Fabricating Two-Dimensional Molecular Gradients via Asymmetric Deformation of Uniformly-Coated Elastomer Sheets**

By *Jan Genzer*,* *Daniel A. Fischer*, and *Kirill Efimenko**

Tuning the surface characteristics of materials has become of paramount interest in many fields of science and technology. While most applications involve surfaces that are chemically homogeneous, in other instances, surfaces are needed that comprise two or more chemically heterogeneous regions. Applications of the latter family of structures include tools for chemical separations, substrates for selective adsorption, and specimens for lithography and other microfabrication technologies. Recently, there has been an increased interest in generating and utilizing so-called "gradient substrates", in which the surface energy varies gradually across the sample surface.[1–3] Numerous studies established that such structures offer a unique geometry for probing cell/substrate interactions,[1] phase behavior in thin liquid (including polymer) films,[4,5] and directed motion of liquids.[6–9] Recent reports also demonstrated that "gradient substrates" prove useful in molecular templating and multi-variant studies.[10–12]

Over the past four decades, multiple strategies for making molecular gradients have been conceived and developed.[1–3] These technologies typically involve variants of liquid or vapor deposition of the gradient-forming species, or physical modification to the existing surfaces via plasma, corona, or ultraviolet/ozone radiation—on the millimeter scale—and scanning probe microscope tips—on the nanometer scale. One unifying feature of all gradient techniques practiced to date is that the molecular gradient is formed on a "stationary" substrate.[1–3] One exception to these methods was the work of Efimenko and Genzer,[13] who demonstrated that one-dimensional (1D) planar molecular gradients with tunable wettabilities can be fabricated by combining the asymmetric vapor deposition method of organosilane precursors[6] and the technology leading to "mechanically assembled monolayers" (MAMs).[14] In the MAMs technique, a flexible substrate, made of cross-linked poly(dimethylsiloxane) (PDMS), is uniformly mechanically extended and exposed to ultraviolet–ozone (UVO) treatment. The UVO process produces hydrophilic moieties on the PDMS surface,[15] which serve as attachment points for short organosilanes. After the organosilane grafting, the strain is removed from the substrate, which returns to its original position causing the grafted molecules to form a densely packed monolayer. The density of the molecules inside the MAMs is tunable—it increases with increasing initial substrate extension, Δx.[14] Because the wettability of the organosilane modified surfaces depends crucially on the interplay between the chemistry and the grafting density of the molecules grafted on the surfaces, the surface characteristics of the MAMs made of a given organosilane can be tuned by simply adjusting Δx.

In this paper, we offer a novel strategy for generating substrates with position-dependent physico–chemical properties. Specifically, we demonstrate that two-dimensional (2D) in-plane variation of gradient-forming molecules can be produced by utilizing MAMs on substrates in combination with in-plane asymmetric stretching of elastomeric substrates uniformly coated with organosilane precursors. We use combinatorial near-edge absorption fine structure (NEXAFS) spectroscopy to map out the resulting in-plane concentration of the MAMs. We also correlate our experimental results with finite element analysis calculations.

PDMS sheets cut into "bone-like" shapes were prepared and uniaxially stretched using a custom-build apparatus (for details see the Experimental section). Figure 1 depicts two different sample stretching scenarios employed in this work. We refer to these two sample geometries as samples S1 (top) and S2 (bottom). Figure 1a displays the photographs of the PDMS sample in the stretching apparatus before stretching. For clarity, the sample contour is highlighted with a thick line. Figure 1b illustrates the geometry of the S1 and S2 samples after imposing a uniaxial extension of $\approx 40\,\%$. The sample deformation upon stretching depends on the initial sample orientation in the stretching apparatus. The contours of the unstretched (solid lines) and stretched (dashed lines) samples for both geometries are superimposed in Figure 1c. A close inspection of the contour profiles in Figure 1c reveals that the largest extension occurs on the parts of the substrate that are continuous between the two opposite sample clamps. The molecular gradients were created by forming MAMs of 1*H*,1*H*,2*H*,2*H*-perfluorodecyltrichloro-silane (F8H2). Because of the spatial distribution of strains on the pre-stretched specimen, the molecular density of the grafted F8H2 in relaxed samples was expected to vary as a function of the position on the substrate. Specifically, the degree of packing of the grafted molecules was estimated to be high (low) on the parts of the substrate exposed to a large (small) strain.

We used combinatorial NEXAFS spectroscopy to determine the in-plane concentration of the F8H2 moieties grafted on the PDMS substrates.[16] The NEXAFS experiments were carried out on the NIST/Dow Soft X-ray Materials Characterization Facility at the National Synchrotron Light Source at Brookhaven National Laboratory.[17] We first measured a NEXAFS spectrum from a sample covered with a dense homogeneous monolayer of F8H2 on PDMS-UVO. In Figure 2, we plot the NEXAFS partial electron yield signal collected at the fluorine K-edge. The spectrum reveals the exis-

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ADVANCED MATERIALS

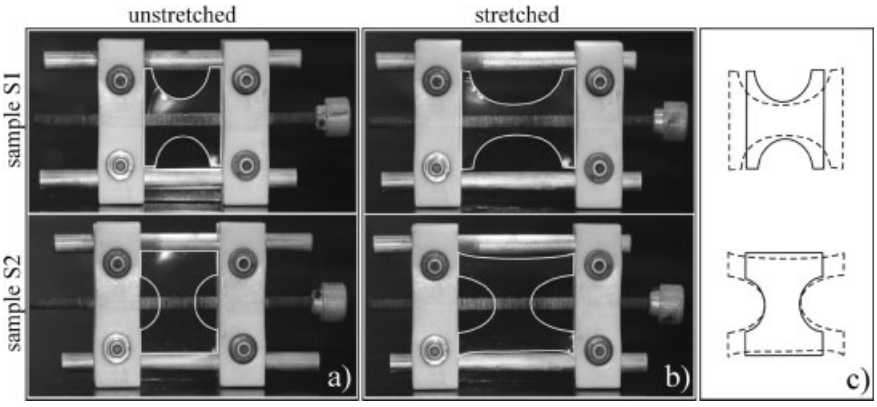

Fig. 1. Photographs of the PDMS sheets clamped in the stretching apparatus before stretching (a) and after imposing a uniaxial strain of 40 % (b). The contours of the unstretched (solid lines) and stretched (dashed lines) samples are reproduced in (c) of the figure. Two sample geometries were used: sample S1 (top row) and S2 (bottom row).

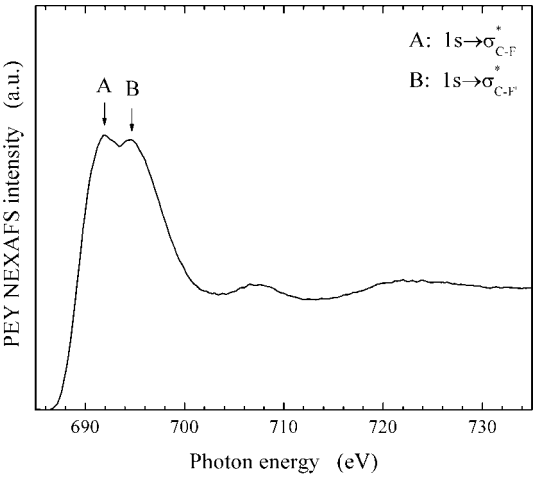

Fig. 2. Partial electron yield NEXAFS intensity collected at the fluorine K-edge of a sample comprising a F8H2 self-assembled monolayer grafted on top of the PDMS network modified with ultraviolet/ozone radiation. The arrows in the figure denote the positions of the 1s → σ* C–F and C–F′ excitations.

tence of two strong intensity signals at ≈ 692.0 and ≈ 694.5 eV, corresponding to the 1s → σ* C–F (peak A) and C–F′ (peak B) excitations, respectively, superimposed on top of a broad fluorine excitation edge. The combinatorial NEXAFS experiments were performed by scanning the specimens in the vertical and horizontal directions with 1 mm increments. After each step, a set of intensities were collected at E_{pre} = 685.0 eV, E_{CF} = 692.0 eV, and E_{post} = 735.0 eV, where E_{pre}, E_{CF}, and E_{post} are the energies corresponding to the pre-edge, C–F, and post-edge signals, respectively. The C–F data were normalized using a standard procedure: $I_{CF,norm} = (E_{CF} - E_{pre})/(E_{post} - E_{pre})$.[18]

In Figure 3, we plot $I_{CF,norm}$ as a function of the position on samples S1 and S2. The darker areas in the plot denote regions on the substrates with higher concentration of the C–F bond. The data in Figure 3 reveal that the concentration of fluorine on the samples varies spatially.[19] Specifically, in sample S1, the concentration of fluorine is highest in the middle of the sample and decays towards the edges of the specimen. In sample S2, the edges of the sample contain a larger number of the F8H2 molecules, relative to the center. The ratio between the highest and lowest NEXAFS intensity signal in samples S1 and S2 was 1.35 and 1.26, respectively. Recall, that the regions of the substrates with the highest fluorine signal correspond to the locus of the maximum strain imposed after stretching. Importantly, there is a gradual in-plane variation of the F8H2 concentration ranging between the high and low F8H2 density regions on the substrate.

In order to correlate the results of the combinatorial NEXAFS mapping experiments, the distribution of stresses in the S1 and S2 samples were calculated using a commercial software package Robot Millennium (RoboBAT Group/ISS Inc).[20] The input parameters comprised the sample dimensions, and the estimates of the PDMS modulus (E = 0.1 MPa for the M_n = 28 kDa used in this study), and Poisson's ratio (ν = 0.5). The results of the calculated stress distributions in the samples are shown as contour plots in Figure 4. For simplicity, we only show the stress components along the stretching direction. The stress increase is characterized by darker colors in Figure 4. Because of the applicability of the linear elasticity model (recall that PDMS is a model elastic material), the results in Figure 4 provide also a direct measure of the strain distributions in the sample along the stretching direction. By comparing visually the results in Figure 4 with those in Figure 1c and Figure 3, we conclude that the calculated results agree qualitatively well with the estimated strain distributions based on the sample contours and the concentration of the F8H2 molecules obtained measured by the combinatorial NEXAFS, respectively.

In summary, we have developed a new method for generating two-dimensional planar molecular concentration gradi-

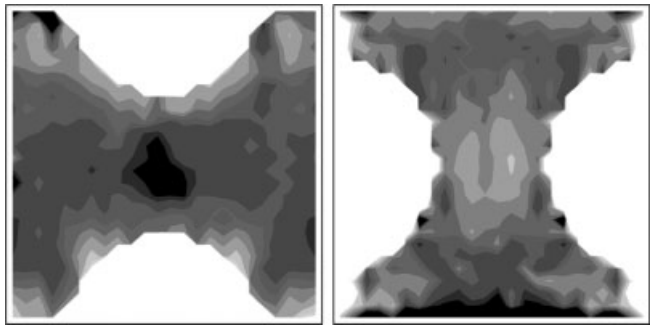

Fig. 3. Normalized partial electron yield NEXAFS C–F peak intensity map recorded from samples S1 (left) and S2 (right) after grafting F8H2 and strain release. The darker regions in the plot denote regions of the substrate with higher intensity of the fluorine signal. The ratio between the highest and lowest NEXAFS C–F peak intensity signal for the S1 and S2 sample was 1.35:1.00 and 1.26:1.00, respectively.

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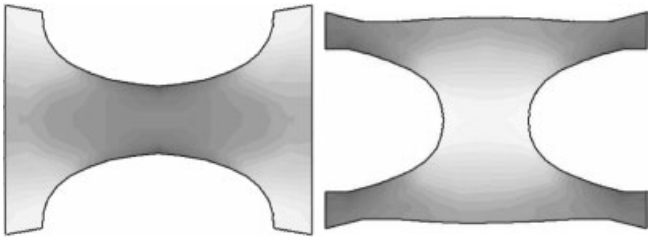

Fig. 4. Calculated strain maps in the stretched PDMS sheets for geometries corresponding to samples S1 (left) and S2 (right). The darker regions in the plots denote regions with larger strains.

ents. In contrast to most previous techniques that generated gradients of molecular precursors ex situ and transferred them onto the substrate, we employed an in-situ methodology, which is based on mechanical deformation of the substrate covered with a uniform array of grafted organosilane molecules. We envisage that in addition to the "conventional" applications of chemical molecular gradient listed in the introduction, our technique can be employed in visualization of strain distribution in elastic materials.

Experimental

The substrates comprising sheets of PDMS networks are prepared by casting mixtures of monodisperse vinyl-capped PDMS homopolymers (M_n = 28.0 kDa) with tetrakisdimethylsiloxysilane [21] and a minute amount of a Pt catalyst into thin films (thickness ≈ 0.5 mm) and curing them at 55 °C for about 1 h. After the network formation, the PDMS sheets are cut into "bone-like" shapes (base dimensions: 25 mm × 25 mm) and uniaxially stretched.

The stretching apparatus comprises a pair of parallel Teflon sample holder clamps. The PDMS film is positioned perpendicular to the longitudinal axes of the clamps. The motion of the sample holders along two parallel steel rods is controlled through a screw; one-half of the length of the screw is right-threaded and the other half is left-threaded. By rotating the screw in one direction, one is able to separate the sample clamps and thus stretch the film. Conversely, by rotating the threaded member in the opposite direction, the clamps are brought inward, thus releasing the strain from the PDMS specimen.

The two asymmetrically stretched PDMS substrates were treated with UVO for 20 min, which generated the surface-bound hydroxyl groups. The substrates were subjected to a spatially uniform vapor of 1*H*,1*H*,2*H*,2*H*-perfluorodecyltrichlorosilane (F8H2) for 15 min at ambient conditions. During this procedure, the F8H2 molecules were grafted to the PDMS-UVO substrates. After grafting the substrates were washed thoroughly with methanol and deionized water in order to remove any physisorbed F8H2 molecules. The strain was slowly removed from the substrates (≈ 0.5 mm min^{-1}), which returned to their original shapes causing the grafted F8H2 molecules to pack.

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[20] We thank Marc A. Leonard (E/T Engineering Technologies, Inc.) for performing the calculation and David N. Erel (NCSU) for his assistance with drawing the contour plots.
[21] For this PDMS molecular weight, the PDMS/tetrakisdimethylsiloxysilane ratio was 10:17. Our independent experiments [K. Efimenko, J. Genzer, unpublished results] indicated that at this ratio, the network possessed the highest elasticity.

Reduced Operating Voltages in Polymer Light-Emitting Diodes Doped with Rare-Earth Complexes**

By *Matthew R. Robinson*, *Jacek C. Ostrowski*, *Guillermo C. Bazan*,* and *Michael D. McGehee**

Several polymer light-emitting diode (PLED) designs make use of blends of a conducting polymer with a rare-earth (lanthanide) complex.[1–6] This strategy provides a means of adding desirable optical properties to the device without sacrificing beneficial properties inherent in the neat polymer. Specifically, rare-earth complexes exhibit a characteristic narrow emission spectrum that is largely independent of the local environment. Europium(III) β-diketonate complexes have been used to obtain narrow red emission potentially useful for organic light-emitting diodes (OLEDs) and full-color displays.[1] Complexes with erbium and neodymium are also promising for near-infrared emission—useful for telecommunications applications.[2–4]

When europium complexes are used as guests, the narrow red emission is obtained with increased electroluminescence (EL) efficiency at the expense of increased operating voltage.[1,7] This increase in voltage is commonly attributed to the fact that guest molecules act as traps for carriers (electrons and/or holes) resulting in recombination directly on the guest.[1,8–11] In other words, the carrier trapping may cause an

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