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Supporting Information

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Supplementary Figures for "Diffusional Self-Organization in Exponential LBL Films into Composite "Accordions" with Micro+Nanoscale Periodicity**"

By

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1. Supplementary Figures:

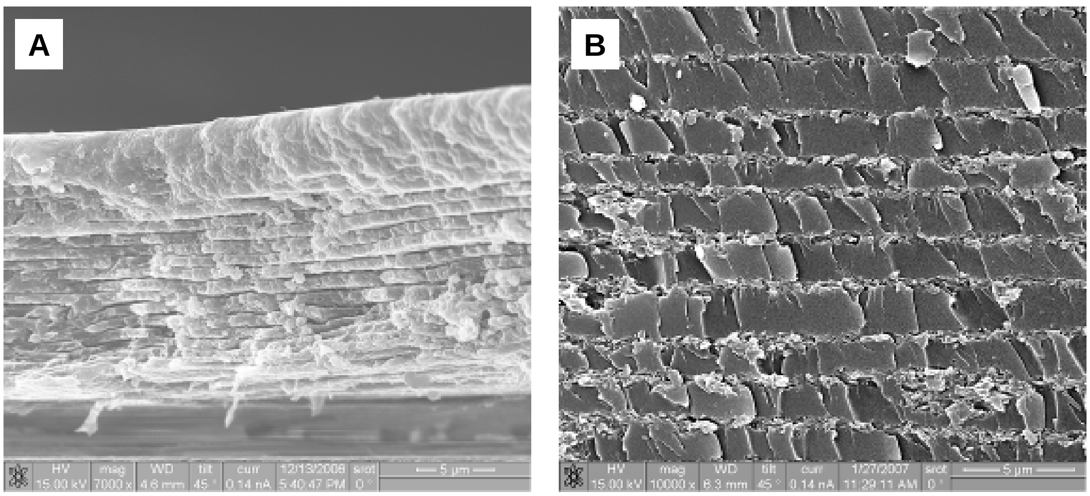

Figure S1. Comparison of PDDA/MTM/PDDA/PAA films with A) 30 sec (30-cycle film) and B) 10 min (close-up of a 100-cycle film) depositions.

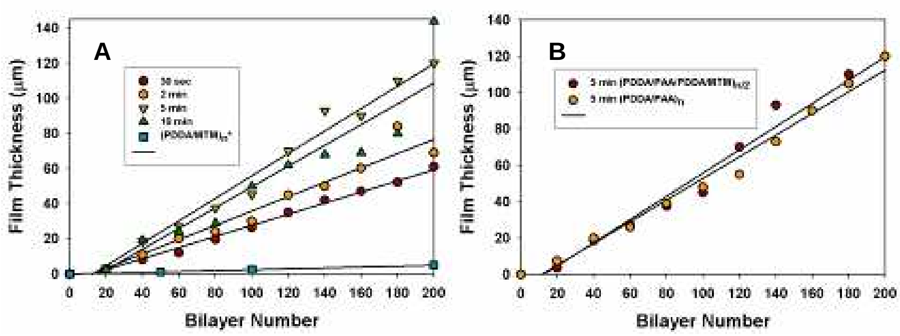

Figure S2. Compilation of thicknesses evolution of e-LBL and l-LBL films as a function of number of deposited layers and with different deposition intervals. A) Comparison of thicknesses from SEM for $(PDDA/MTM/PDDA/PAA)_n$ films with the specified deposition intervals prepared on microscope glass slides. The $(PDDA/MTM)_n$ regression is based on the values obtained by Tang et al..[1] B) Comparison of $(PDDA/MTM/PDDA/PAA)_n$ with and without MTM following 5 min depositions.

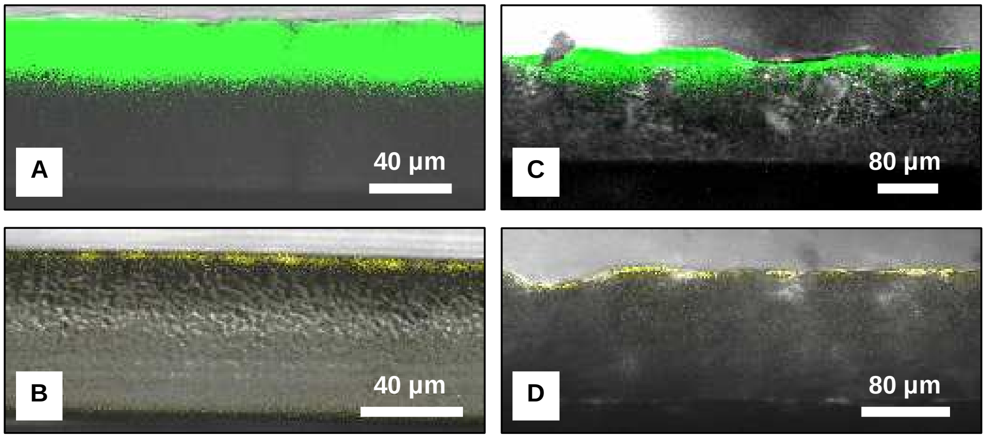

Figure S3. Laser scanning confocal microscopy characterization of dye-labeled polymer diffusion in the e-LBL systems. A) and B): $(PDDA/MTM/PDDA/PAA)_{100}$ with top layers of FITC-PEI and LYC-PAA, respectively. C) and D): $(PDDA/PAA)_{200}$ with top layers of FITC-PEI and LYC-PAA, respectively.

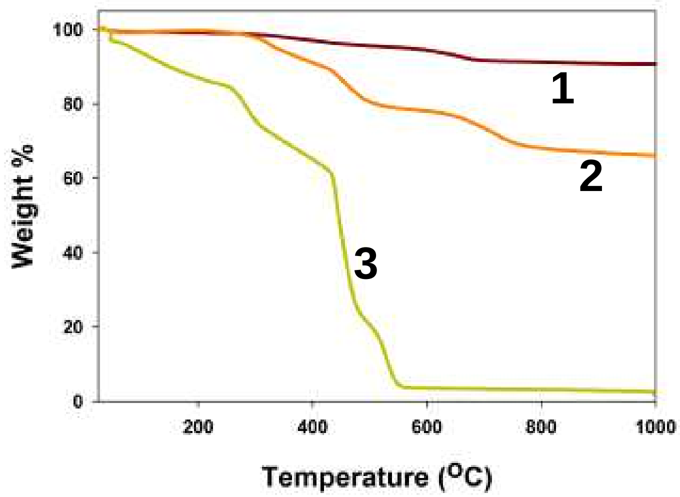

Figure S4. Thermo-gravimetric analysis results for: 1) pure MTM powder, 2) $(PDDA/MTM)_{300}$, and 3) $(PDDA/MTM/PDDA/PAA)_{100}$ with 30 sec deposition.

2. SAXS Analysis of Film Structure:

Small angle X-ray scattering (SAXS) was used to reveal information about morphologies of $(PDDA/PAA)_{200}$, $(PDDA/MTM)_{300}$, and $(PDDA/PAA/PDDA/MTM)_{100}$ films. The $(PDDA/PAA)_{200}$ film does not contain clay and thus only diffuse scattering from the polymers is observed (Fig. S5a). For the films containing clay, scattering was observed in the q_z direction, indicating clay platelets oriented parallel to the substrate. In the $(PDDA/MTM)_{300}$ film a sharp peak was observed in the corresponds to a basal spacing of 1.45 nm (Figs. S5b, d), which is similar to literature values of the basal spacing for Na^+-

montmorillonite.[2] A less prominent peak was also observed corresponding to a larger basal spacing at 2.09 nm, indicating significant intercalation of polymer between clay sheets. While there is clearly significant scattering from the montmorillonite in the $(PDDA/PAA/PDDA/MTM)_{100}$ film, the lack of a distinct peak indicates either a wide range of intercalated basal spacings or exfoliation of the clay platelets (Figs. S5c, d). In the $(PDDA/MTM)_{300}$ film the positively charged PDDA intercalates the montmorillonite interlayer gallery by exchanging with the Na^+ ions. In this case any further intercalation of PDDA into the interlayer gallery will lead to an excess positive charge.

We can further quantify the orientation of the clay platelets by using Herman's orientation parameter (f).[3-5] To calculate the orientation parameter, azimuthal scans were taken over a small window around the q value. This parameter ranges from 1 to -½, in which a value of zero indicates a completely random distribution of orientations. When f is 1 or -½ the system is completely aligned parallel or perpendicular, respectively, to the chosen reference direction (in this case, normal to the substrate). Herman's orientation parameters as high as 0.8 have been reported for clay platelets in blown polypropylene-montmorrilonite nanocomposite films.[6] The values for the orientation parameter were as follows:

$(PDDA/MTM)_{300}$ for spacing between 1.38 and 1.51:	0.38 ± 0.10
$(PDDA/MTM)_{300}$ for spacings between 1.97 and 2.28 nm:	0.29 ± 0.11
$(PDDA/PAA/PDDA/MTM)_{100}$ for spacings between 1.38 and 1.51:	0.11 ± 0.06

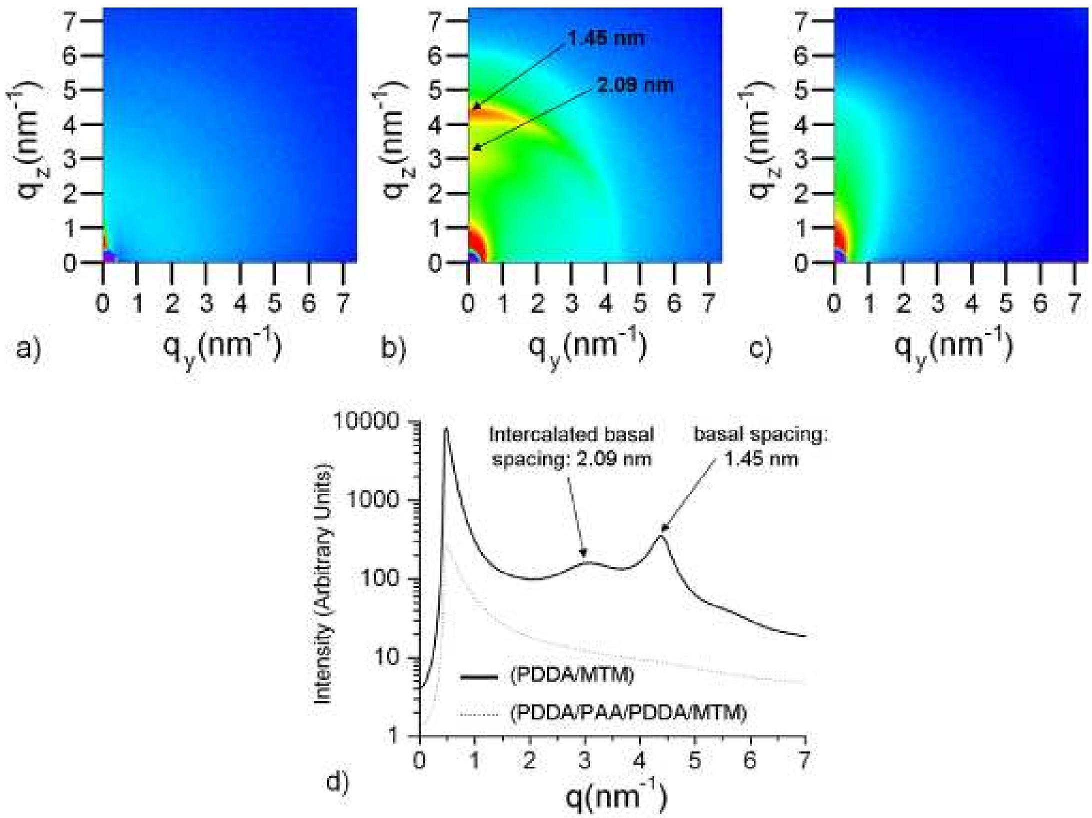

Figure S5. 2-D SAXS patterns of free-standing films of: a) $(PDDA/PAA)_{200}$; b) $(PDDA/MTM)_{300}$; and c) $(PEI/PAA/PEI/MTM)_{100}$. The scattering features of interest are indicated by arrows and the corresponding spacings are noted. d) 1-D SAXS patterns of free-standing films of $(PDDA/MTM)_{300}$ and $(PDDA/PAA/PDDA/MTM)_{100}$. These plots are radial integrations of the 2-D images shown in b) and c). The intensities were shifted for clarity. A strong peak indicating a basal spacing of 1.45 nm and an additional peak indicating a intercalated basal spacing of 2.09 nm is observed in the PDDA/MTM film. The lack of a clear scattering peak from the montmorillonite in the PDDA/PAA/PDDA/MTM film indicates a lower degree of organization either a wide range of intercalated basal spacings or exfoliation of the clay platelets.

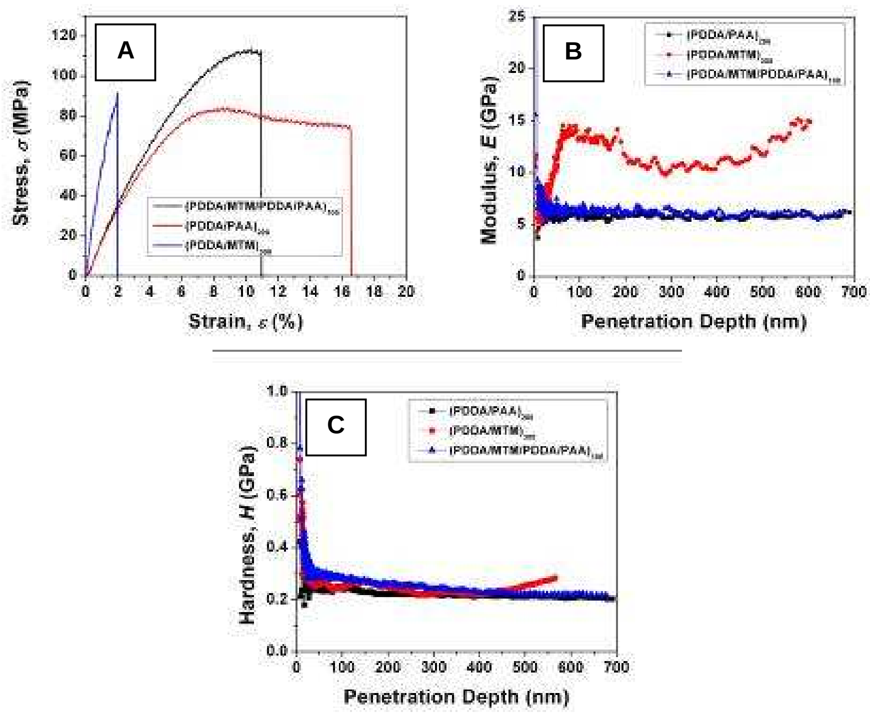

Figure S6. Representative results from tensile and nanoindentation tests for $(PDDA/MTM)_{300}$ with 5 min depositions, $(PDDA/PAA)_{200}$ with 30 sec depositions, and $(PDDA/MTM/PDDA/PAA)_{100}$ with 30 sec depositions.

Reference:

[1.] Z. Tang, N. A. Kotov, S. Magonov, B. Ozturk, *Nature Materials* **2003,** *2*, 413.

[2.] G. Brown, *The X-ray Identification and Crystal Structures of Clay Minerals*; Mineralogical Society: London, 1961.

[3.] R.-J. Roe, *Methods of X-ray and Neutron Scattering in Polymer Science*; Oxford University Press: New York, 2000.

[4.] B. Finnigan, K. Jack, K. Campbell, P. Halley, R. Truss, P. Casey, D. Cookson, S. King, D. Martin, *Macromolecules* **2005**, *38*, 7386.

[5.] J. L. Lutkenhaus, E. A. Olivetti, E. A. Verploegen, B. M. Cord, D. R. Sadoway, P. T. Hammond, *Langmuir* **2007**, *23*, 8515.

[6.] K. C. Cole, F. Perrin-Sarazin, G. Dorval-Douville, *Macromol. Symp.* 2005, 230, 1.