

Supporting Information

Influence of polymer molecular weight on the parabolic and linear growth regime of PDADMAC/PSS multilayers

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All PEMs are prepared in 0.1 M NaCl solution, and measured in salt-free solution with multiple angle ellipsometry. In all Figures, the lines are fits to equations (3) and (4). For each combination of molecular weights, the same values for N_{trans} and α are used for d and Δd . When a film has three growth zones, equations (3) and (4) are modified as described in the text.

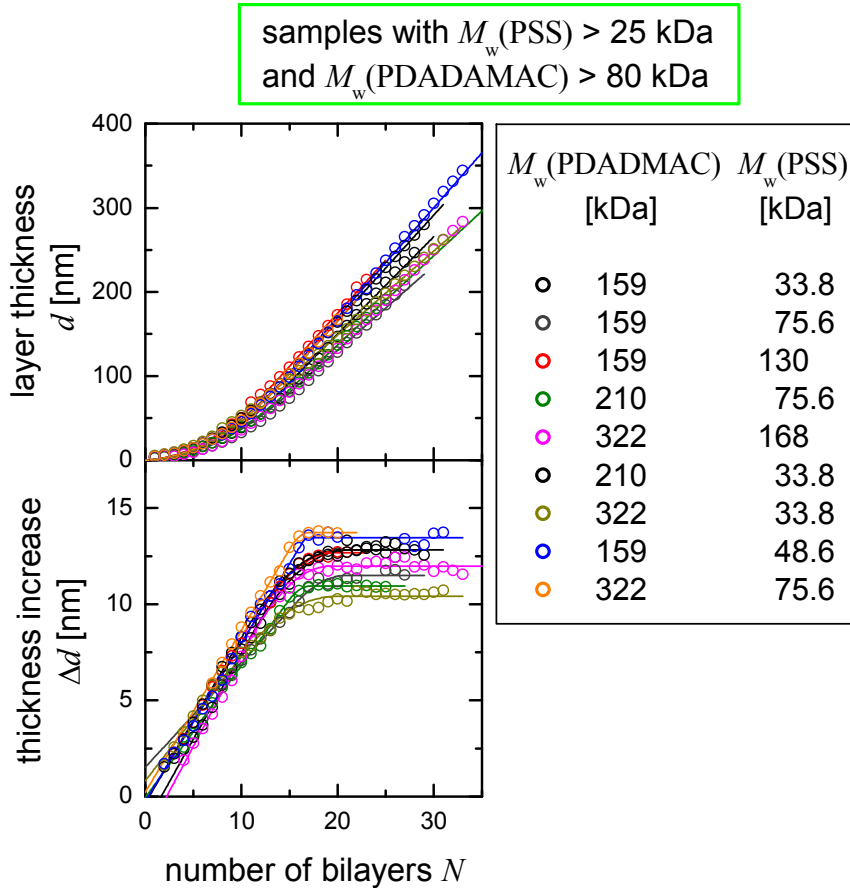


Figure S1: Thickness of the PDADMAC/PSS films (top) and thickness of top layer pair (bottom) vs number of deposited layer pairs N for different molecular weights as indicated. All molecular weights are above the respective threshold value, therefore the molecular weight has (within error) no influence on the film growth (green region in Fig. 3, and in Tables 1 and 2).

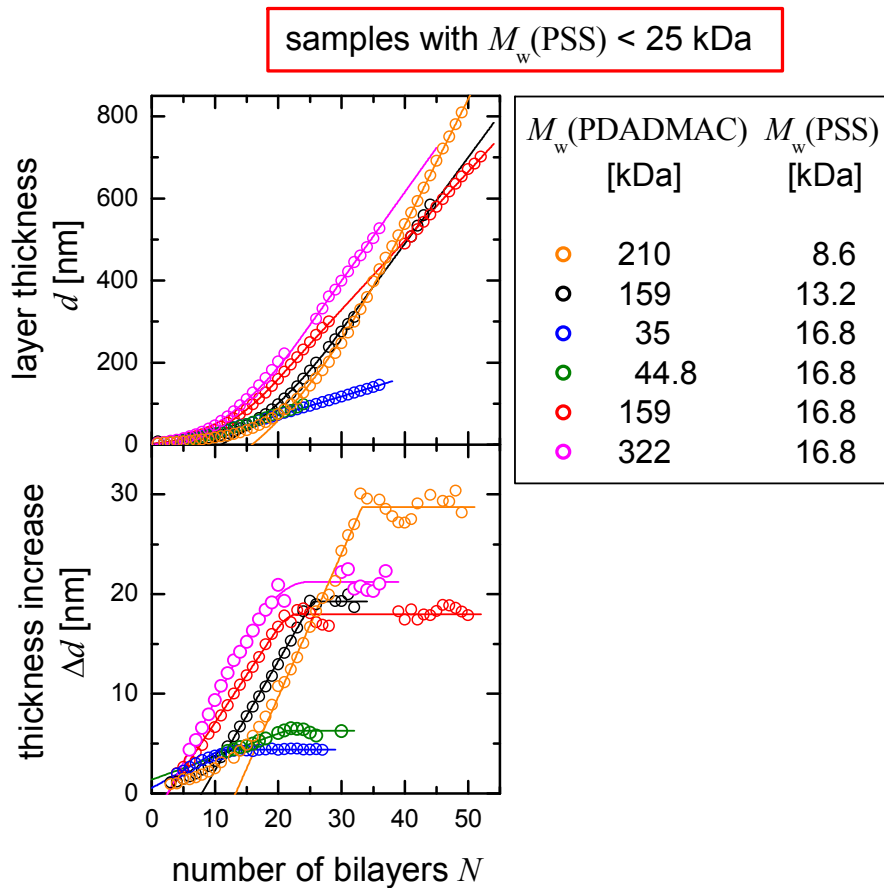


Figure S2: Thickness of the PDADMAC/PSS films (top) and thickness of top layer pair (bottom) vs number of deposited layer pairs N for different molecular weights as indicated. The molecular weight of PSS is below its threshold value, the molecular weight of PDADMAC is either above (159, 210 or 322 kDa) or below the threshold value (35 and 44.8 kDa). The former are the measurements depicted in the red region of Fig. 3 and of tables 1 and 2; they show three growth regimes (exponential, parabolic, linear). The measurement with $M_w(\text{PDADMAC}) = 35 \text{ kDa}$ is depicted in the blue region of Fig. 3. However, the film with $M_w(\text{PDADMAC}) = 44.8 \text{ kDa}$ is in between. While d_{BL} is decreased as expected for PDADMAC with low molecular weight, N_{trans} is increased, as expected for low molecular weight PSS.

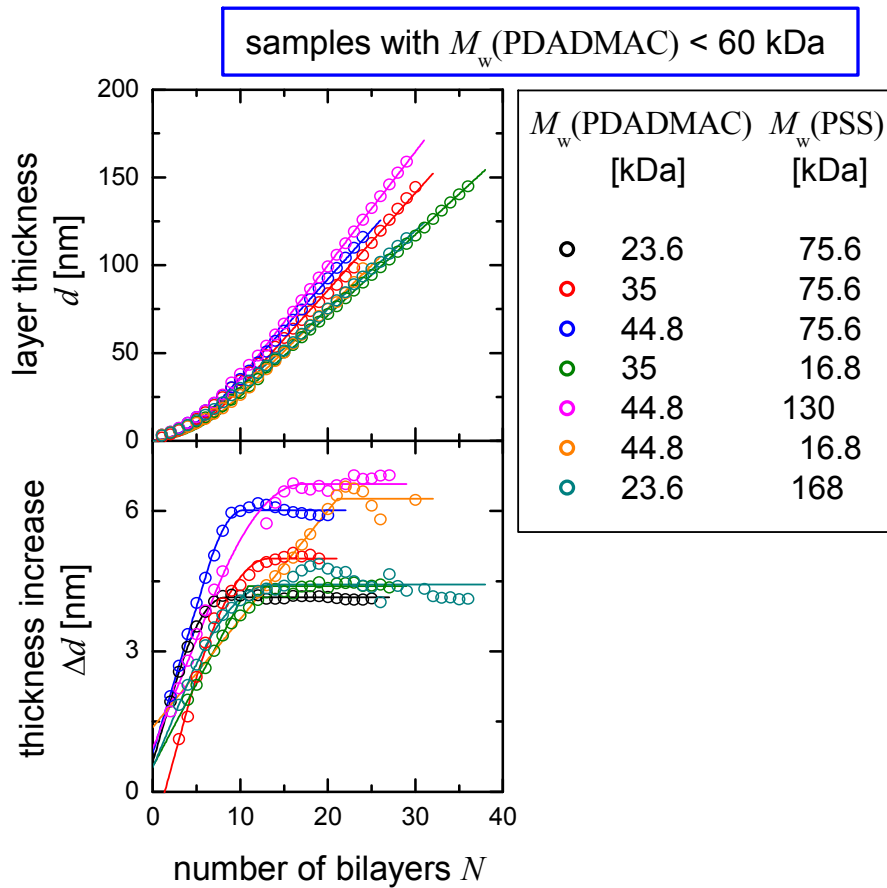


Figure S3: Thickness of the PDADMAC/PSS films (top) and thickness of top layer pair (bottom) vs number of deposited layer pairs N for different molecular weights as indicated. The molecular weight of PDADMAC is below its threshold value, the molecular weight of PSS is either above (75.6, 130 or 168 kDa) or below the threshold value (16.8 kDa). With the exception of the film prepared from $M_w(\text{PDADMAC})/M_w(\text{PSS})=44.8/16.8$ all measurements are depicted in the blue region of Fig. 3 and of tables 1 and 2. The film made from $M_w(\text{PDADMAC}) = 44.8 \text{ kDa}$ does show a low d_{BL} as expected for PDADMAC with low molecular weight. However, N_{trans} is increased, as expected for low molecular weight PSS.

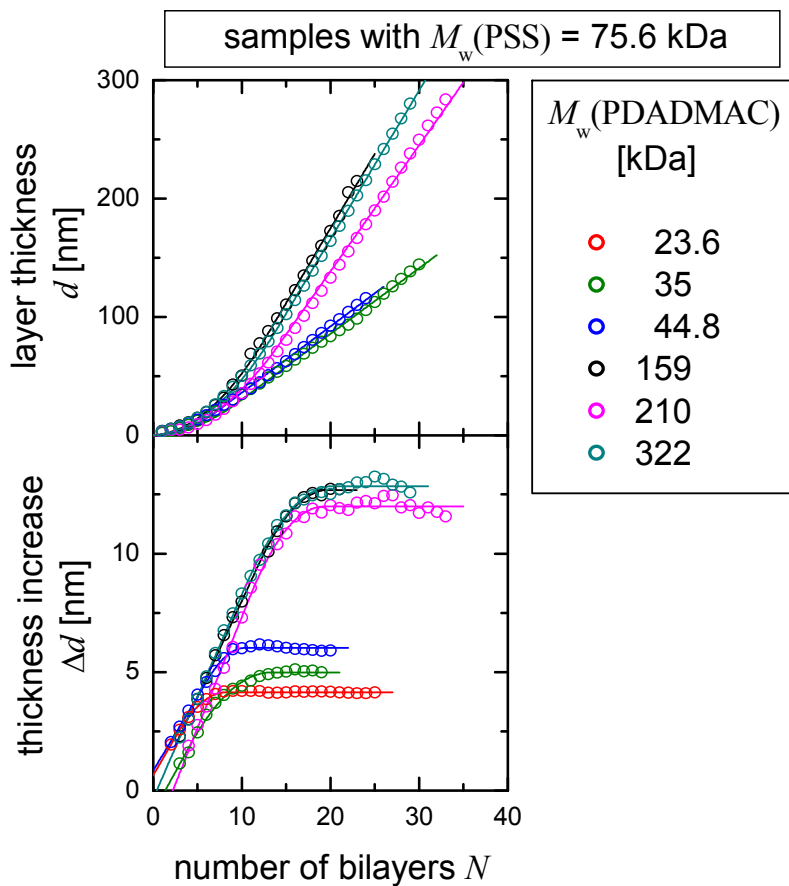


Figure S4: Thickness of the PDADMAC/PSS films (top) and thickness of top layer pair (bottom) vs number of deposited layer pairs N for different molecular weights as indicated. The molecular weight of PSS is 75.6 kDa, the molecular weight of PDADMAC is varied. The values of d_{BL} and N_{trans} obtained from least square fits are depicted in Fig. 3, bottom. On increase of $M_w(\text{PDADMAC})$, both d_{BL} and N_{trans} increase, until the threshold value of 80 kDa is reached. Then, both d_{BL} and N_{trans} are constant.

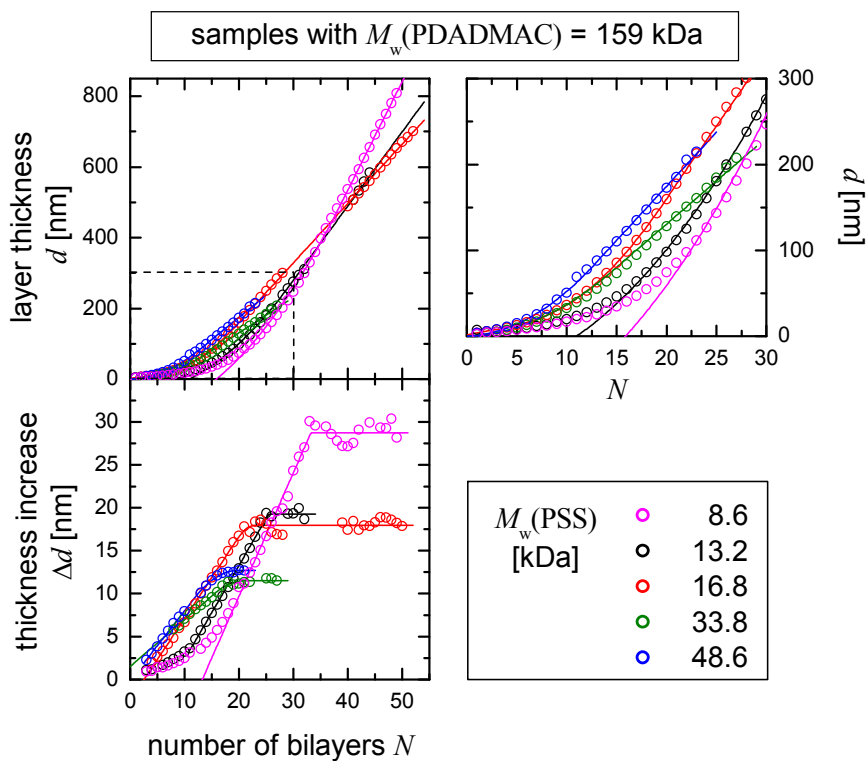


Figure S5, left: Thickness of the PDADMAC/PSS films (top) and thickness of top layer pair (bottom) vs number of deposited layer pairs N for different molecular weights as indicated. Right: Enlargement of the dashed frame of the plot on the left side, top (to visualize the exponential growth regime). The molecular weight of PDADMAC is 75.6 kDa, the molecular weight of PSS is varied. The values of d_{BL} and N_{trans} obtained from least square fits are depicted in Fig. 3, bottom. On increase of $M_w(\text{PSS})$, both d_{BL} and N_{trans} decrease, until the threshold value of 25 kDa is reached. Then, both d_{BL} and N_{trans} are constant.