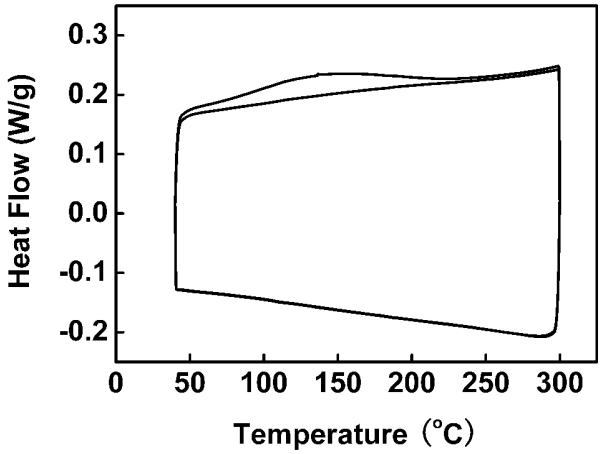
Supplementary Material (ESI) for Soft Matter

Thermochemical properties of free-standing electrostatic layer-by-layer assemblies containing poly(allylamine hydrochloride) and poly(acrylic acid)

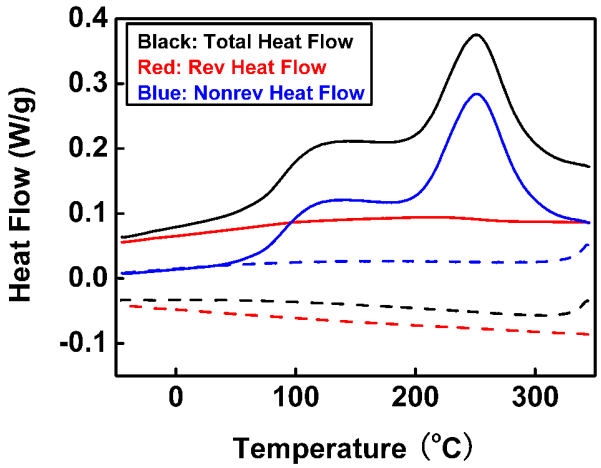
Lin Shao and Jodie L. Lutkenhaus

Department of Chemical Engineering, Yale University, New Haven, Connecticut. 06520

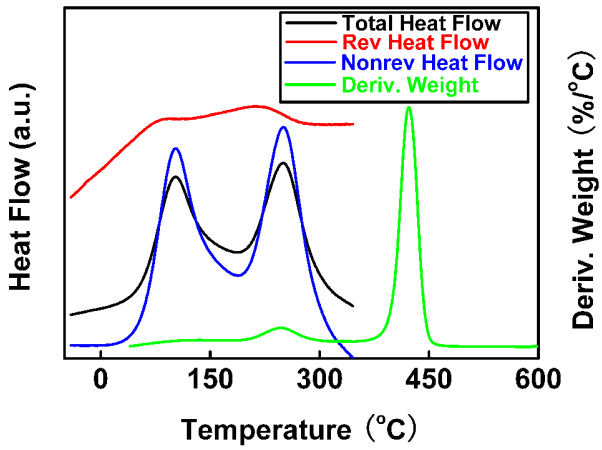
E-mail: jodie.lutkenhaus@yale.edu



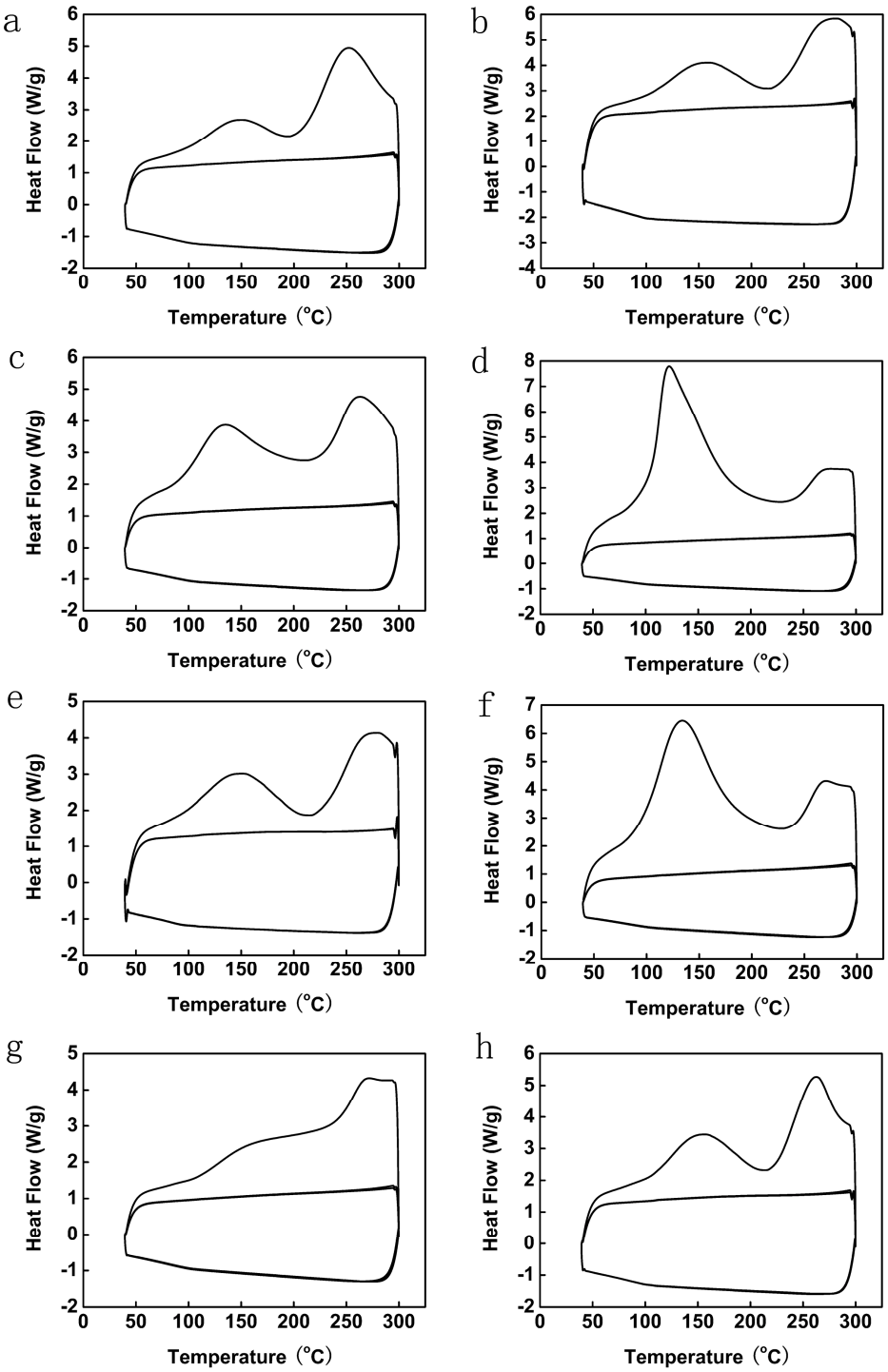
Supporting Figure 1. DSC thermogram of a free-standing $PAH_{7.5}/PAA_{3.5}$ LbL film, which had been exposed to air for three hours following a prior DSC test. Heating and cooling rate is 10 °C/min.



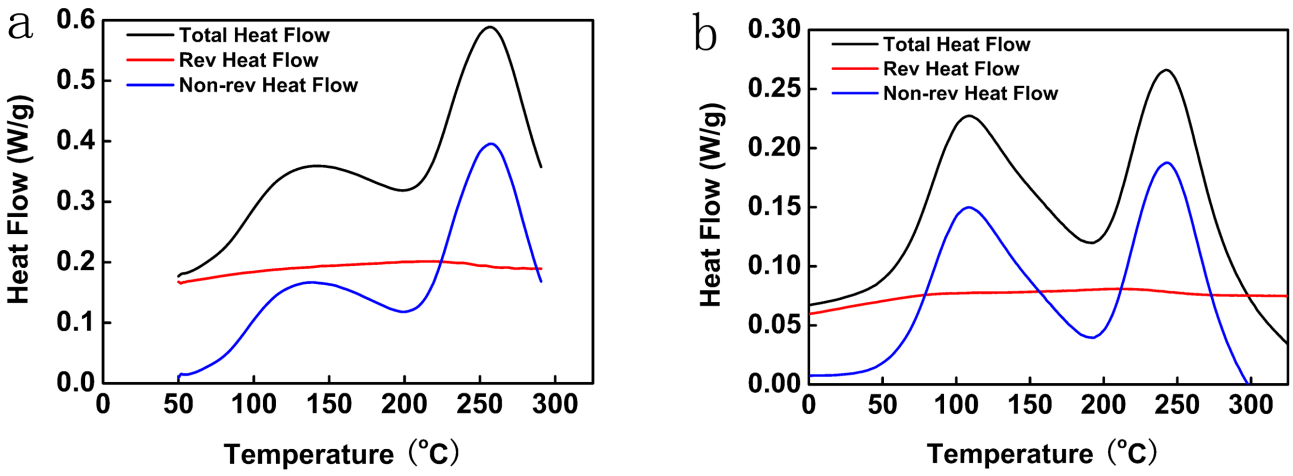
Supporting Figure 2. MDSC heating (solid line) and cooling (dashed line) of a free-standing $PAH_{7.5}/PAA_{3.5}$ LbL film. Heating and cooling rate is 3 °C/min.



Supporting Figure 3. MDSC and TGA thermograms of a free-standing $PAH_{7.5}/PAA_{3.5}$ LbL film. The left y-axis is heat flow, where the MDSC curves have been stretched along the y-axis for clarity. The right y-axis is the derivative of weight with respect to temperature from TGA.



Supporting Figure 4. DSC thermograms of free-standing PAH/PAA LbL films fabricated from assembly solutions of various pH values. (a) $PAH_{4.5}/PAA_{2.5}$ LbL film; (b) $PAH_{4.5}/PAA_{3.5}$ LbL film; (c) $PAH_{7.5}/PAA_{2.5}$ LbL film; (d) $PAH_{7.5}/PAA_{3.5}$ LbL film; (e) $PAH_{4.5}/PAA_{4.5}$ LbL film; (f) $PAH_{7.5}/PAA_{4.5}$ LbL film; (g) $PAH_{6.5}/PAA_{6.5}$ LbL film; (h) $PAH_{8.5}/PAA_{7.5}$ LbL film. Heating and cooling rate is 50 °C /min. All PAH/PAA LbL films investigated showed two thermal events (~120 and ~250 ºC) upon heating, which suggested that all PAH/PAA LbL films undergo anhydride formation and amidation upon heating. In all samples, no apparent glass transition was observed. The kink in the cooling curve at 50 – 100 ºC is an artifact from the instrument.



Supporting Figure 5. MDSC thermograms (a) of a free-standing $PAH_{6.5}/PAA_{6.5}$ LbL film at a heating rate of 5°C /min and (b) of a free-standing $PAH_{4.5}/PAA_{3.5}$ LbL film at a heating rate of 3°C /min.

Supporting Table 1. Weight loss in different temperature range

PAA	40-190 °C	190-25 °C	250- 345 °C	345-550 °C
	5.9%	9.9%	24.3%	44.3%
	loosely bound water; water from of anhydride formation (intramolecular)	water from anhydride formation (intermolecular)	decarboxylation of anhydride groups	scission of the main polymer backbone
PAH	40-150 °C	150-370 °C	370-550 °C	
	3.3%	50.0%	41.7%	
	loosely bound water	scission of the amine side-chains	scission of the polymer backbone	
LbL	40-150 °C	150-330 °C	330-550 °C	
	5.1%	16.2%	67.4%	
	loosely bound water	Water loss from amidation and anhydride formation, decarboxylation, scission of the amine side-chains	scission of the polymer backbone	