

Synthesis of Geometrically Well Defined, Molecularly Thin Polymer Films**

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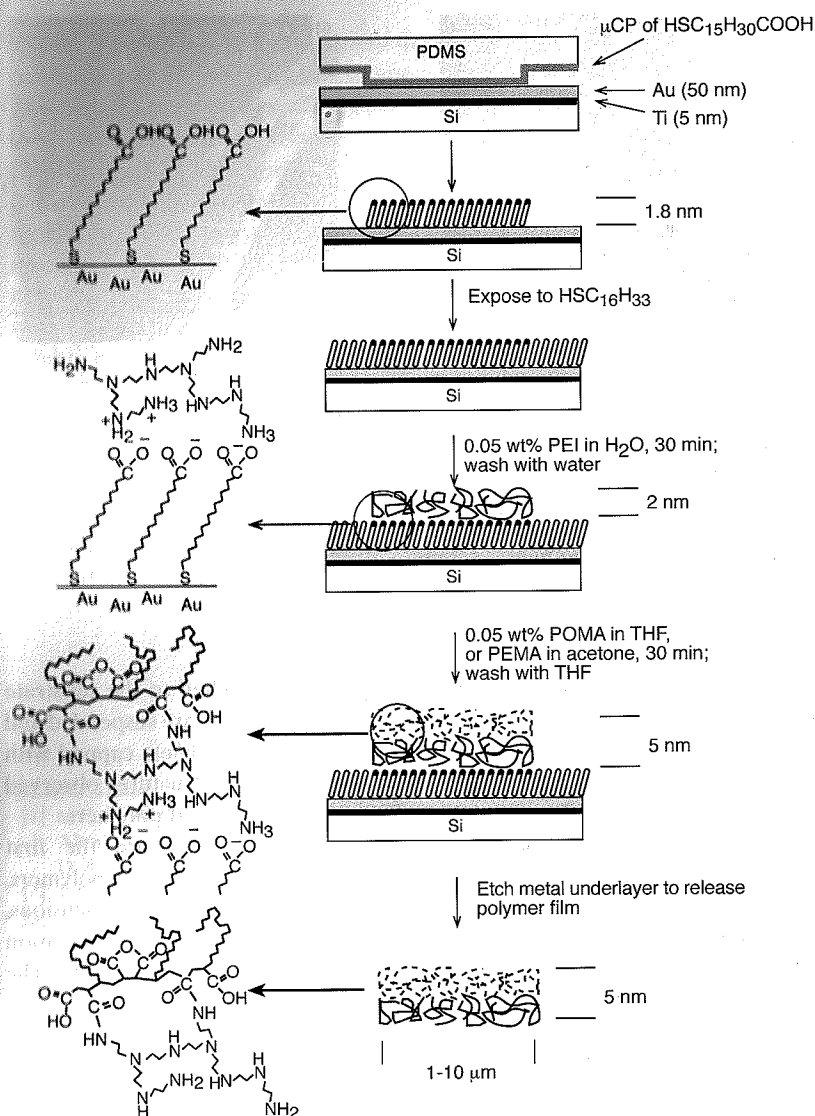
Here we demonstrate a general method for the fabrication of molecularly thin polymer films with well-defined (in-plane) dimensions. The strategy for the synthesis of these materials starts with a sequence of reactions on a patterned self-assembled monolayer (SAM). This pattern, defined by microcontact printing, determines the size and shape of the polymer films on the micrometer scale. The out-of-plane thickness and composition is defined on a nanometer scale by the sequence of chemical reactions.

These molecularly thin polymer films with in-plane cross-linking are a subset of the class of "two-dimensional polymers".^[1] Synthetic routes to two-dimensional polymers include polymerization of reactive monomers in SAMs^[2] and lipid bilayers,^[3] at oil-water^[4] and air-water interfaces,^[5] and polymerization of monomers that form self-assembled layered structures.^[6] Although certain of these approaches have generated two-dimensional polymeric structures, they have not controlled their lateral (in-plane) dimensions. Our strategy for the fabrication of two-dimensional polymers relies on the work of Grainger et al.,^[7] Crooks et al.,^[8] and others,^[9] who examined covalently bound polymer mono- and multilayers on surfaces. Rubner et al.^[10] and Decher^[11] also examined structures made up of electrostatically associated layers of polymers. Möhwald et al. described covalently linked hollow shell multilayers^[12] and Hammond et al. studied electrostatically deposited multilayers on patterned SAMs.^[13] We do not know of any attempts to release these polymeric multilayers into suspension following assembly on a surface.

We began the fabrication of the two-dimensional polymers by using microcontact printing (μ CP)^[14] to pattern a SAM; this patterned SAM served as a template for the growth of the polymer films (Scheme 1). The synthesis involves four steps: 1) patterning a gold surface by μ CP with COOH- and CH₃-terminated SAMs;^[15] 2) deposition of an amine-containing polymer (polyethyleneimine, PEI) by ionic adsorption onto the CO₂⁻-terminated areas;^[16] 3) cross-linking the adsorbed PEI covalently by allowing it to react with a polymeric anhydride (poly(octadecene-*alt*-maleic anhydride), POMA, or poly(ethylene-*alt*-maleic anhydride), PEMA);^[17] and 4) releasing the film from the surface by dissolving the gold substrate completely in 5 mM sodium dodecylsulfate (SDS)/30% aqua regia/0.5% HF in water.^[18] We examined polymeric films patterned into hexagons with 10- μ m sides and 10-

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Scheme 1. Schematic outline of the process used to obtain patterned thin polymer films. Fluorescence-labeled polymer films were synthesized by treating fluoresceinamine with the bilayers (PEI/POMA) prior to release from the surface. Printing was achieved with a poly(dimethylsiloxane) (PDMS) stamp.

μm central holes, in sheets with $10 \times 10 \mu\text{m}$ square holes, and in $20 \mu\text{m}$ wide lines. To aid in characterizing the polymer films we coupled fluoresceinamine to the PEI/POMA bilayer.^[19] Polymer films capped with this fluorophore showed green fluorescence.

Ellipsometry on homogeneous, unpatterned films of polymer prepared by the procedure of Scheme 1 (excluding microcontact printing and final release) gave a thickness of 1.5–2.0 nm for the film formed by reaction with PEI, and 4–5 nm for the bilayer formed by reaction with POMA.^[20]

The thickness of the polymer bilayers, as determined by atomic force microscopy (AFM), is approximately 5 nm.^[20] The layers appeared to be flat and continuous, that is, without holes or defects at the scale we could observe ($\approx 150 \text{ nm}$). The PEI is highly branched, and after covalent cross-linking by POMA or PEMA, the resulting two-dimensional polymer is a tightly interwoven network.

We released the thin films from the support by dissolving the metal underlayer in a mixture of aqua regia, HF, and SDS in water. We believe that the etching of the metal underlayer does not significantly damage the films, because the polymers did not dissolve or change appearance after prolonged exposure to the etchant. We added SDS to the etching solution because it seems to provide extra stability to the polymer films in suspension, perhaps by forming a mono- or bilayer on the top and bottom. This SDS layer could also aid the suspension of the polymer sheets. We were not able to release the sheets under mild conditions (for example, aqueous solutions with high ionic strengths). We speculate that the size of the sheets, the cooperative effect of a large number of electrostatic interactions between the polymers and the surface, the insolubility of the polymer sheets, spontaneous amide formation between the SAM and the polymer layer, and other unknown pinning points might contribute to the strong adhesion of the polymer sheets to the surface.

For characterization, the released polymeric structures were deposited on a surface and examined by AFM and optical microscopy. X-ray photoelectron spectroscopy (XPS) on redeposited thin films showed only traces of Ti and Au; this observation is compatible with the idea that the structures we observe are free polymers, unsupported by metallic films. We estimate that the molecular weight of a 5 nm thick film is around $3 \times 10^6 \text{ Da } \mu\text{m}^{-2}$.^[21]

We released hexagonal sheets with $10 \mu\text{m}$ sides and central holes $10 \mu\text{m}$ in diameter. Figure 1a shows an optical image of these hexagons after they had been transferred to a glass slide. The films have a clearly recognizable hexagonal shape. Some narrow creases are visible; the center sheet was apparently folded and deformed, perhaps during deposition on the surface. The sheetlike structures in Figure 1b remained mostly flat and extended in suspension. The original $10 \times 10 \mu\text{m}$ square holes in the sheet are deformed but recognizable. The fiberlike structure on the left of the image is probably a rolled-up sheet. The square pattern in the background is the image left from the patterned surface. Figure 1c shows an AFM image of a sheet with $10 \times 10 \mu\text{m}$ square holes that was released and redeposited without adding SDS to the etching solution. We performed this experiment to measure the thickness of the polymer films with AFM. The AFM measurements gave a thickness for the polymer layer of approximately 10 nm. This value is in satisfactory agreement with the thickness of 5 nm estimated before release from the surface. The difference might be due to solvation by a thin

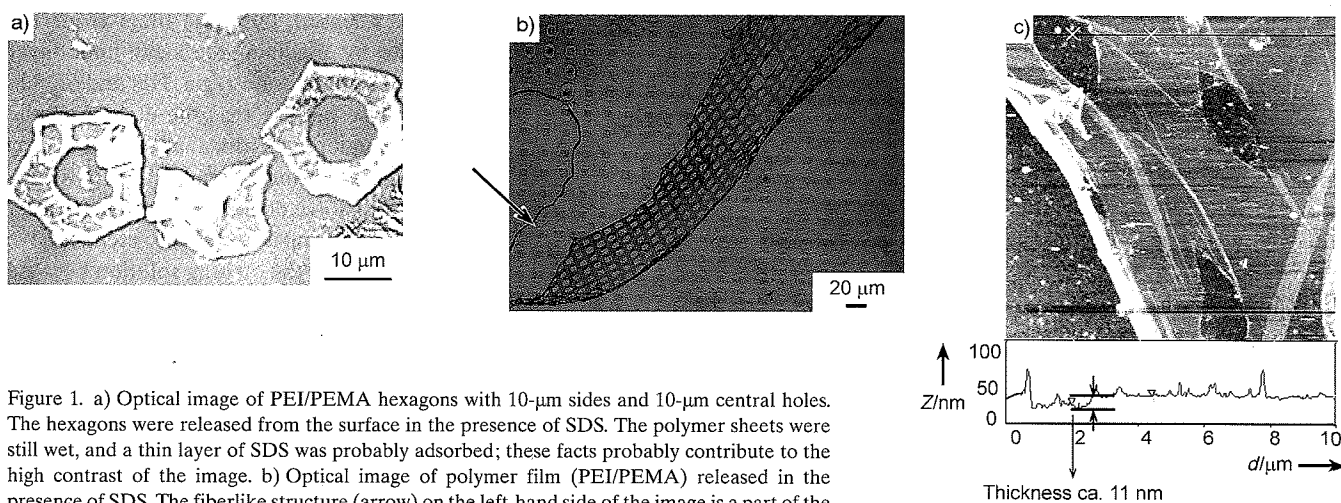


Figure 1. a) Optical image of PEI/PEMA hexagons with 10- μm sides and 10- μm central holes. The hexagons were released from the surface in the presence of SDS. The polymer sheets were still wet, and a thin layer of SDS was probably adsorbed; these facts probably contribute to the high contrast of the image. b) Optical image of polymer film (PEI/PEMA) released in the presence of SDS. The fiberlike structure (arrow) on the left-hand side of the image is a part of the sheet that crumpled. The faded pattern in the background is a remainder of the patterning of the surface by μCP . c) AFM image of a two-dimensional sheet of polymer film (PEI/POMA) with (deformed) $10 \times 10 \mu\text{m}^2$ holes.

layer of adsorbed water, reorganization of the polymers in the film on release from the surface, or cumulative uncertainties in the measurements.

The influence of SDS on the stability of the released films became clearer in a series of experiments (Figures 2a–d) in which we released 20 μm wide lines in the absence of SDS. Figure 2a shows an AFM image of a released polymer film that was deposited onto a surface. The original polymer lines folded after release from the surface. The height profile shows that the thinnest parts of the polymer films are approximately 8–10 nm thick. The profile suggests that the variations in thickness along the line scan correspond to the pleating of layers that are 8–10 nm thick. This thickness is realistic when relief of strain in the film (with lateral shrinking and perpendicular thickening) upon release from the substrate is taken into account. Figure 2b shows an optical image of partially released 20- μm lines. On the right and left, the two-

dimensional polymer lines are still attached to the substrate and remain flat. In the center, the polymers are suspended and folded. Fluorescence images of polymer sheets capped with fluorescein (Figure 2c) confirm that the structures observed under the microscope (Figure 2d) are indeed polymers.

The thin polymer films described here are the first examples of a new class of two-dimensional organic polymers, characterized by well-defined shape and lateral dimensions, by thicknesses of 5–20 nm, and by controllable composition in the direction perpendicular to the plane of the film. The synthesis of the polymers on the surface ensures high dimensional reproducibility (or, in the context of macromolecular science, monodispersity). The molecular weight can be controlled by means of the μCP process, either by the pattern used (for example, by the shape of the polymer) or by the number of layers used in the fabrication of the polymer (for example, PEI/POMA, PEI/POMA/PEI/POMA, etc.). The

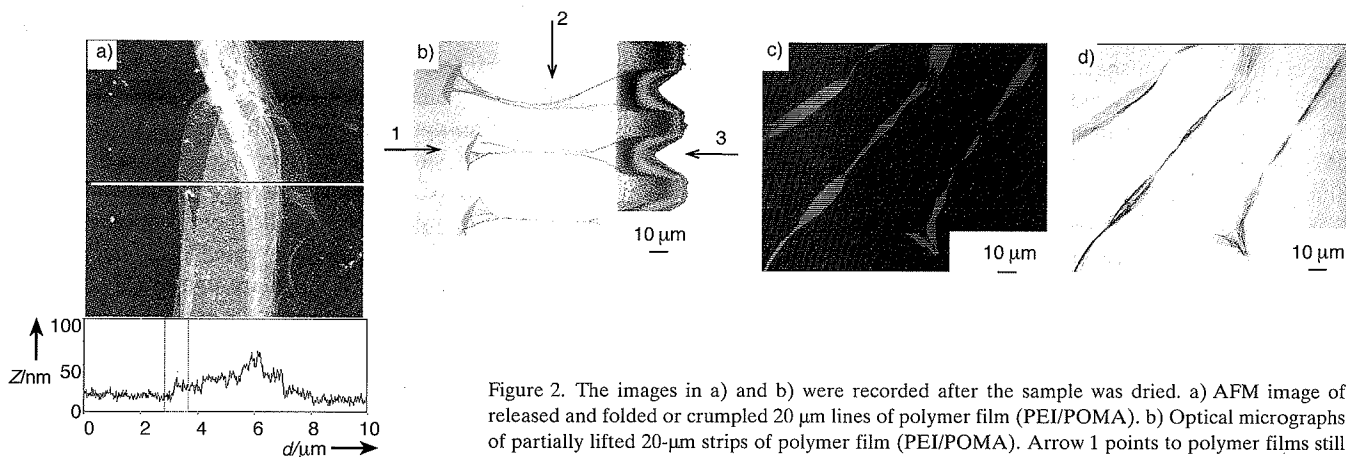


Figure 2. The images in a) and b) were recorded after the sample was dried. a) AFM image of released and folded or crumpled 20 μm lines of polymer film (PEI/POMA). b) Optical micrographs of partially lifted 20- μm strips of polymer film (PEI/POMA). Arrow 1 points to polymer films still attached to the surface; the section indicated by arrow 2 has detached from the support and redeposited on the surface; arrow 3 points to a part of the metal underlayer that was unetched. The images in c) and d) were taken from wet samples. c) Fluorescence image of released 20- μm lines of fluorescence-labeled polymer film (PEI/POMA) floating in water. d) Optical image of the same polymer films as in (c).

composition of the polymer sheets depends on the type of polymers used and the presence or absence of a capping layer. The patterns used here resulted in polymer films that can be classified either as materials or as macromolecules. More familiar systems that combine macroscopic and molecular dimensions are liposomes, SAMs, and Langmuir–Blodgett films.^[22] The smallest patterns that can now be formed by μCP are approximately $0.01\ \mu\text{m}^2$; the two-dimensional polymers derived from these patterns will have $M_r \approx 100\ \text{MDa}$ and would begin to approach the molecular weight of very large soluble polymers such as polyacrylamide (20 MDa)^[23] and λ -phage DNA (32 MDa).^[24] This study represents a first step towards the fabrication (rather than synthesis) of polymers with well-defined nanosize shapes and dimensions. The combination of (nano)lithographic techniques and surface chemistry will allow the fabrication of a wide range of different shapes and chemical functionalities for these macromolecules.

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- [17] The patterned substrate was placed in a 0.05 wt% solution of PEI (branched, $M_r = 750\,000$) in isopropyl alcohol for 20 min. The surface was briefly (<30 s) sonicated in water and dried under a stream of nitrogen. This polymer layer was cross-linked by reacting the amine-terminated surface with a 0.05 wt% solution of POMA ($M_r = 30\,000$) in THF, or PEMA ($M_r = 100\,000$ – $500\,000$) in acetone. The excess polymer was removed by briefly (<30 s) sonicating the sample in THF or acetone and washing with CH_2Cl_2 .
- [18] We added 0.5% HF to remove the underlying film of Ti that was used to promote adhesion of gold to SiO_2 .
- [19] PEI, POMA, PEMA, and fluoresceinamine were purchased from Aldrich and used without further purification.
- [20] Full characterization of patterned polymer multilayers is described in W. T. S. Huck, L. Yan, A. Stroock, R. Haag, G. M. Whitesides, *Langmuir* **1999**, *15*, 6862.
- [21] The volume of a 5-nm thick $1\ \mu\text{m}^2$ film is $5 \times 10^{-15}\ \text{cm}^3$. The density of PEI is $1.05\ \text{g cm}^{-3}$, and the density of POMA is $0.97\ \text{g cm}^{-3}$. Assuming an average density for the polymer film of $1.01\ \text{g cm}^{-3}$, the molecular weight is $1.01 \times 6.02 \times 10^{23} \times 5 \times 10^{-15} \approx 3\ \text{GDa}$.
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