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Stretching the Stamp: A Flexible Approach to the Fabrication of Miniaturized DNA Arrays**

Matthias Geissler,* Emmanuel Roy, Jean-Sébastien Deneault, Mélanie Arbour, Gerardo A. Diaz-Quijada, André Nantel, and Teodor Veres

DNA arrays have emerged as key tools in genomic research to measure relative expression levels of genes among different samples in parallel and with minimal sample consumption.^[1] In addition, they are also becoming popular in other areas such as biomedical diagnostics, cellular analysis, and drug development. DNA arrays typically comprise a set of synthesized gene sequences immobilized on a solid support, which are subjected to hybridization with specific target genes. In most cases, a fluorescence marker such as Cy3 ($\lambda_{\text{ex}} = 550 \text{ nm}$, $\lambda_{\text{em}} = 570 \text{ nm}$) or Cy5 ($\lambda_{\text{ex}} = 650 \text{ nm}$, $\lambda_{\text{em}} = 670 \text{ nm}$) is linked to the target DNA, which allows for the detection of hybridization events through fluorescence readout of the array. The number of DNA probes per surface area is an important criterion for their efficacy: the higher their density, the more information can be extracted from a single experiment. DNA microarrays are commonly fabricated by spotting minute amounts of DNA solution onto a proper substrate by using either metal pins^[1a] or microactuated dispensing systems.^[1a,2] To this end, the resolution of most commercial spotting techniques is limited to arrays containing ≈ 100 to 5000 spots per cm^2 depending on the specifications of the tools, the conditions of spotting, and the characteristics of the substrate. Arrays of higher density (e.g., spots 100 nm in diameter or below) have been realized by using cantilever probes,^[3] yet reliability and throughput of this technology need to be improved before it may become suitable for production purposes. An alternative fabrication scheme is in situ synthesis, which employs light-sensitive chemistry in conjunction with photolithographic techniques to construct a

desired oligonucleotide at selected sites on a substrate.^[1a,4] This technique can yield arrays of high density ($>10^5$ spots per cm^2) but the process is costly and time consuming, and the yield of each synthesis step can be prone to variation.

Herein, we describe a fabricating scheme based on soft lithography^[5] in conjunction with conventional microspotting to produce miniaturized DNA arrays in an experimentally simple and cost-efficient way (Figure 1). This process uses a planar elastomeric stamp, which is stretched in a uniform biaxial manner (e.g., the change in length (ΔL) is equal in both x and y directions). A “standard-size” DNA microarray is then

Figure 1. Schematic illustration of a stretch-based miniaturization protocol for DNA microarrays.

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generated at the surface of the stamp at strain by using mechanical microspotting with a metal pin. Once completed, the strain is released, allowing the stamp to recover its original size (e.g., L_0). During relaxation, the diameter (d) of each spot and the periodicity (p) should both be reduced at the same time. The miniaturized array is then transferred onto a solid support (e.g., a modified glass slide) via conformal contact, as commonly done in microcontact printing (μ CP).^[6–8] Although unique as an entity, the underlying concept – that is, size reduction through elastomeric deformation – is not novel, and has been demonstrated in a number of ways. For example, Whitesides and co-workers have created complex polymer microstructures by replica molding against an elastomeric mold under bending, stretching, and compression.^[9] Xia and Whitesides have shown how mechanical deformation of a poly(dimethylsiloxane) (PDMS) stamp can be used to tailor both geometry and size of a μ CP pattern formed from alkanethiols on gold.^[10] Genzer and Efimenko have demonstrated how elastomeric deformation can influence the properties of a silane monolayer grafted onto PDMS.^[11] Stretching has also been used to alter the shape of nanostructures embedded in a polymer matrix,^[12] or to tune the spacing between colloidal spheres in a 2D array.^[13] Rogers and co-workers have used stretching and compression to induce periodic wavelike geometries into submicrometer single-crystal silicon elements on a flexible substrate.^[14] More recently, Liu and co-workers have proposed a concept called stepwise contraction and adsorption nanolithography (SCAN)^[15] – a miniaturization protocol that uses PDMS in a cascade of stretch and transfer cycles to achieve a reduction in feature size. The work presented in this study takes advantage of elastomers that offer mechanical flexibility superior to that of standard PDMS-based materials, making it possible to obtain a high degree of miniaturization in a single step.

We fabricated stamps from three commercial grades of styrenic block copolymers: Versaflex CL30, Versaflex CL2000X, and Synprene RT-3820M (Table 1). These materials derive their elastomeric character from the presence of hard polystyrene domains in a soft matrix of poly(ethylene/butylene) or polybutadiene,^[16] and can withstand relatively large elongations without substantial permanent deformation. Moreover, these elastomers can be processed thermally through molding or embossing techniques in order to fabricate stamps (see Experimental Section for details). As indicated by their wetting properties, pristine surfaces of these materials are generally low in energy and lead to a rather pronounced hysteresis between advancing (θ_{adv}) and receding (θ_{rec})

Figure 2. Photographs showing a) the central area of the set-up at pre-elongation level, b) a high-precision screw that was used to induce elongation, and c) the pin spotter during the process of printing a DNA microarray on a stretched stamp.

contact angles. It is possible, however, to render the surface of RT-3820M hydrophilic through oxygen plasma treatment. Stretching of stamps was accomplished by using a home-built tool (Figure 2a) that consisted of four uniaxial translocation stages mounted on a ground plate in a face-to-face configuration. Each stage was equipped with a set of aluminum clamps bearing a complementary V-shape lock-in profile to hold the stamp in place during elongation. A polymer spacer was incorporated to limit mechanical damage of the stamp at the touching points. The segment of the stamp to be elongated was confined by the distance between two opposite clamping units. Re-adjustment of the pre-elongation level was usually necessary in order to compensate for stress-induced bending of the stamp as a result of the clamping process. Typical values of L_0 were 12.6 to 13.0 mm in either direction. Elongation was done in a manual fashion through the use of high-precision screws located at the periphery of each stage (Figure 2b). The travel distance of each screw was 25.4 mm, allowing for a maximum elongation of $\Delta L \approx 400\%$. Once adjusted, the stages retained their precise position for the duration of spotting. Arrays were generated in the central area of the stamp using an

Table 1. Selected properties of elastomers used in this study.

Brand name	Elongation at break [%] ^[a]	Tensile stress at 300% elongation [kPa] ^[a]	Wettability	
			θ_{adv} [°]	θ_{rec} [°]
Versaflex CL30	780 ^[b]	1448 ^[b]	107 ± 3	66 ± 5
Versaflex CL2000X	1100 ^[b]	200 ^[b]	104 ± 3	62 ± 8
Synprene RT-3820M	760 ^[c]	600 ^[c]	59 ± 4 ^[d]	<10 ^[d]

[a] According to test method ASTM D412 as provided by the supplier. [b] Data were accessed online at <http://www.glsCorp.com/home.html>.

[c] Data were accessed online at <http://www.polyone.com/index.asp>. [d] Measured after oxygen plasma treatment for 2 min at a power of 5 W sccm^{-1} , and a pressure of 50 mTorr.

automated microarray spotter equipped with a single pin (Figure 2c).

Figure 3a shows an array that was obtained by spotting a Cy3-labeled ssDNA onto an amino silane-modified glass slide (GAPS II) serving as a reference. Spots were $\approx 140\ \mu\text{m}$ in diameter, and their high uniformity in fluorescence intensity was indicative of an equal distribution of DNA molecules across the spotted regions. We set the value of p to $160\ \mu\text{m}$, which allowed for a close arrangement of spots while maintaining sufficient separation between them. Printing of DNA onto a hydrophobic stamp with no strain applied (Figure 3b) resulted in spots with high-intensity regions of 40 to $70\ \mu\text{m}$ in diameter depending on the spotting conditions (e.g., the speed at which the pin approached the stamp and the time of contact between the two). Usually, each spot was surrounded by a faint corona (visible only at higher detector gains). We attribute this finding to de-wetting of the polar ink solution on the surface of the hydrophobic stamp. The variation in p was relatively low (e.g., 10% or less), indicating that liquid largely remained confined to the spotted regions. Spotting onto elongated stamps was done as described above and allowed for the production of miniaturized arrays of high quality with different oligonucleotides on a variety of substrates. The example shown in Figure 3c derived from

Figure 3. Fluorescence micrographs of DNA arrays. a) A Cy3-labeled 15mer (5'-Cy3-CGG GCA GCA TCA AGC-3') spotted directly onto a GAPS II slide. b) A Cy5-labeled 15mer (5'-Cy5-GCT TGA TGC TGC CCG-3') spotted onto a stamp made of CL30 with no strain applied, followed by printing onto a GAPS II slide. c) A miniaturized array comprising 12×18 spots of an amino-modified 15mer (5'-Cy3-CGG GCA GCA TCA AGC-(CH₂)₆-NH₂-3') on an epoxy-functionalized glass substrate. During spotting, a strain of 280% was applied to a stamp made of CL30. The diameter of resultant spots varies between 25 and $10\ \mu\text{m}$ as it decreased progressively with the number of prints performed by the pin (here, from the lower right to the upper left corner). The inset shows the de-wetting morphology that is typical for spots produced on a hydrophobic elastomer. Contact between stamp and substrate lasted for 1 min.

spotting an amino-modified oligonucleotide onto a hydrophobic stamp at 280% strain (in both x and y directions) followed by transfer of the miniaturized array onto an epoxy-modified glass substrate.^[17] Here, the average spot diameter was about $18\ \mu\text{m}$ due to stretch-induced reduction, yet variation in d across the array was pronounced (e.g., $>40\%$) due to depletion of the pin during the spotting process. The signal-to-noise ratio was generally excellent despite a notable increase in fluorescence background for those regions that have been in contact with the stamp (data not shown). The value of p (e.g., $\approx 60\ \mu\text{m}$) was uniform over the entire array, even though a slight distortion was introduced during stretching and/or printing of the stamp. We hybridized printed DNA using a complementary strand that was labeled with Cy5, yielding intense and uniform fluorescence emission from the respective spots in the array (data not shown). Although this finding confirms the integrity of the miniaturized array, in-depth investigation of the transfer yield and binding efficiency is yet to be achieved.

To assess the performance of our approach, we inspected the effect of strain on p and d for two different materials, CL2000X and hydrophilized RT-3820M (Figure 4). As can be

Figure 4. Plots of a) spot diameter and b) periodicity along with extrapolated array density as a function of elongation length. The data was established by printing arrays comprising 5×5 spots of fluorescently labeled 15mers ($20\ \mu\text{m}$ in DMSO/water) onto stamps fabricated from Versaflex CL2000X (squares) and plasma-treated Synprene RT-3820M (circles), respectively. Stamps were placed by hand onto GAPS II slides providing contact for 1 min.

expected from their respective wetting properties (Table 1), the values for the initial spot size differed notably: while d_0 was $\approx 55 \mu\text{m}$ for CL2000X, spots typically exceeded $160 \mu\text{m}$ (e.g., $d_0 > p_0$) for hydrophilized RT-3820M, and fused together in many cases. Interestingly, stretching diminished the effect of hydrophilicity, and for $\Delta L = 310\%$, we obtained $d \approx 15 \mu\text{m}$, which was comparable to those arrays produced with its hydrophobic counterpart. In this case, size reduction was particularly pronounced, yielding $\Delta d > 90\%$ (inset of Figure 4a). The trends in p (Figure 4b) are directly related to the elastic properties of the materials: low values of elongation (e.g., $\Delta L < 150\%$) yielded a largely linear relationship, whereas higher elongations increasingly resulted in nonlinear responses of both elastomers. These findings are in good agreement with the general stress–strain behavior of rubber–elastic materials, for which the ratio of stress and strain (that is, the modulus) remains constant only for very low strains.^[18] However, we did not find notable variations in p within any of the printed arrays, suggesting that the central area of the stamp (e.g., $6 \times 6 \text{ mm}^2$ as defined by the width of each clamping unit) was stretched in a relatively uniform manner, irrespective of the applied strain. On the other hand, we observed largely non-uniform stress–strain behavior towards the periphery of the stamp, which could be visualized, for example, through distortion exerted upon arrays that were spotted outside the center of the stamp (data not shown). We generally obtained lower values of p when the stamp was made from CL2000X, which may be explained by a slight difference in the elastic properties of the two materials, as indicated by their respective values of tensile stress (Table 1). Extension of CL2000X by $\approx 360\%$ resulted in $p \approx 50 \mu\text{m}$, which corresponds to a 69% reduction of the initial setting. Array densities were directly calculated from p^2 and included as extrapolated values in Figure 4b. For example, by using a $\approx 360\%$ elongation with CL2000X, we achieved a 10-fold increase in array density, from $\approx 3.76 \times 10^3$ to $\approx 3.66 \times 10^4$ spots per cm^2 . Higher densities may be achieved by increasing ΔL , and/or reducing p_0 . A series of experiments using settings of 140 to $80 \mu\text{m}$ revealed, however, that the latter possibility had its limitations: a reduction of p_0 to below $120 \mu\text{m}$ typically resulted in a declining number of spots being present in the printed array. We attribute this finding to indentation of the flexible polymer surface upon contact with the metal pin. When the distance between neighboring spots became shorter, printed liquid was dragged away from its original place mainly by gravitational force as the pin moved across the surface – an effect that was promoted in part by the hydrophobic nature of the elastomer. While optimization of the spotting parameters may be helpful in overcoming this problem to some extent, a noncontact technique such as high-resolution ink-jet printing should generally be better suited for this purpose. It was possible to tune the shape of resultant spots to some extent by departing from the uniform biaxial mode of stretching that was described above. For example, when we preferentially elongated the stamp in one dimension, we were able to achieve elliptical and even quasi-linear DNA features in a regular arrangement (data not shown). Although these findings may contribute to the formation of DNA arrays in a potentially useful manner, stretch-induced alteration of shape was beyond the scope of the present study, and is awaiting further investigation.

In summary, we have described a simple and straightforward miniaturization scheme for producing DNA microarrays based on elastomeric deformation and conventional pin spotting. The degree of reduction was dependent mainly on the elongation length and the particular surface chemistry of the elastomer. For example, when a stamp made of pristine Versaflex CL2000X was elongated by 360%, the initial values of p and d were reduced by 70 and 80%, respectively, increasing the density of resultant array by one order of magnitude. The method emphasizes the formation of arrays with dimensions in the range of several tens of micrometers for both spot size and periodicity, which makes them potentially useful for microarray-based point-of-care diagnostics using lab-on-a-chip devices.^[19] The non-uniform nature of the elongation process may, however, be an obstacle to achieving ever smaller feature sizes using this approach, yet the use of stamp materials with even higher elasticity, improved tool designs, and sharper pins^[3] should all enable further reduction of the critical dimensions that may extend well into the submicrometer regime. Also, the adaptation of the concept underlying SCAN^[15] – that is, repeating stretch and transfer steps multiple times – should be helpful for this purpose, provided that the yield of transferred material remains sufficiently high for each printing step. The relatively low mobility of oligonucleotides on the surface of the stamp was a prerequisite for the demonstrations presented in this paper, suggesting that the process may equally be applied to the miniaturization of arrays with other chemical or biological species. While the DNA strands used within this study remained intact and accessible to hybridization, stress-induced damage may become an issue when handling and manipulating more fragile biological samples using this approach.

Experimental Section

Materials and Compounds: Versaflex CL30 and CL2000X were both obtained from GLS Corp. (McHenry, IL). Synprene RT-3820M was provided by PolyOne Canada, Inc. (Valleyfield, QC). Translocation stages for the stretch tool were bought from Thor Labs, Inc. (Newton, NJ); high-precision screws came from Mitutoyo (Mississauga, ON). All oligonucleotides were purchased from Integrated DNA Technologies, Inc. (Coralville, IA), and were used without further purification. For spotting experiments, we used a $20 \mu\text{M}$ solution of oligonucleotide in DMSO/water 50:50 (v/v). GAPS II and epoxy-modified glass slides were purchased from Corning (Acton, MA) and Erie Scientific (Portsmouth, NH), respectively.

Fabrication of Stamps: Planar stamps were fabricated from elastomer pellets using hot embossing in conjunction with a home-built 4" aluminum gasket (1 mm in height) with void areas that were $25 \times 75 \text{ mm}^2$ in size. Two 4" silicon wafers (Silicon Quest International, Inc., Santa Clara, CA) modified with 1H,1H,2H,2H-perfluorooctyl-trichlorosilane (Sigma-Aldrich Corp., St. Louis, MO) served as top and bottom plates of the mold, which was mounted in an EVG 520 embossing tool (EV Group, Schärding, Austria). Embossing was done at elevated temperatures (e.g., 170°C for CL30), a force of $2 \times 10^3 \text{ N}$ applied to the entire area of the wafer, and a pressure of $1 \times 10^{-3} \text{ mbar}$. Upon release from

the mold, stamps were cut into pieces of $\approx 25 \times 25 \text{ mm}^2$ that were used for experiments.

Printing and Hybridization of DNA Arrays: Spotting was performed with a VersArray Chipwriter Pro from Bio-Rad (Hercules, CA) under controlled environmental conditions (e.g., 24°C , 52% humidity). All experiments were performed with a single SMP3 microspotting pin from ArrayIt Microarray Technology (Sunnyvale, CA), which was cleaned thoroughly with DI water after each printing cycle in order to avoid cross contamination between different DNA samples. We usually pre-printed a number of spots onto a separate glass slide to remove excess solution from the pin. After spotting, stamps were allowed to dry for $\approx 5 \text{ min}$. Following relaxation, stamps were placed by hand onto the substrate. In most cases, contact formed immediately, and propagated across the entire surface without the need to apply any external pressure. Hybridization was done by spreading $25 \mu\text{L}$ of a $20 \mu\text{M}$ solution of the complementary DNA strand (labeled with Cy5) in hybridization buffer (8X SSPE containing 0.04% polyvinylpyrrolidone and 40% formamide, all obtained from Sigma-Aldrich) over the surface through contact with a microscope cover slide, followed by incubation at room temperature in a light-protective container for 1 h. Upon removal of the cover slip, substrates were first rinsed with 1X SSC containing 0.1% SDS (Sigma-Aldrich), then with water, and finally dried with a stream of nitrogen gas.

Instrumentation: Angles of contact were measured with a contact-angle goniometer from Kerenco Instruments, Inc. (El Paso, TX) using deionized water ($18.2 \text{ M}\Omega \text{ cm}$) as the probe liquid. Oxygen plasma treatment of stamps was done with a Plasma-lab80Plus from Oxford Instruments (Bristol, UK). Fluorescence readout of samples was done with a ScanArray Lite microarray scanner from Perkin Elmer Corp. (Woodbridge, ON) operated at excitation wavelengths of 543 and 633 nm for Cy3 and Cy5 fluorescent dyes, respectively. The limit in resolution was $5 \times 5 \mu\text{m}^2$. Close-up views of spots were taken with an Eclipse TE2000-U inverted fluorescence microscope from Nikon (Melville, NY) equipped with an EM-CCD camera from Hamamatsu (Bridge-water, NJ).

Keywords:

DNA arrays · elastic deformation · microspotting · soft lithography

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