Electronic Supplementary Information (ESI)

Non-destructive determination of functionalized polyelectrolyte placement in layer-by-layer films by IR ellipsometry

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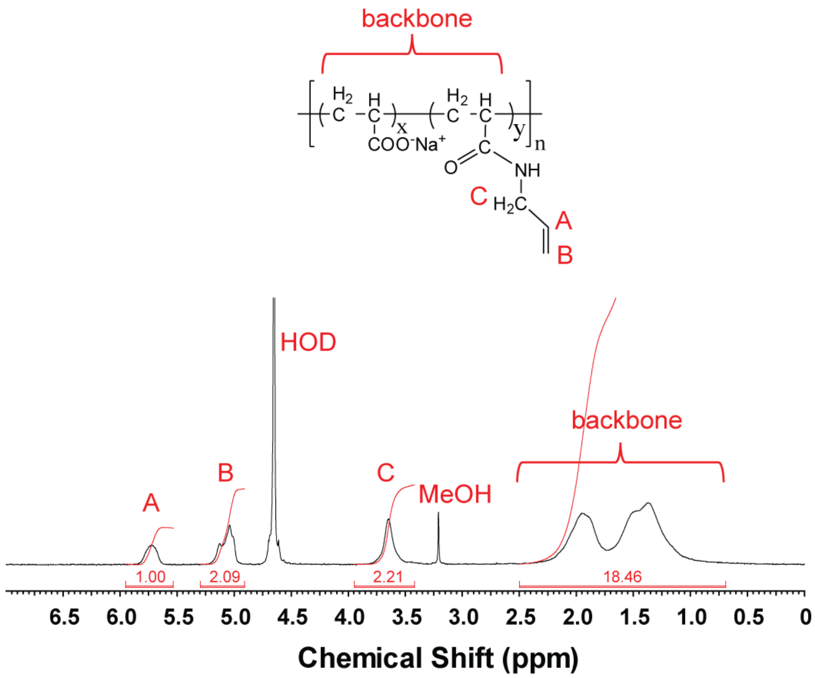

Figure S1. ^{1}H NMR spectra for the allyl-PAA in D_2O.

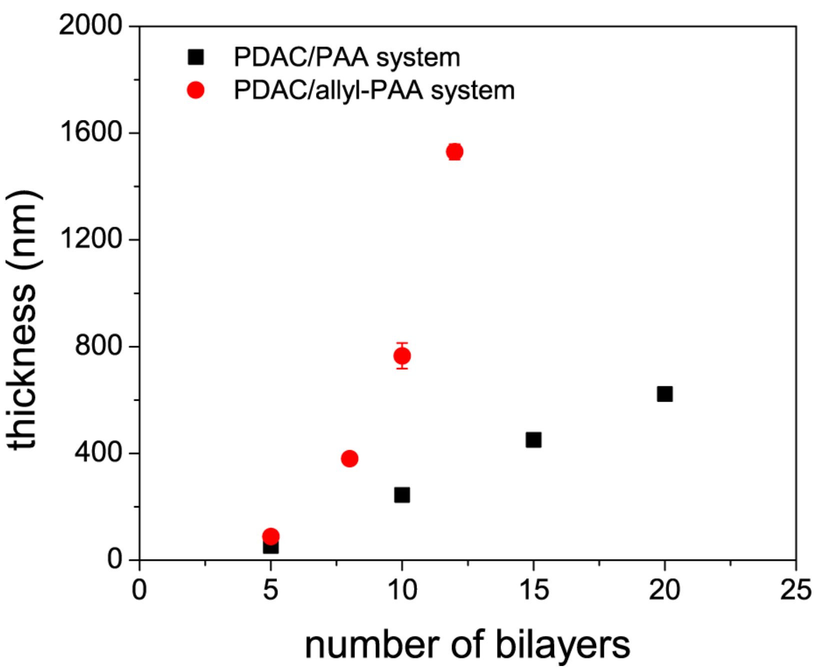

Figure S2. Kinetics for the film growth by Layer by layer (LbL) deposition of (■) PDAC/PAA and (●) PDAC/allyl-PAA. Linear growth is observed for PDAC/PAA, while the growth rate with the PDAC/allyl-PAA increases as additional bilayers are deposited.

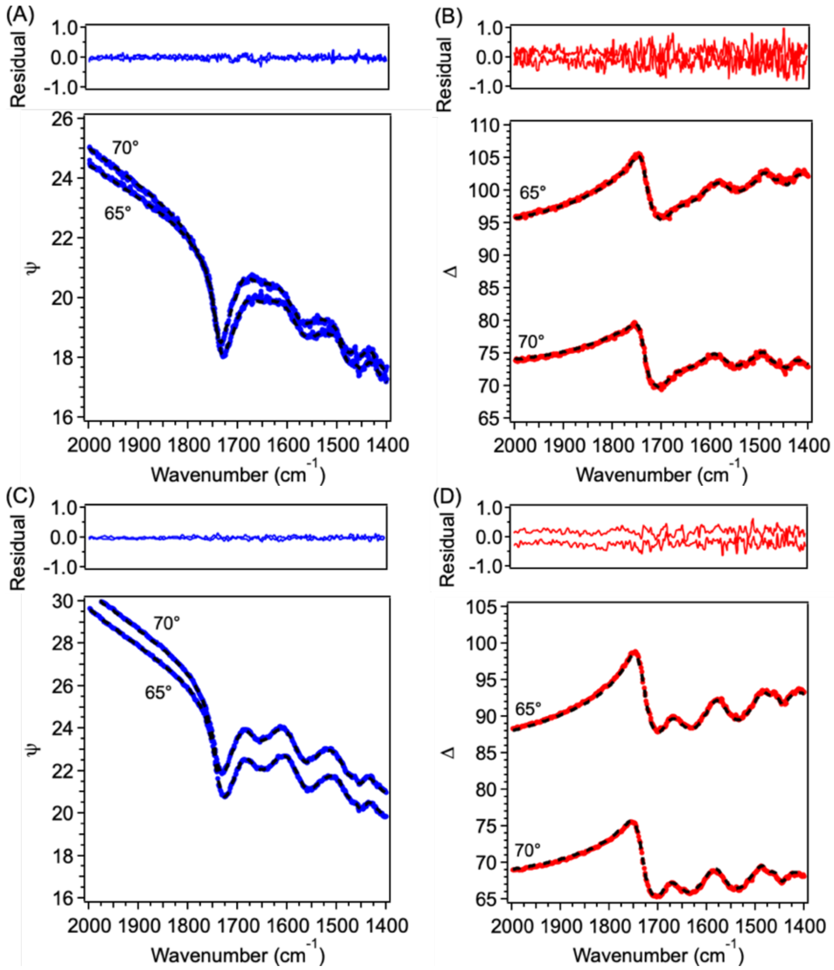

Figure S3. Ellipsometric angles (Ψ, Δ) for (a,b) 495nm $(PDAC/PAA)_{17}$ and (c,d) 643 nm $(PDAC/allyl\text{-}PAA)_9$ films as a function of wavenumber in the IR. The dashed black lines are the best fits to the ellipsometric data using a Kramers-Kronig consistent general oscillator model that describes the absorption in the films as Gaussian oscillators.

There was some difference in the fitting between the two films where additional oscillators were needed to fit the finer structures of $(PDAC/allyl\text{-}PAA)_9$. Some of the added oscillators can be attributed to the allyl group and some small shifts in the absorption of groups adjacent to the added allyl groups.

Table S1. Gaussian oscillators fit to describe the ellipsometric data for the $(PDAC/PAA)_{17}$ and $(PDAC/allyl\text{-}PAA)_9$ films.

Oscillator #	$(PDAC/PAA)_{17}$			$(PDAC/allyl\text{-}PAA)_9$		
	Amplitude	Energy (cm^{-1})	Width (cm^{-1})	Amplitude	Energy (cm^{-1})	Width (cm^{-1})
1				0.52558	1240.4	76.764
2				0.083935	1343.7	62.183
3	0.30346	1386.2	93.435	0.28087	1391.5	264.95
4				0.043343	1396.7	36.482
5	0.16996	1451.3	20.815	0.11589	1449.9	19.033
6	0.255599	1475.7	30.877	0.077308	1472.6	23.631
7	0.090084	1510.1	37.45	0.086498	1529.5	39.035
8	0.25539	1560	57.02	0.23154	1557.2	43.168
9				0.073201	1644.4	41.502
10	0.23554	1684.5	127.68	0.29855	1659.1	116.74
11	0.53075	1718.1	34.629	0.34894	1715.1	39.616
12				0.089734	1961.2	761.98

It should be noted that experimentally determining the optical constants for the different individual components can be critical to obtaining reasonable fits. This is also true of substrates where any doping of the silicon will alter the absorption in the IR due to mobile charge carriers and thus initial fits of the silicon by IR SE is recommended. Similarly, glass substrates should also be fit independently prior to examination of polymer films when using IR SE as the surfaces of glass can have different optical properties than the bulk.

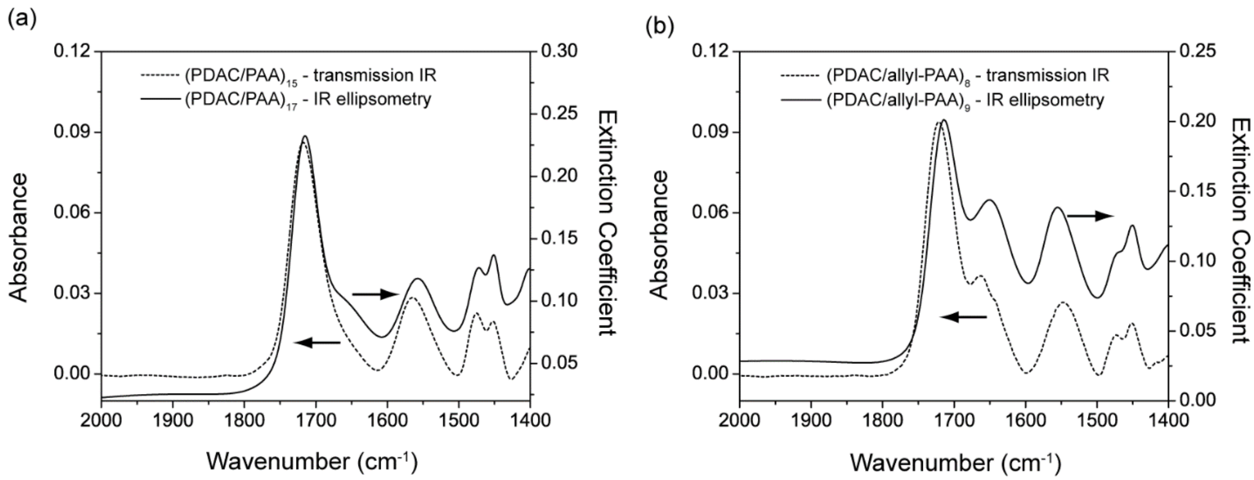

Figure S4. Comparison of the (- - -) transmission IR spectra and the (—) extinction coefficients determined from IR-VASE for (a) PDAC/PAA and (b) PDAC/allyl-PAA films.

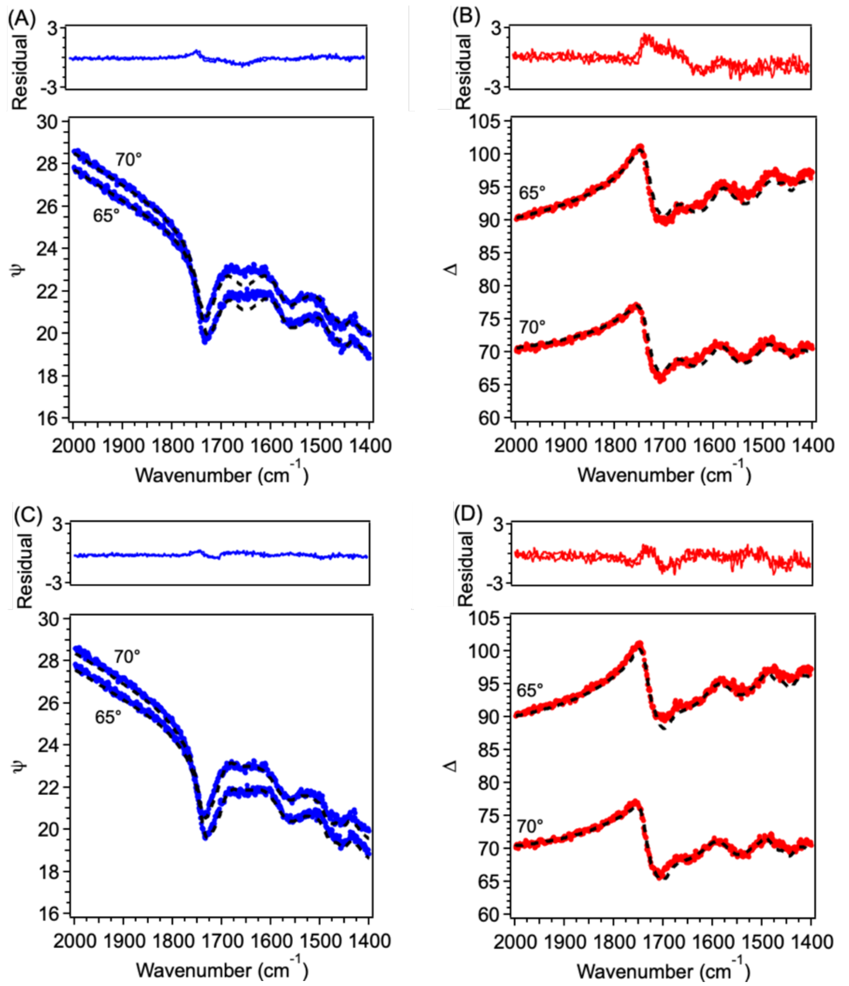

Figure S5. Ellipsometric angles (Ψ, Δ) for (PDAC/allyl-PAA)$_2$ on (PDAC/PAA)$_{12}$ with fits using (a,b) optical constants from PDAC/allyl-PAA alone, (c,d) optical constants from PDAC/PAA alone.

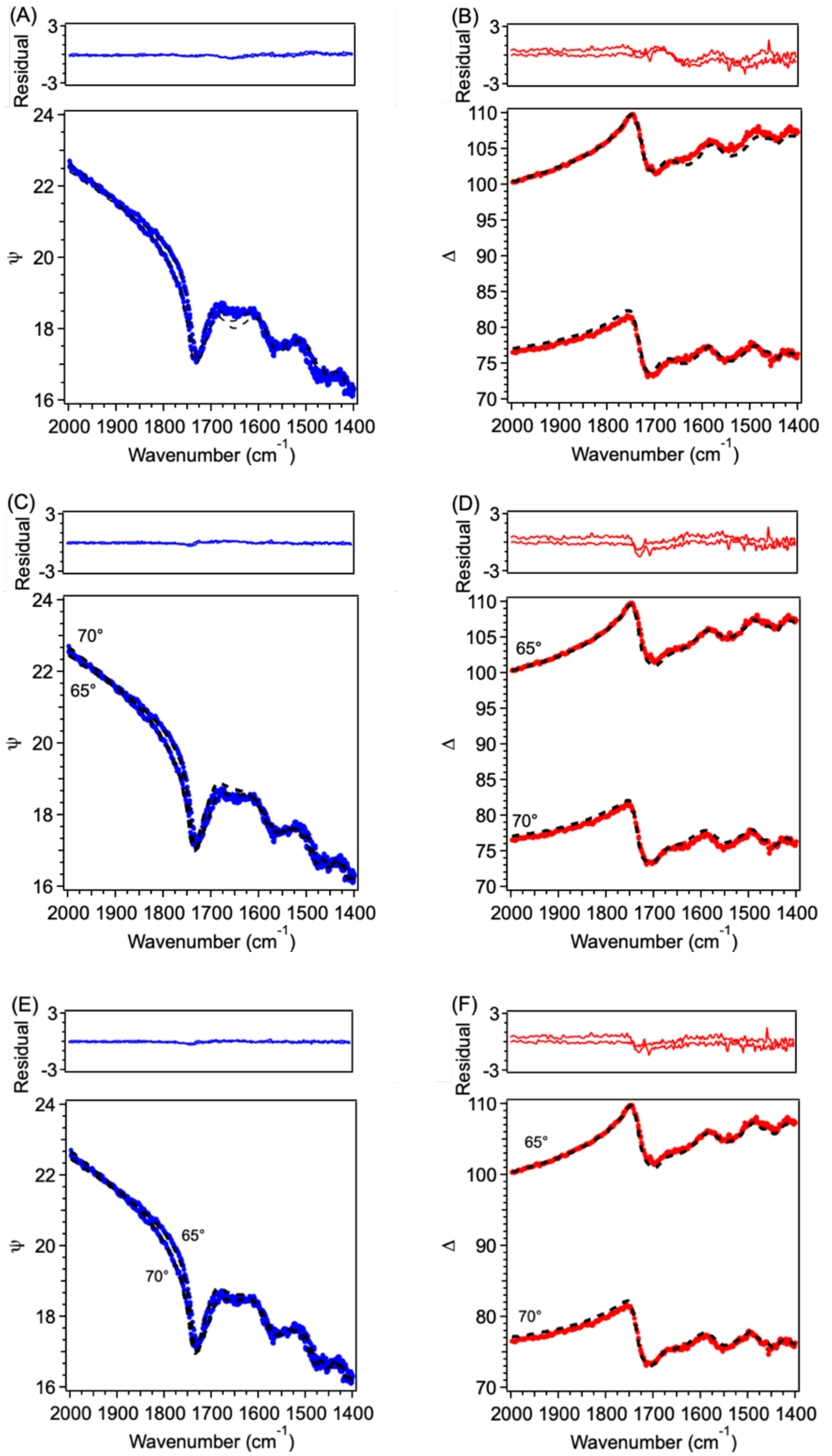

Figure S6. Ellipsometric angles (Ψ, Δ) for $(PDAC/PAA)_5$ on $(PDAC/ allyl\text{-}PAA)_6$ with fits using (a,b) optical constants from PDAC/allyl-PAA alone, (c,d) optical constants from PDAC/PAA alone, and (e,f) to a bilayer model with a graded interface. The compositional profile used for the fits in (e,f) is shown in Figure 4A.

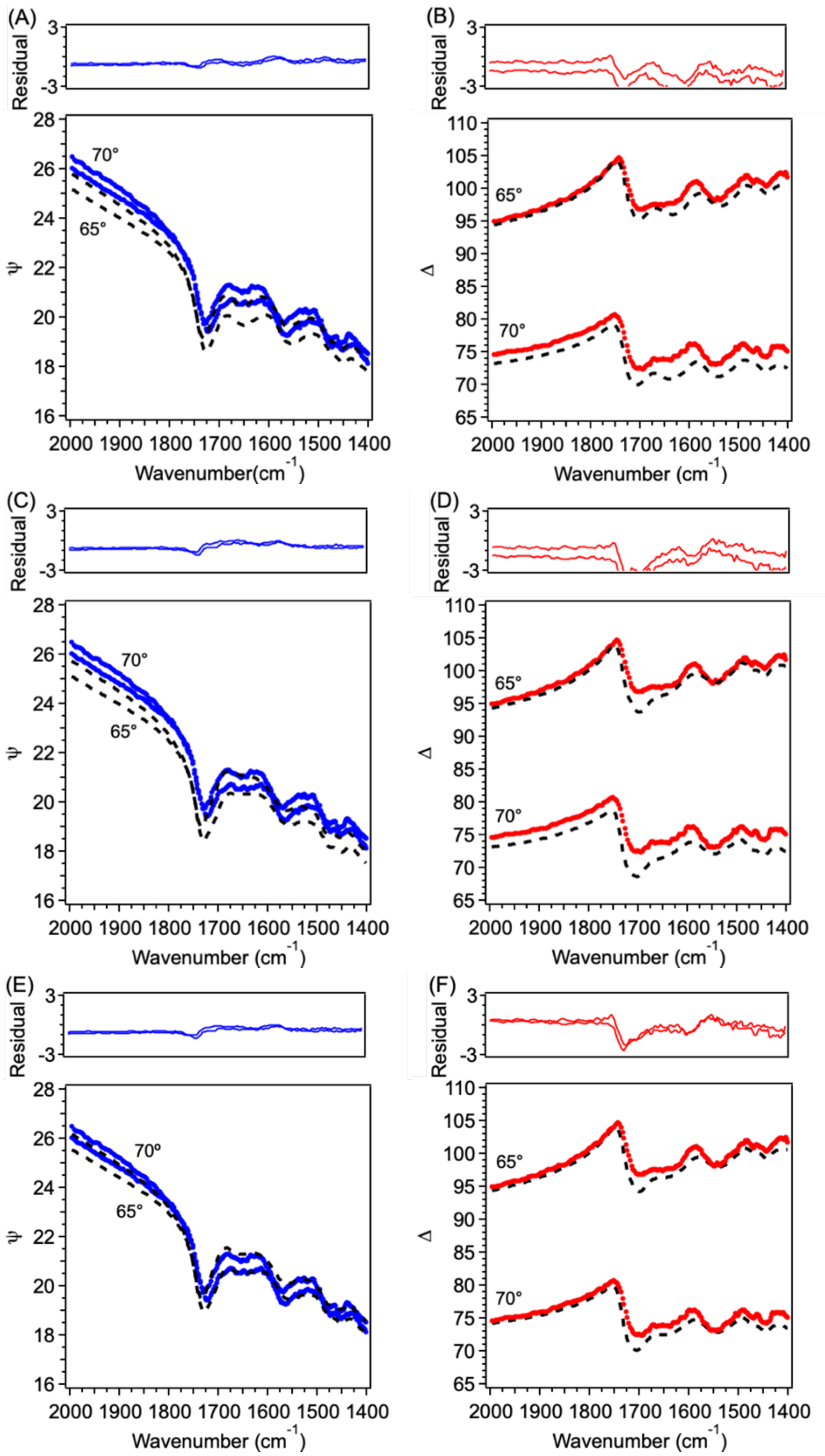

Figure S7. Ellipsometric angles (Ψ, Δ) for $(PDAC/PAA)_2$ on $(PDAC/\ allyl\text{-}PAA)_2$ on $(PDAC/PAA)_8$ with fits using (a,b) optical constants from PDAC/allyl-PAA alone, (c,d) optical constants from PDAC/PAA alone, and (e,f) to a trilayer model with graded interfaces.