

Electronic Supplementary Information for:

Towards tailored topography: Facile preparation of surface-wrinkled gradient poly(dimethyl siloxane) with continuously changing wavelength

Kai Uwe Claussen,^{a,§} Moritz Tebbe,^{b,§} Reiner Giesa^a, Alexandra Schweikart^b, Andreas Fery^b,
and Hans-Werner Schmidt*^a

^a*Department of Macromolecular Chemistry I, University of Bayreuth, 95440 Bayreuth, Germany. Fax: +49 921 55-3206; Tel: +49 921 55-3200; E-mail: hans-werner.schmidt@uni-bayreuth.de*

^b*Department of Physical Chemistry II, University of Bayreuth, 95440 Bayreuth, Germany. Fax: +49 921 55-2059; Tel: +49 921 55-2753; E-mail: andreas.fery@uni-bayreuth.de*

Experimental Section

PDMS Gradient Sample Preparation

Due to big differences in viscosity, the siloxane cannot be mixed with the curing agent in the employed disposable static mixer.³⁰ As a consequence, the preparation of compositional gradients of Sylgard 184 (DOW Corning) cannot be achieved by varying the flow rate of siloxane and curing agent while processing the mixture through the static mixing element. Therefore, the siloxane and curing agent had to be mixed before using the syringe pumps. In contrast to other PDMS systems³⁰, Sylgard 184 has a pot life of several hours what allowed us

to mix the siloxane and curing agent in 10:1 (PDMS-hard) and 25:1 (PDMS-soft) ratios before processing. The static mixer performed well at these similar viscosities.

Sylgard 184 was purchased from DOW Corning. The PDMS system was mixed in a 10:1 (PDMS-hard) and a 25:1 (PDMS-soft) ratio (w/w) of siloxane and curing agent. After degassing, two 10 mL glass syringes with luer lock connectors were filled with both the highly viscous mixtures and mounted on a high precision syringe pump system (Cetoni Nemesys). The syringes were connected by tubing to a custom-designed mixing head with an attached disposable static mixer (Quadro Sulzer[®]). PDMS mixtures with discrete and gradient composition were prepared by application of a certain flow profile for the 10:1 and 25:1 mixture at a constant total flow rate of 25 $\mu\text{L/s}$. For instance, the discrete composition PDMS-hard 20% was prepared using a flow rate of 5 $\mu\text{L/s}$ (PDMS-hard) and 20 $\mu\text{L/s}$ (PDMS-soft). In the case of PDMS gradient samples, an optimized on/off flow profile was used as shown in Fig. 2a. Mixtures were cast into rectangular Teflon[®] molds (140x10x1 mm³) mounted on a linear motion slide. The molds were uniformly filled in 56s by synchronization of the mold movement (2.5 mm/s) and the total flow rate of 25 $\mu\text{L/s}$. After processing, mixtures were cured at room temperature over night and post-cured for 2 h at 150°C. The thickness of the samples was measured with a caliper and ranged from 0.90-1.00 mm. Over each individual sample the thickness was uniform.

Embedding of Gradient Specimens

Normal procedures for wrinkling PDMS substrates involve the uniaxial straining of the samples and subsequent oxygen plasma treatment.² In the case of PDMS gradient specimens, the applied load does not distribute uniformly across the sample due to the mechanical gradient. This avoids the transfer of the continuously changing substrate's modulus into a stepless varying wrinkle wavelength. Therefore, the prepared gradient specimens (140x10x1 mm³) were cut in two stripes (140x5x1 mm³). Each stripe (PDMS gradient

specimen) was then embedded into a mixture of PDMS-hard that was cured afterwards, uniaxially stretched to 125% of its initial length and subsequently treated with oxygen plasma for 5 min (0.2 bar, 100 W, plasma technology) (Fig. 3). Straining the sample, the surrounding matrix (Fig. S1) provides a constant force field to the gradient specimen, ensuring an uniform strain of the entire sample. In this way, the wrinkle wavelength changed in dependency on the Young's modulus of the substrate according to equation (1).

The sharp interface between the embedded gradient specimen and the matrix reminds of the postulated γ -branching occurring at the transition between different wavelengths.²⁹

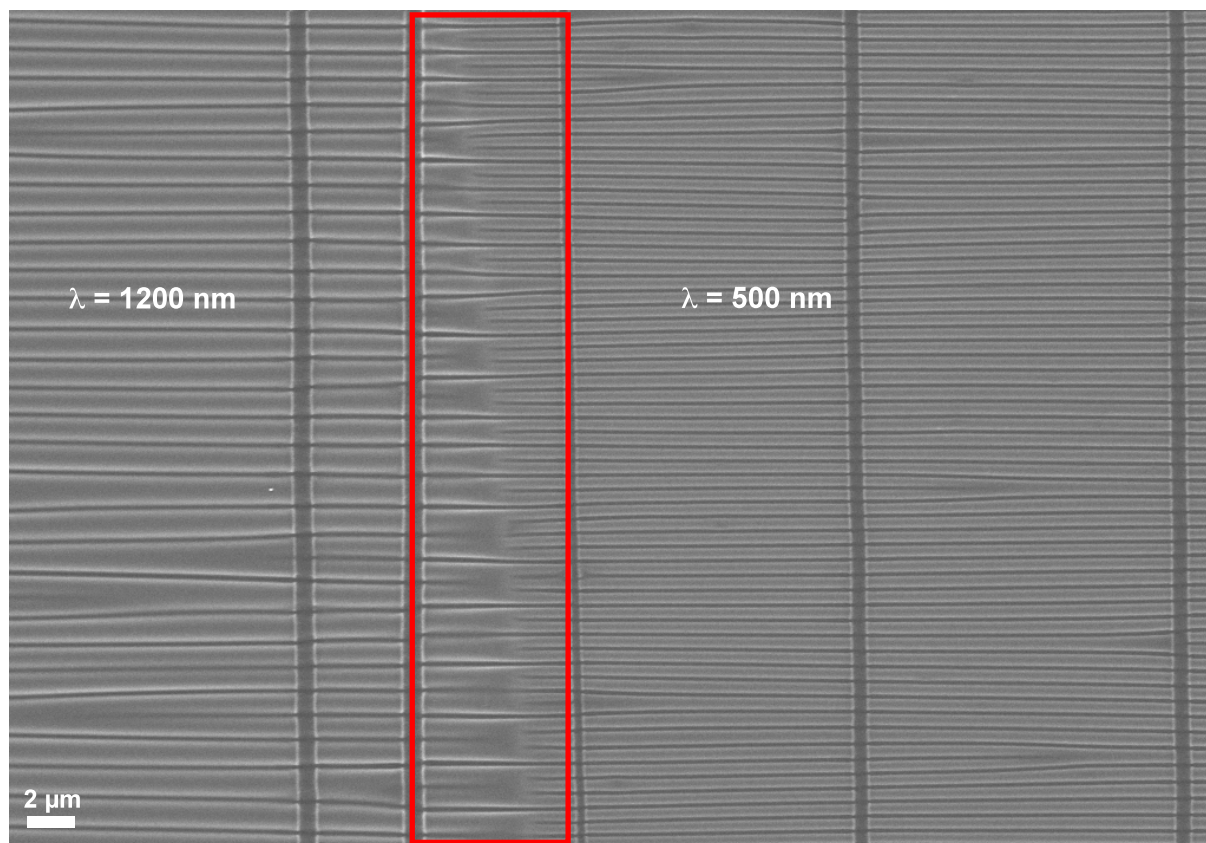


Fig. S1 Interface (see red rectangle) between embedded polymer gradient sample (left) and surrounding matrix (right). The transition between the different wavelengths reminds of γ -branching.²⁹

Mechanical Testing

The Young's modulus in compression of samples with discrete composition was measured in an unconfined compression test³² using a Rheometric Scientific DMTA IV with 17 mm compression plates. Cylindric samples (5 mm diameter, 1 mm thickness) were placed between the plates and at a strain rate of $5 \cdot 10^{-4} \text{ s}^{-1}$ the compressive force was recorded versus deflection. Tensile tests of samples with discrete composition were carried out on an Instron 5565 universal tester with pneumatic clamps and a 100 N load cell. Rectangular samples of $140 \times 10 \times 1 \text{ mm}^3$ (clamping distance $L_0 = 100 \text{ mm}$) were subjected to tensile tests at a strain rate of 200 mm/min (see ISO 37:2005) and the moduli reported were calculated from the initial slope. For statistical reasons, at least 5 specimens were tested for compressive modulus and tensile testing.

SEM Analysis

The wrinkle wavelengths were determined via SEM (Zeiss, Leo 1530). Using the embedded gradient specimens (two stripes, each with a dimension of $140 \times 5 \times 1 \text{ mm}^3$) 28 samples each with a length of 10 mm were cut for SEM analysis. For statistical reasons, each wrinkled sample was imaged at three different spots. The spot position in the middle of the sample was kept constant relative to the horizontal sample plane (and parallel to the wrinkle waves). The resulting images were evaluated with imageJ with respect to their gray value profiles. Note that the SEM images in Fig. 4 A to C are sinusoidal buckled as proven by AFM measurements of comparable systems (N. Pazos-Pérez, W. Ni, A. Schweikart, R. A. Alvarez-Puebla, A. Fery, L. M. Liz-Marzán, *Chem. Sci.* **2010**, *1*, 174. Highly uniform SERS substrates formed by wrinkle-confined drying of gold colloids). The contrast in SEM images must not be misinterpreted; the tip and the bottom of each wrinkle show lower gray values due to stronger scattering/absorption effects compared to the less curved slopes.

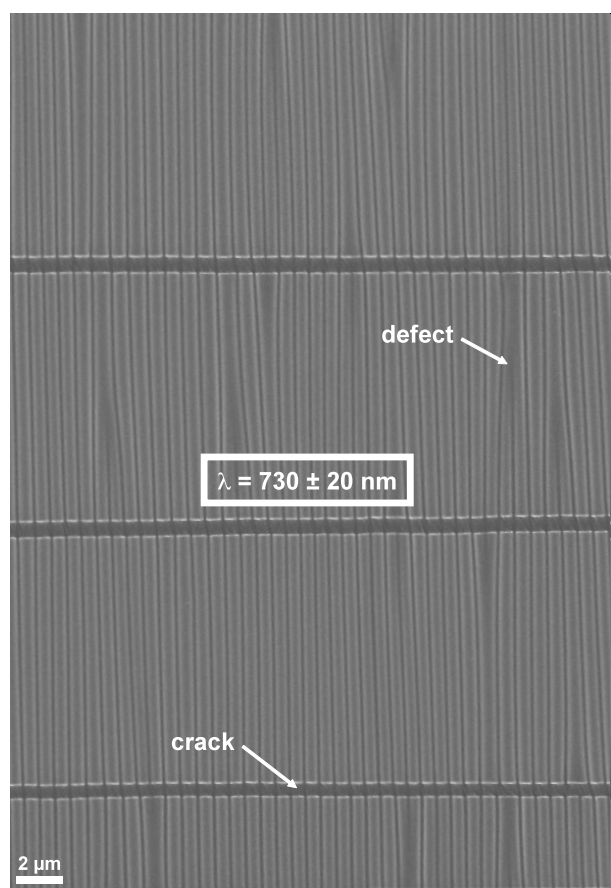


Fig. S2 This image was taken at the sample position A at 0.5 cm of the PDMS gradient shown in Fig. 4. Over a large surface area ($80 \times 120 \mu\text{m}^2$) the wrinkle wavelengths are highly uniform ($\lambda = 730 \pm 20 \text{ nm}$). Cracks perpendicular to the wrinkles are a well known phenomenon.²

Calculation of layer thickness

According to equation (1) the wrinkle wavelength λ depends linearly on the layer thickness h . A varying layer thickness with the factor of 1.7 would be necessary for a change in wrinkle wavelength from 700 to 1200 nm. To exclude a varying layer thickness, the dependency of the layer thickness h_f on the sample position had to be investigated. Unfortunately, the film thickness could not be measured by analysis of the cross-section via SEM due to the brittle SiO_x -layer and the resulting inaccuracy of the thickness determination. Therefore, the thickness was calculated. According to equation (1) the thickness h was determined with the measured wrinkle wavelength λ and the substrate's tensile modulus that was correlated to the measured compressive modulus using exponential fits (Fig. 1). The error analysis (covariance

propagation law) comprised seven defective values for the determination of h_f but yielded only small errors. The layer thickness was found to be almost constant along the gradient sample (Fig. S3). Therefore, the continuously changing wrinkle wavelength can be exclusively attributed to the change of the Young's modulus along the length of the sample.

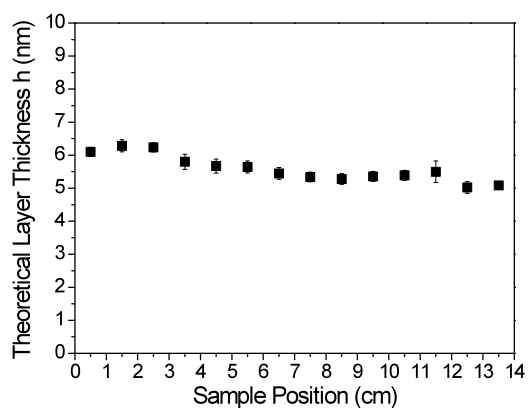


Fig. S3 Film thickness in dependency on the sample position. The mechanical gradient caused by a continuously changing crosslinker amount does not significantly affect the sample thickness. Therefore, the variation of wrinkle wavelength can be exclusively attributed to the change of the substrate's Young's modulus.