.

The formation of topological peculiarities, ring(s) around a single peak, could be mostly associated with the geometrically nonuniform mass transport due to the competition between electric-field distribution and the thickness of the SBR film. As indicated above, the radial component of the pressure gradient acting on the polymer film is stronger for thin films and could be one of the factors responsible for a trough ring nanostructure formation. To evaluate the mass transport of material under the AFM tip, the volume of displaced SBR was calculated using data extracted from the AFM images. The calculations were performed using WSxM software.[18] The features' characteristics can be defined as being comprised of a central peak circumscribed by a trough region, which is in turn surrounded by a ring of raised material as shown in Fig. 7(b). Figure 7(a) shows the corresponding dependence of the volume change in each feature component (i.e., the peak, trough, and ring) with bias voltage for features created using the sharp tip (5 nm). Every data point is cal-

Nature (London) **403**, 403 (2000).

[6] K. A. Leach, Z. Lin, and T. P. Russell, Macromolecules **38**, 4868 (2005).

[7] S.-Y. Jang, M. Marquez, and G. A. Sotzing, Synth. Met. **152**, 345 (2005).

[8] S. F. Lyuksyutov, R. A. Vaia, P. B. Paramonov, S. Juhl, L. Waterhouse, R. M. Ralich, G. Sigalov, and E. Sancaktar, Nat. Mater. **2**, 468 (2003).

[9] I. Dolog, R. R. Mallik, and S. F. Lyuksyutov, Appl. Phys. Lett. **90**, 213111 (2007).

[10] P. B. Paramonov, S. F. Lyuksyutov, O. V. Mayevska, M. A. Reagan, R. A. Vaia, S. Juhl, K. Umemura, H. Tobari, and M. Hara, Langmuir **22**, 6555 (2006).

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