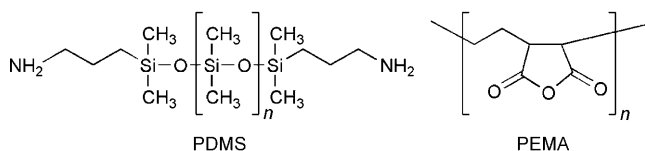


Covalent Layer-by-Layer Assembly and Solvent Memory of Multilayer Films from Homobifunctional Poly(dimethylsiloxane)**

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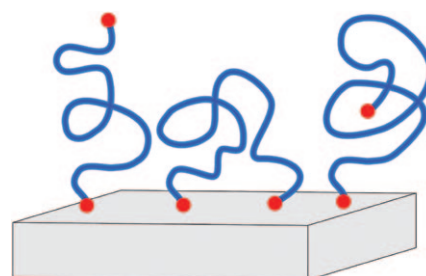
Layer-by-layer (LbL) assembled films have attracted attention as multicomposite conformal coatings either for the purpose of functionalizing surfaces with a large variety of different components or for the fabrication of electrical or optical thin-film devices.^[1–17] While most work on LbL films is based on electrostatic interactions, the use of covalent bonds has been reported as well.^[18–32]

Poly(dimethylsiloxane) (PDMS; Scheme 1), the most commonly used silicone-based organic polymer, is an elastomer whose unique molecular structure and physicochemical properties make it suitable for a broad range of applications, including lubricants, sealants, adhesives, eye contact lenses,



Scheme 1. The two types of polymers used for covalent LbL deposition: 3-aminopropyl-terminated homobifunctional poly(dimethylsiloxane) (PDMS) with $n \approx 34$ and $n \approx 364$, and poly(ethylene-*alt*-maleic anhydride) (PEMA) with $n \approx 800$ –4000. A monofunctional PDMS (PDMS-mono; not shown) with a single aminopropyl end group was also used.

microfluidic devices, or stamps for microcontact printing.^[33] Although polyelectrolyte multilayers have been assembled on PDMS objects in various geometries,^[34–45] there have not yet been any reports on the fabrication of multilayer films containing end-functionalized PDMS as a constituent. One of the reasons for a lack of experimental work in this area is most likely due to the fact that the end groups of polymers are notoriously difficult to react, firstly because the end groups constitute only a very small fraction of the chain and secondly because they are predominantly hidden inside the polymer coil for statistical reasons (Scheme 2, example on the right).



Scheme 2. Idealized depiction of the essential conformations of homobifunctional macromolecules attached to a surface by reactive chain ends. The red dots represent primary amino groups in this case, which react with anhydride groups present on the surface (not shown). Extended conformations are statistically less favorable, and in particular those in which the second end group is easily available for further reaction (left). In loop conformations (center), both chain ends are attached. Statistically more favorable conformations are those in which the second end group is hidden inside the polymer coil and is thus difficult to access (right).

The problem of end-group reactions is even more pronounced on surfaces than in solution because of the additional confinement in space. This difficulty for carrying out reactions on surfaces is well-known from much simpler related systems, for example, solid-phase peptide synthesis, in which incomplete yields of individual reaction steps may cause sequence defects in the final oligopeptide products.^[46] If consecutive chemical reactions do not proceed with exactly 100 % yield, the surface density of available functional groups will decrease dramatically with an increasing number of reaction steps.

A second important problem for fabricating multilayer films from homobifunctional reagents lies in the fact that backfolding of the second chain end followed by a reaction with the underlying reactive surface may further lead to a substantial decrease of functional groups available for attaching further layers. Although brush-like structures of

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polymer monolayers with dangling second end-groups are easily obtained in grafting-to reactions using monofunctional chains, the second chain end of homobifunctional components can be captured by the underlying reactive surface and the formation of loops may become strongly favored, especially at low polymer concentrations (Scheme 2, center).

The problem of fabricating multilayer films of small homobifunctional components was only overcome by employing electrostatic interactions using rigid bola-shaped amphiphiles^[47] and for covalently attached small chromophores by introducing so-called polymeric capping layers that are capable of planarization and of compensating the loss of functional groups.^[48,49]

Herein, we make use of a capping approach while using mid-sized homobifunctional molecules, namely amino-terminated PDMS with number-average molecular weights of 2500 g mol⁻¹ and 27000 g mol⁻¹, which corresponds to a degree of polymerization of 34 and 364, respectively. As material for the capping layer, through which high lateral densities of reactive chemical functional groups are redeemed even after reactions of homobifunctional reagents with moderate or poor yield or after significant loop formation, we chose poly(ethylene-*alt*-maleic anhydride) (PEMA; Scheme 1) with a commercially available molar mass of 100000–500000 g mol⁻¹.

The length of the PDMS monomer repeat unit was estimated from MO-calculations to be 0.235 nm (see Supporting Information), and this value was used to estimate the contour lengths of the PDMS polymers used in this study. With a molar mass of 74.15 g mol⁻¹ for the (CH₃)₂SiO monomer repeat unit of PDMS and the length of this unit of 0.235 nm, we calculated values for the degrees of polymerization and for the contour lengths (Table 1).

Table 1: Estimated contour lengths of the polymers used as derived from semiempirical MO calculations (PM3) of extended oligomers.

Polymer	$\overline{M}_n$ [g mol ⁻¹] ^[a]	$\overline{DP}_n$ ^[b]	Estimated contour length
PDMS-mono	2200	30	7 nm
PDMS-2500	2500	34	8 nm
PDMS-27000	27000	364	86 nm

[a] Molar mass. [b] Degree of polymerization.

The two types of PDMS used for covalent LbL assembly with PEMA are homobifunctional PDMS of different molecular weight (Table 1) having an aminopropyl group attached at each end of the linear chain. To demonstrate how well capping layers work in this case and even at difficult conditions, commercial PDMS derivatives were used without further purification. It can therefore not be excluded that multilayer growth proceeds partially by parasitic reactions, and unequivocal proof that both PDMS end groups are required for successful covalent LbL assembly can thus only be established by showing that monofunctional PDMS only leads to the formation of a monomolecular brush-like layer under exactly the same conditions. For this purpose, we investigated monomolecular layers of aminopropyl-terminated poly(dimethylsiloxane) (PDMS-mono), which has a

reactive amino group attached at only one end. Impurities of PDMS molecules without any terminal amino group do not interfere because they do not chemisorb at all. However, a single chemisorption cycle may not be sufficient to obtain a dense monolayer by chemisorption of PDMS-mono. We therefore carried out several consecutive chemisorption steps at identical conditions until a plateau for the monolayer thickness was reached. Figure 1 shows that this plateau is reached after 10 consecutive chemisorption cycles. When the plateau is reached, the monolayer possesses a thickness of 6.8 nm. This value is slightly less than the estimated contour length of the monofunctional PDMS and suggests the formation of a rather dense layer in which the chains are in a somewhat stretched conformation.

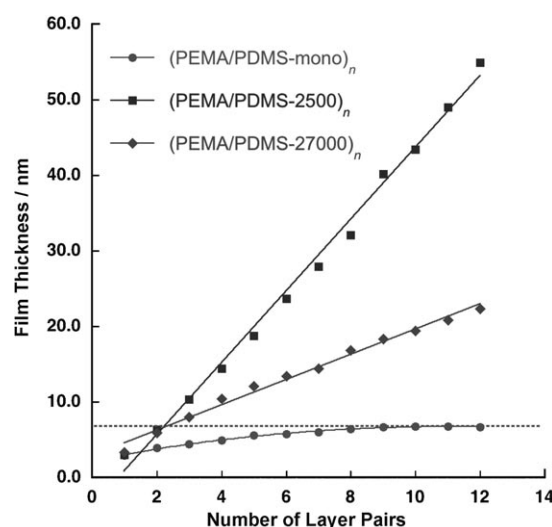


Figure 1. Comparison of the build-up of films using PDMS of differing molar mass having one or two amino end groups. Polymer concentrations: 1.0 mg mL⁻¹.

The optimization of chemisorption times in different solvents showed that regular film growth occurred at immersion times of 30 minutes per layer for PEMA dissolved in tetrahydrofuran and 50 minutes per layer for PDMS dissolved in toluene. Films prepared at these conditions are optically homogeneous and do not visibly scatter any light. The multilayer films are smooth enough to permit determination of thickness and surface roughness by small angle X-ray reflectometry up to a film thickness corresponding to the resolution of our instrument (about 60 nm). Thicker films show very homogeneous interference colors (Figure 2; left). The root-mean-square surface roughness was determined by atomic force microscopy and was in general about 5–10 % of the film thickness; typical AFM images are shown in Figure 2.

The multilayer growth is actually more interesting than shown in Figure 1 because the two polymers involved must be deposited from different solvents. PEMA layers are always attached in THF, whereas the PDMS layers are always deposited from toluene. The raw growth increments (PEMA/PDMS)₁ are 2.8 nm after PEMA deposition (Figure 3, from slope of curve with ●) and 5.7 nm after PDMS-27000 deposition (Figure 3, from slope of curve with ◆) for polymer

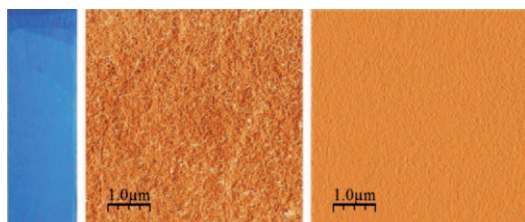


Figure 2. Left: Image of a thick multilayer film composed of PEMA and PDMS-2500 on a silicon wafer showing a homogeneous blue interference color. The original sample size was 12 mm × 42 mm, the film was covalently assembled from polymer solutions with a concentration of 300 mg mL⁻¹. The slightly more intense color at the top is an artifact of the meniscus region during immersion. AFM images of a multilayer film after deposition of 6 layer pairs are shown in deflection (center) and phase modes (right).

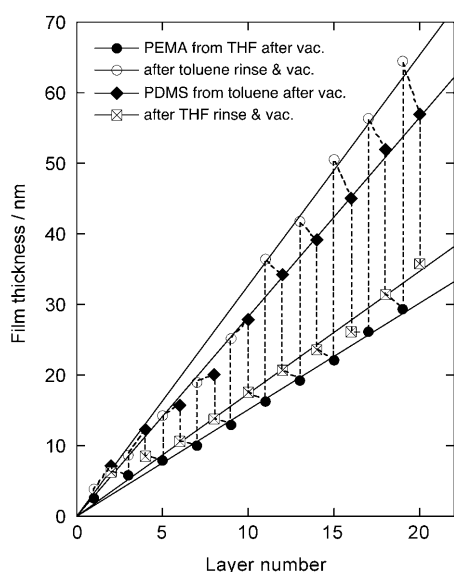


Figure 3. Full growth curve for a multilayer film deposited from solutions of 50 mg mL⁻¹ using optimized adsorption times of 30 min for PEMA and 50 min for PDMS-27000 including swelling/de-swelling of the films at the steps of solvent change. The dotted line connects all the data points in the sequence as they were taken. The thickness data after drying in air are not shown as they are identical to the data after drying for 10 min in vacuum. Thickness data for small layer numbers usually show a larger error than data taken at larger layer numbers.

concentrations of 50 mg mL⁻¹. The individual thickness increments of the PEMA and PDMS layers cannot directly be determined due to the strong swelling/de-swelling of the films in the two solvents. When the solvent is changed from THF to toluene after the adsorption of a layer of PEMA, the films swells by a factor of 2.2 (determined by taking the ratios of the corresponding slopes). Correspondingly, when the solvent is changed from toluene to THF after the adsorption of a layer of PDMS, the film shrinks by a factor of 0.61, again calculated from the ratios of the corresponding slopes. The thickness of the multilayers in the dry state is identical after either drying in air or drying in vacuum, indicating that the volume changes in the film associated with the swelling/de-swelling may take place without solvent remaining in the films. This marked

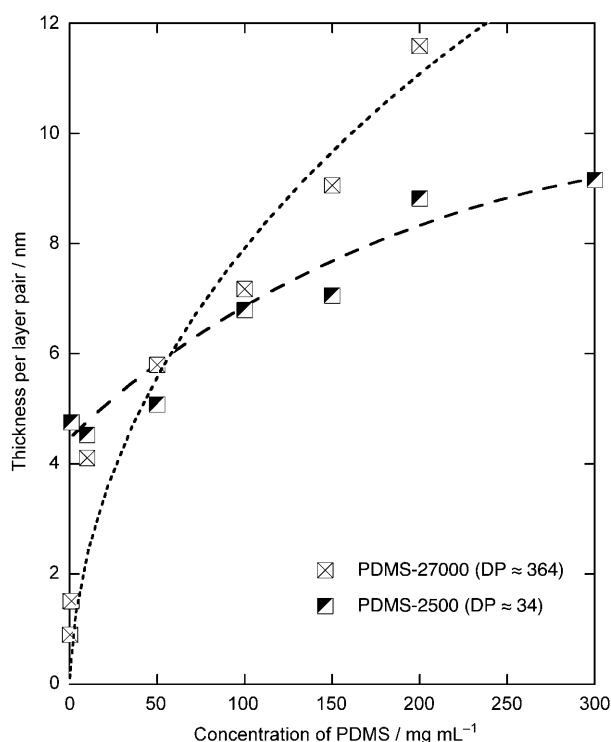


Figure 4. Comparison of the average growth increments of layer pairs for the multilayer build-up as a function of the molar mass and the polymer concentration. A value for 300 mg mL⁻¹ could not be determined for PDMS-27000 as solutions were too viscous. The solid lines act as a guide to the eye.

memory effect for solvent occurs throughout the whole film and not only in the last layer(s), and is attributed to the change of polymer conformations induced by the change of solvent quality for the corresponding polymers. A typical growth curve of (PEMA/PDMS)_n films showing the swelling/de-swelling effects in full detail is depicted in Figure 3.

Figure 4 depicts the influence of the polymer concentration on the film thickness. It can be seen that the average thickness increment per layer pair (PDMS/PEMA)₁ correlates well with the molar mass of the polymers and that, as expected, the film thickness approaches a plateau of about 10 nm with increasing polymer concentration in the case of PDMS-2500. Assuming a thickness of 1–2 nm for a PEMA layer leaves an upper limit of the thickness of the PDMS-2500 layer of 7–8 nm, which corresponds well to the thickness of a monolayer of PDMS (Figure 1) and also to the contour length of the polymer. The plateau value of the thickness increment per layer pair could not be determined in the case of the PDMS-27000 derivative due to the strongly increasing viscosity of solutions above concentrations of 200 mg mL⁻¹.

At first glance it seems surprising that the longer polymer only forms thicker films at high polymer concentrations whereas the shorter polymer forms thicker films at small polymer concentrations. However, Figure 1 shows that films of both polymers have a regular growth with the slope of the shorter polymer being more than 2.5 times larger than the slope of the polymer with a tenfold higher molar mass. The average thickness increments obtained from Figure 1 are 4.8 nm per

layer pair for the case of PDMS-2500 and 1.7 nm per layer pair for the case of PDMS-27000 at a polymer concentration of 1.0 mg mL^{-1} . This fact indicates that the increased chain length favors polymer conformations in which the chain ends are less-accessible for reaction (Scheme 2, right). The fact that the end groups of macromolecules are increasingly difficult to react with increasing molar mass is a frequent phenomenon in polymer chemistry. Consequently we observe that the reduced reactivity of PDMS-27000 slows down its attachment compared to PDMS-2500 and also the attachment of PEMA in the next layer. Both reactions contribute to a reduced thickness increment in comparison with PDMS-2500. Note that we use optimized adsorption times of 30 minutes in the case of PEMA and of 50 minutes in the case of any PDMS, and never allowed the reactions to go to completion. Only when we substantially increased the polymer concentrations did we observe a change of growth regime in which the bifunctional PDMS with the higher mass also forms thicker films. The crossover between both regimes occurs at concentrations between 50 and 100 mg mL^{-1} ; in this range both polymers show almost identical thickness increments of about 6 nm per layer pair (Figure 4). However, the largest value of the thickness increment of about 12 nm remains about 30 times smaller than the contour length of longer polymer. This indicates a much less stretched conformation of the PDMS chains in the multilayer films in comparison with the monolayer of PDMS-mono.

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