

Supporting information:

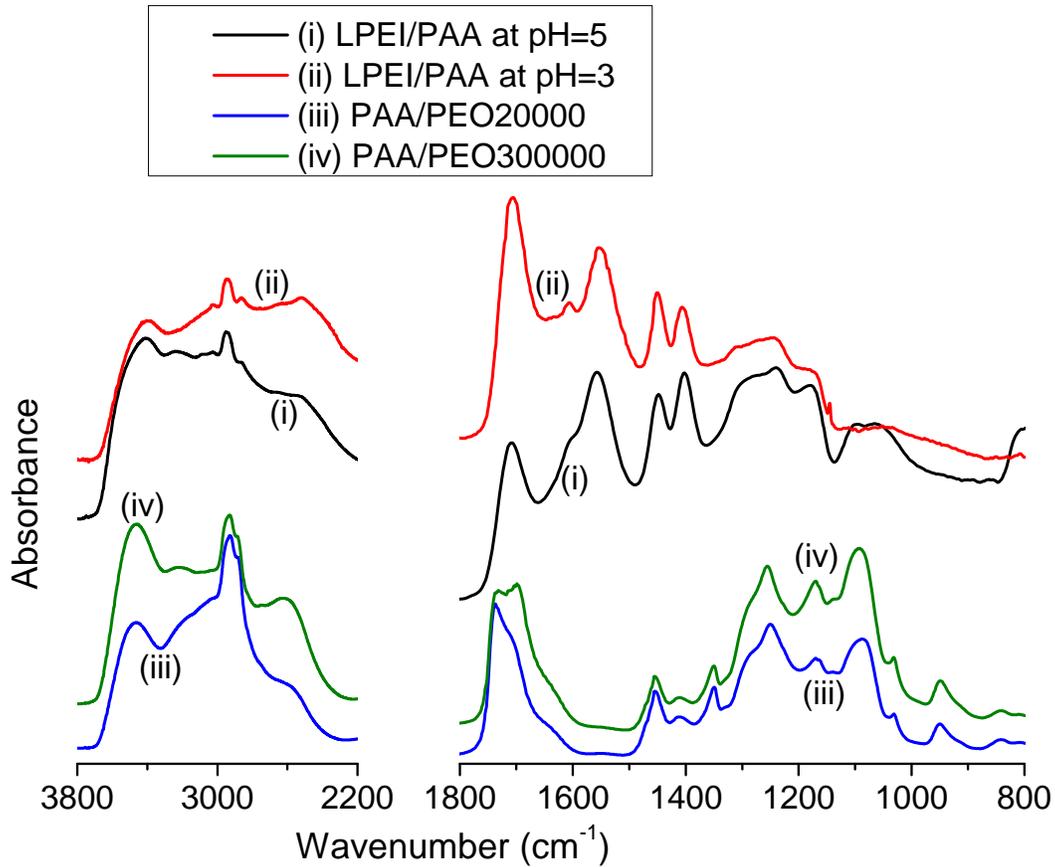


Figure S1 - FTIR data for various bilayer LBL films with electrostatic bonding LPEI/PAA (i) & (ii) or hydrogen bonding PAA/PEO (iii) & (iv).

Figure S1 presents the infrared spectra for the dried bilayer samples of LPEI/PAA and PAA/PEO in the region of hydroxyl O-H and carbonyl C=O stretching, typical for carboxylic group in PAA molecules. It can be clearly seen that ionized  $\text{COO}^-$  peaks ( $1554\text{ cm}^{-1}$ ) are absent from the spectra of the PAA/PEO samples, indicating a high degree of COOH protonation even assembled at pH=3. Evidence of hydroxyl-hydrogen bonding is found with the broad band around  $3100\text{ cm}^{-1}$  observed in PAA/PEO20K sample. On the other hand, broad composite band centered around  $2620\text{ cm}^{-1}$  was seen the in PAA/PEO300K sample, which was attributed to the harmonic coupling of the O-H stretching ( $\nu_s$ ) and  $\text{H}\cdots\text{O}$  stretching ( $\sigma_s$ ) mode) [1]. Broad bands at  $840\text{ cm}^{-1}$  were also

observed in the spectra of both PAA/PEO samples, indicating the disorder structure of PEO molecules in the hydrogen bonding bilayer film [2].. The COOH peak in PAA/PEO300K was seen to split into two peaks of carboxylic acid – ether oxygen interaction ( $1732\text{ cm}^{-1}$ ) and carboxylic acid dimer ( $1699\text{ cm}^{-1}$ ) with the intensity of the latter being slightly higher. On the other hand, the carboxylic acid – ether oxygen peak was seen to dominate in the PAA/PEO20K sample.

Bands at  $949$  and  $842\text{ cm}^{-1}$  correspond to the C-O stretching and  $\text{CH}_2$  rocking mode for PEO molecules in the presence of LiTF salt [3]. Especially, the low-intensity but sharp peaks at  $1032\text{ cm}^{-1}$  originated from the symmetric stretching of  $\text{SO}_3$  group, indicating “free” triflate ions due to formation of PEO-LiTF complexes. This suggests the incorporation of Li salt into the PAA/PEO bilayer.

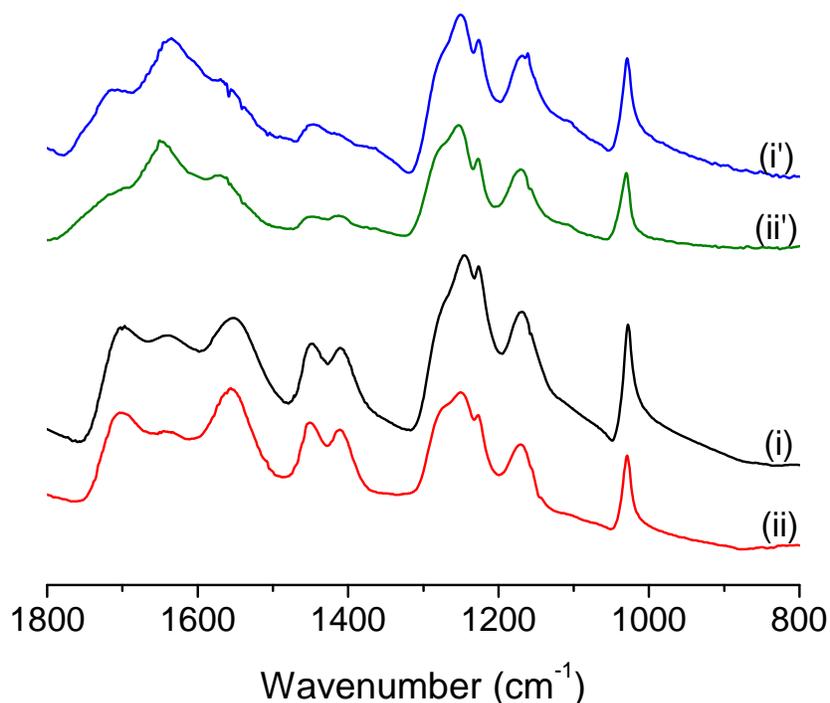


Figure S2 – IR spectroscopic data of dry-state tetralayer samples with PEO 20K (i, i') and PEO 300K (ii, ii') in original state (i, ii) and after being heated to  $180^\circ\text{C}$  (i', ii').

Figure S2 shows the spectra of the dry-state samples measured after being heated to 180°C for 15 minutes. Strong bands indicative of amide formation by thermal cross-linking between the amine and carboxylic groups (LPEI/PAA) could be observed at 1635 and 1651  $\text{cm}^{-1}$  for tetralayer with PEO 20K and 300K, respectively. These new peaks were accompanied by the disappearance of both COOH ( $\sim 1730 \text{ cm}^{-1}$ ) and COO<sup>-</sup> ( $\sim 1555 \text{ cm}^{-1}$ ) bands. On the other hand, bands at 1249  $\text{cm}^{-1}$  also grew sharper which was probably contributed by the stronger CH<sub>2</sub> twisting mode from PEO molecular chains indicative of a structural change.

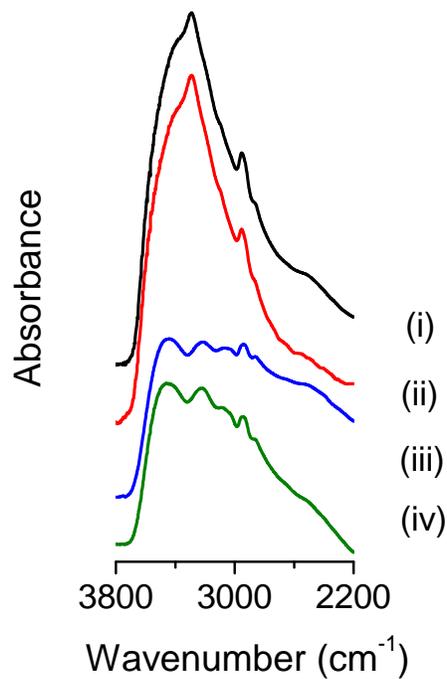


Figure S3 – FTIR data for tetralayer LBL films with PEO molecular weight of 20K (i, iii) and 300K (ii, iv) in wet (i, ii) and dry (iii, iv) -state.

Figure S3 presents the hydroxyl stretching region (3800-2200  $\text{cm}^{-1}$ ) of the wet-state samples with the dominance of sharp bands at 3289  $\text{cm}^{-1}$  and shoulder bands at  $\sim 3400 \text{ cm}^{-1}$ . The broad O-H stretching absorption band centered at 3200  $\text{cm}^{-1}$  has been correlated to a distribution of various modes for the hydroxyl groups in the neat PAA

films [1]. In the blends with PEO at higher concentration of PAA, this band can be resolved into two bands centered at  $\sim 3450$  and  $\sim 3100$   $\text{cm}^{-1}$ . For the higher concentration PEO blends, the lower band was observed and correlated to the existence of hydrogen bonding only between the acid groups and ether oxygen atoms. The higher O-H absorption bands observed in the wet-state samples indicated the dominant existence of non-cyclic single or multiple hydrogen bonds and cyclic dimers as compared to the free hydroxyl groups. This was caused by the higher moisture content in the samples due to the exposure humidity (90%RH for 2 hours) which led to more flexibility in the polymer chains and weakening of the intermolecular H-bond. For the dry-state samples, the O-H absorption bands were clearly observed at  $\sim 3445$ ,  $\sim 3219$ , and  $\sim 3068$   $\text{cm}^{-1}$  which indicates a mixture of all of the mentioned modes for the hydroxyl groups.

1. X. Lu and R. A. Weiss, *Macromolecules* 28 (1995) 3022.
2. J. Y. Lee, P. C. Painter, and M. M. Coleman, *Macromolecules* 21 (1988) 346.
3. R. Frech, S. Chintapalli, P. G. Bruce, and C. A. Vincent, *Macromolecules* 32 (1999) 808.