

## Structure Formation in Multilayered Films Prepared by the Layer-by-Layer Deposition Using PAA and HM-PEO

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### Introduction

The layer-by-layer (LbL) assembly is a well-established technique to prepare thin and versatile multilayered films based on various intermolecular interactions between pairing polymers. Thin and highly tunable platform can thus be easily achieved by the LbL assembly. In present study, poly(acrylic acid) (PAA) and hydrophobically modified poly(ethylene oxide) (HM-PEO) multilayers based on the hydrogen bonding between the component polymer pair have been prepared by the LbL deposition method and observed their unique properties and film morphology.

### Experimental

**Materials.** Hydrophobically modified poly(ethylene oxide) (HM-PEO,  $M_w = 35,000$  and  $20,000$  respectively), a urethane-coupled polyethylene oxide end-capped with alkyl groups ( $C_{22}$ ), was synthesized according to the method reported in the literature. Poly(acrylic acid) (PAA,  $M_w = 90,000$ ) was purchased from Polysciences Inc., and used as received. HCl and NaOH were used for pH adjustment. Teflon-AF 2400 (1 wt% solution) was obtained from DuPont Fluoroproducts and hexamethyl diisilazane (HMPS) was purchased from Aldrich. Both chemicals were used as received. Silicon wafer, Teflon, polypropylene (PP) and PDMS were used as substrate. Before using substrates, silicon wafer was cleaned under oxygen plasma (100 W, 0.1- 0.5 Torr, 5 min). Teflon and PP substrates were sonicated in Mili-Q water for 15 minutes prior to film deposition. PDMS were used as made.

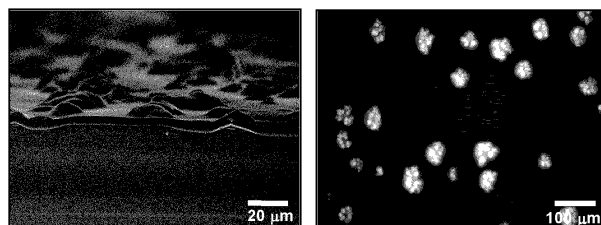
**Dip-Assembled Polyelectrolyte Multilayers.** All polyelectrolyte solutions were made as 0.02 M concentrations with respect to repeat unit in Mili-Q water. Films were obtained with Carl Zeiss DS50 programmable slide stainer. Substrates were first exposed to HM-PEO solution for 15 minutes, then to three baths of Mili-Q water for 2, 1, 1 minute respectively for washing weakly adsorbed polymer chains. HM-PEO coated substrates were exposed to PAA solution with same procedure. All baths were kept at pH 2.5 to prevent ionization of PAA. This cycle was repeated to build up polyelectrolyte multilayers. To investigate temperature effect on growth and surface properties of multilayers, polyelectrolyte multilayers were made at room temperature (25 °C) and 35 °C, respectively. After assembly, the films were dried by nitrogen blowing. Free-standing films were obtained by peeling away from substrate with tweezers directly.

**Morphology Characterization.** All thickness, roughness and 3D topography of assembled multilayers surfaces were characterized with Tencor P10 profilometer using 2 mm stylus tip and 5 mg stylus force. Thickness and roughness were measured by scratching the film down to the substrate. The average values were reported by measuring more than three times. The optical and fluorescence images of assembled multilayers were obtained with Zeiss Axioplan 2 fluorescence microscope (Carl Zeiss Inc.). Contact angle measurements were made on multilayer surfaces by using a VCA-2000 contact angle system (AST Products, Inc.). Scanning Electron Microscopy (SEM) images were obtained with JSM 6060 scanning electron microscope (JEOL Co.). Images of Free-standing films were captured with Nikon Coolpix 2500.

**Composition Analysis.** Free-standing polyelectrolyte multilayers were characterized with TGA and DSC. Samples were heated by TA Instruments Q50 from room temperature to 700 °C with nitrogen purge. Heating rate was 10 °C/min. TA Instruments Q1000 was used to obtain the DSC data. Second scan values were reported from -90 °C to 110 °C at a rate of 10 °C/min with a nitrogen purge. To minimized humidity effect, all samples were dried for 30min in nitrogen purge before measured.

### Results and discussion

To investigate the effect of alkyl chains linked with urethane group on the both end of PEO chain, we compare the pure PEO/PAA and the HM-PEO/PAA multilayer system within similar molecular weight. The bilayer thickness of HM-PEO/PAA multilayers was 8 times higher than PEO/PAA multilayers and the surface structures were obtained within building up procedure. Individual HM-PEO micelles were connected through the bridging PEO chains to form temporary networks on multilayer surface and induced peculiar surface morphology on HM-PEO/PAA multilayers above the critical number of bilayers. These were studied with optical microscope as well as fluorescence microscope with pyrene dyes that allows us to monitor the sites of HM-PEO micelles.



**Figure 1.** The cross-sectional SEM image and fluorescence microscope image of (HM-PEO35k/PAA)<sub>30</sub> multilayers

It is also noted that the film morphology can also be controlled by changing the solvent polarity. By adding alcohol into water, the water polarity decreases and the hydrophobic association between alkyl chains is effectively suppressed, yield the disappearance of such unique surface structures. In addition to the solvent effect, the surface structure was also shown to be tunable with temperature, molecular weight of HM-PEO and the assembly method.

To study the temperature effect on multilayer fabrication, HM-PEO/PAA multilayers were built up at 25 °C room temperature and 35 °C, respectively. Hydrophobic associations were accelerated at 35 °C, due to the increasing flexibility of PEO chains and the decreasing hydrogen bonding between PEO and PAA. Low molecular weight HM-PEO20k which was end-capped same alkyl chains was used to observe the molecular effect on multilayers. Small grains were formed densely on surface of the HM-PEO20k/PAA multilayers than HM-PEO35k/PAA multilayers due to the restricted chain rearrangement and connectivity between HM-micelles owing to the short PEO chain.

Because HM-PEO has hydrophobic moiety which reduce the adsorption energy between multilayer and substrate, free-standing HM-PEO/PAA multilayers were obtained by direct peel off from many kind of substrate. Their composition and thermal properties were also obtained using TGA and DSC measurements. By these measurements, we noticed that the composition of HM-PEO/PAA multilayers was changed as a function of the number of bilayers.

### Conclusions

Dip assembled HM-PEO/PAA multilayers yield unique film morphologies in comparison with PEO/PAA multilayers due to the micellar formation of HM-PEO owing to the hydrophobic attraction between alkyl chains end-capped with the PEO chains. Free-standing multilayered HM-PEO/PAA thin films can also be obtained, which allow us to characterize the composition and physical properties of such thin polymer multilayers in more detail. It is noted that the introduction of hydrophobic moieties in the multilayers facilitates the peel-off from many different types of substrates, yielding free-standing multilayers. HM-PEO/PAA multilayer will be good candidate to alternative solid polymer electrolyte in fuel cell instead of Nafion membranes and especially large area free-standing polymer electrolytes have great potential for many applications on device.

### References

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