Electronic Supplementary Material (ESI) for Soft Matter.

Electronic Supporting Information for:

# Interpolymer Complexes of Poly(Sulfonic Acid)s and Poly(Ethylene Oxide): An Unexpected Association

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# 1. Assignments of FTIR bands for PSSA/PEO and Nafion/PEO

**Table S1. Summary of absorption bands in the IRRAS spectra of PSSA/PEO LbL film in Figures 4a and 5a in the main text.**

| Wavenumber / $cm^{-1}$ | Polymer | Assignment | Refs. |
|---|---|---|---|
| 946 | PEO | $CH_2$ rocking | 1 |
| 1035 | PSSA | symmetric stretching $SO_3^-$ | 2,3 |
| 1100 | PEO | symmetric and asymmetric COC stretching vibrations, CC stretch and $CH_2$ rocking vibrations | 4 |
| 1130 | PSSA | symmetric stretching of the $SO_2$ | 2,3,5 |
| 1184, 1213 | PSSA | antisymmetric stretching $SO_3^-$ | 2,3 |
| 1352 | PEO | wagging $CH_2$ | 1,6 |
| 1453 | PEO | scissor/deformation $CH_2$ | 6 |
| 1650 | PEO and PSSA | water bending mode | 2,3,7 |
| 2848, 2886, 2921 | PEO and PSSA | C-H aliphatic str. | 3 |
| 3053 | PSSA | C-H aromatic str. | 3 |
| 3053 | PSSA/PEO IPC | O-H stretching in $SO_3H$/ether complex | This work |
| 3194 | PSSA/PEO IPC | No definitive assignment, may be related to hydrated $H_3O^+$ | This work, 7,8 |
| 3454 (broad) | | water O-H stretching modes | 9 |

**Table S2**. Summary of absorption bands in the IRRAS spectra of Nafion/PEO LbL film in Figures 4b and Figure 5b in the main text.

| Wavenumber / $cm^{-1}$ | Polymer | Assignment | Ref |
|---|---|---|---|
| 946 | PEO | $CH_2$ rocking | 1 |
| 977 | Nafion | C–O–C and C-F stretching modes | 10 |
| 1065 | Nafion | symmetric stretching $SO_3^-$ | 2,3,10 |
| 1100 | PEO | symmetric and asymmetric COC stretching vibrations, CC stretch and $CH_2$ rocking vibrations | 4 |
| 1163 | Nafion | $CF_2$ symmetric stretching | 10 |
| 1258 | Nafion | $CF_2$ asymmetric stretching | 10 |
| 1300 | Nafion | $CF_2$ backbone | 10 |
| 1352 | PEO | wagging $CH_2$ | 1,6 |
| 1453 | PEO | scissor/deformation $CH_2$ | 6 |
| 1650 (broad) | PEO and PSSA | water bending mode | 2,3,7,10 |
| 2886 | PEO | C-H aliphatic str. | 3 |
| 3065 | Nafion/PEO IPC | O-H stretching in $SO_3H$/ether complex | This work |
| 3183 | Nafion/PEO IPC | No definitive assignment, may be related to hydrated $H_3O^+$ | This work, 7,8 |
| 3454 (broad) | | water O-H stretching | 9 |

## 2. IRRAS Spectrum of PAA/PEO LbL Films

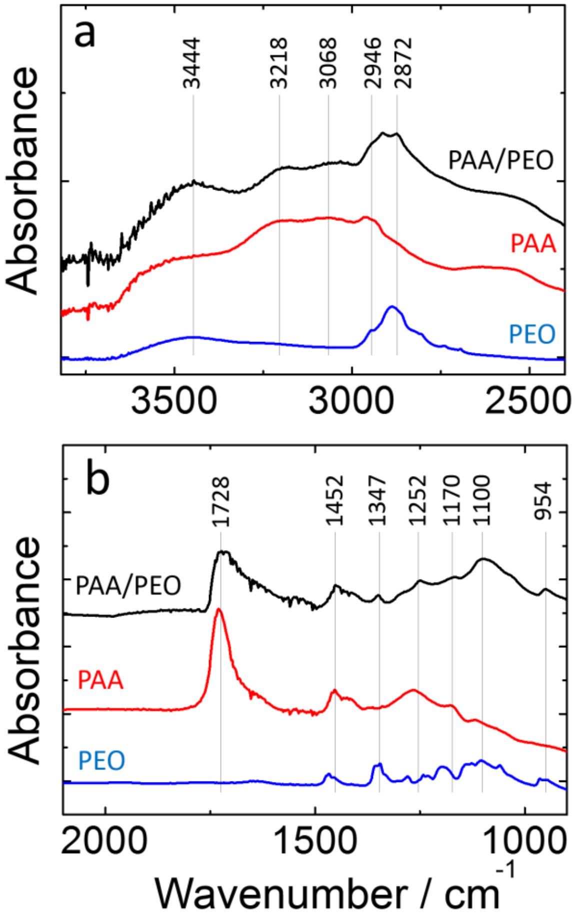


**Figure S1.** Infrared (IRRAS) spectra in the 3600-2400 cm$^{-1}$ (a) and 2100-900 cm$^{-1}$ (b) spectral regions of PAA/PEO LbL (same film as in Figure 3 in the main text) and dropcasted polymer films (PAA and PEO).

**Table S3.** Summary of absorption bands in the IRRAS spectra of PAA/PEO LbL film in Figure S1.

| Wavenumber / $cm^{-1}$ | Polymer | Assignment | Ref |
|---|---|---|---|
| 954 | PEO | $CH_2$ rocking | 1 |
| 1100 | PEO | symmetric and asymmetric COC stretching vibrations, CC stretch and $CH_2$ rocking vibrations | 4 |
| 1170 | PAA | C-O stretching | 11 |
| 1252 | PAA | C-O stretching | 11 |
| 1347 | PEO | wagging $CH_2$ | 1,6 |
| 1452 | PEO | scissor/deformation $CH_2$ | 6 |
| 1452 | PAA | scissor/deformation $CH_2$ | |
| 1728 | PAA | C=O stretching in COOH | 4,12 |
| 2872 and 2946 | PEO and PAA | C-H aliphatic str. | 3,11 |
| 3218 (broad) | PAA | O-H stretching in free and associated COOH | 12 |
| 3454 (broad) | | water O-H stretching<br>O-H stretching in free COOH | 9,12 |

# 3. Additional Information for Electronic Structure Calculations

**Table S4**. Energy of formation of hydrogen-bonded acid/ether complexes determined from electronic structure calculation of small-molecule analogs.

| | B3LYP/aug-cc-pVDZ | MP2/6-311++G(d,p) | MP2/ aug-cc-pVDZ |
|---|---|---|---|
| $\Delta E_{HB}$ / Hartree | | | |
| $CH_3COOH\cdots O(CH_3)_2$ | -0.01222 | -0.01647 | -0.01651 |
| $CH_3SO_3H\cdots O(CH_3)_2$ | -0.01608 | -0.02377 | -0.02217 |
| $C_6H_6SO_3H\cdots O(CH_3)_2$ | -0.01503 | -0.02530 | -0.02715 |
| $\Delta E_{HB}$ / kJ/mol | | | |
| $CH_3COOH\cdots O(CH_3)_2$ | -32.07 | -43.24 | -43.32 |
| $CH_3SO_3H\cdots O(CH_3)_2$ | -42.21 | -62.39 | -58.19 |
| $C_6H_6SO_3H\cdots O(CH_3)_2$ | -39.45 | -66.40 | -71.26 |
| $\Delta E_{HB}$ / $k_BT$ (T = 298 K) | | | |
| $CH_3COOH\cdots O(CH_3)_2$ | -12.94 | -17.45 | -17.49 |
| $CH_3SO_3H\cdots O(CH_3)_2$ | -17.04 | -25.18 | -23.49 |
| $C_6H_6SO_3H\cdots O(CH_3)_2$ | -15.92 | -26.80 | -28.76 |

**Table S5**. Correction of MP2/aug-cc-pVDZ energies with the zero-point energies.

| | MP2/aug-cc-pVDZ | ZPE | Total |
|---|---|---|---|
| $\Delta E_{HB}$ / Hartree | | | |
| $CH_3COOH\cdots O(CH_3)_2$ | -0.01651 | 0.001833 | -0.01467 |
| $CH_3SO_3H\cdots O(CH_3)_2$ | -0.02217 | 0.001234 | -0.02094 |
| $C_6H_6SO_3H\cdots O(CH_3)_2$ | -0.02715 | 0.002643 | -0.02451 |
| $\Delta E_{HB}$ / kJ/mol | | | |
| $CH_3COOH\cdots O(CH_3)_2$ | -43.32 | 4.81 | -38.51 |
| $CH_3SO_3H\cdots O(CH_3)_2$ | -58.19 | 3.24 | -54.95 |
| $C_6H_6SO_3H\cdots O(CH_3)_2$ | -71.26 | 6.93 | -64.32 |
| $\Delta E_{HB}$ / $k_BT$ (T = 298 K) | | | |
| $CH_3COOH\cdots O(CH_3)_2$ | -17.49 | 1.94 | -15.54 |
| $CH_3SO_3H\cdots O(CH_3)_2$ | -23.49 | 1.31 | -22.18 |
| $C_6H_6SO_3H\cdots O(CH_3)_2$ | -28.76 | 2.80 | -25.96 |

# 4. Coupled Chemical Equilibria Model

We consider a simple model of coupled equilibria in order to estimate the effect of the formation of the hydrogen bond on the apparent acid-base equilibrium constant. Let as consider the following equilibria:

$$P-SO_3H \xrightleftharpoons{Ka} P-SO_3^- + H^+ \tag{S1}$$

$$P-SO_3H + PEO \xrightleftharpoons{K_f} P-SO_3H\cdots PEO \tag{S2}$$

, where *P-* indicates the polymeric backbone. The corresponding equilibrium equations (assuming unitary activity coefficients and a homogeneous system) are:

$$Ka = \frac{\left[P-SO_3^-\right]\left[H^+\right]}{\left[P-SO_3H\right]} \tag{S3}$$

and,

$$K_f = \frac{\left[P-SO_3H\cdots PEO\right]}{\left[P-SO_3H\right]\left[PEO\right]} \tag{S4}$$

Let us now denote the fractions of P-$SO_3^-$ and P-$SO_3H\cdots$PEO as $f_c$ and $f_b$, respectively. This substitution allows to rewrite eqs. (S3) and (S4) as,

$$Ka = \frac{f_c\left[H^+\right]}{1-f_c-f_b} \tag{S5}$$

and

$$K_f = \frac{f_b}{(1-f_c-f_b)\left[PEO\right]} \tag{S6}$$

At this stage, for the sake of simplicity, we will assume that the concentration of monomers of PEO and the concentration of sulfonic acid (in all states) are both equal to $c_0$. From stoichiometry considerations, the concentration of free PEO monomers, [PEO], is equal to the total concentration of free sulfonic acid monomers (both charged and uncharged), *i.e.* [PEO] = $c_0(1\text{-}f_b)$, therefore, eq. (S6) becomes:

$$K_f = \frac{f_b}{(1-f_c-f_b)(1-f_b)c_0} \tag{S7}$$

We are interested in determining the apparent p*Ka* of the acid-base equilibrium reaction, p$Ka^{\text{app}}$, which is the pH value for which $f_c = 0.5$. Replacing $f_c = 0.5$ and $[H^+] = Ka^{\text{app}}$ in equations (S5) and (S7) results in:

$$Ka = \frac{Ka^{app}}{1-2f_b} \tag{S8}$$

and,

$$K_f = \frac{f_b}{(0.5-f_b)(1-f_b)c_0} \tag{S9}$$

We rearrange eq. (S8) to,

$$pKa^{app} = pKa - \log_{10}(1-2f_b) \tag{S10}$$

The value of $f_b$ required to obtain p$Ka^{\text{app}}$ from eq. (S10) can be determined from eq. (S9), which is a quadratic equation in $f_b$. Finding the physically meaningful root of this equation results in:

$$f_b = \frac{\left(\frac{3}{2}+\frac{1}{K_f c_0}\right)+\left[\left(\frac{3}{2}+\frac{1}{K_f c_0}\right)^2-2\right]^{1/2}}{2} \tag{S11}$$

Figure S4 shows the predicted shift in p*Ka* (Δp*Ka* = p$Ka^{\text{app}}$ - p*Ka*) and $f_b$ as a function of the product $K_f \cdot c_0$. For $f_b >$ ~0.25, the prediction is that Δp*Ka* increases by one unit every ten-fold increase of $K_f$. The threshold value, $f_b > 0.25$, is of the same order of magnitude as the range of $f_b$ = 0.1-0.5 measured by Granick and coworkers in hydrogen-bonded LbL films of PAA with PEO and PVPON.[4]

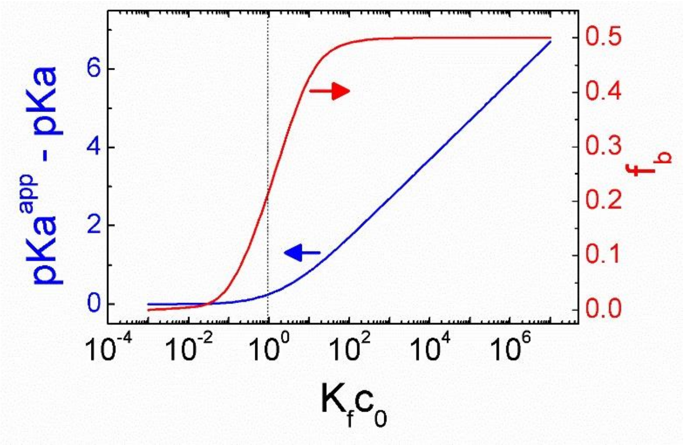
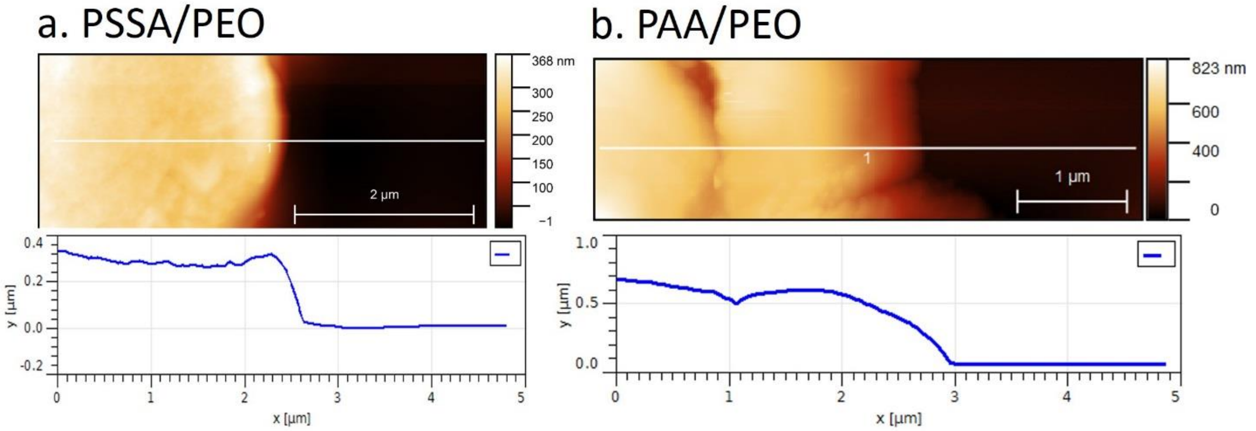


**Figure S2**. Shift in ∆p*Ka* (blue curve, left axis) and fraction of associated acid groups (red curve, right axis) as a function of the product $K_f \cdot c_0$, where $K_f$ is the formation constant of the hydrogen-bonded complex and $c_0$ is the concentration of monomers in the IPC.

## 5. Determination of Film Thickness with AFM



c. Nafion/PEO

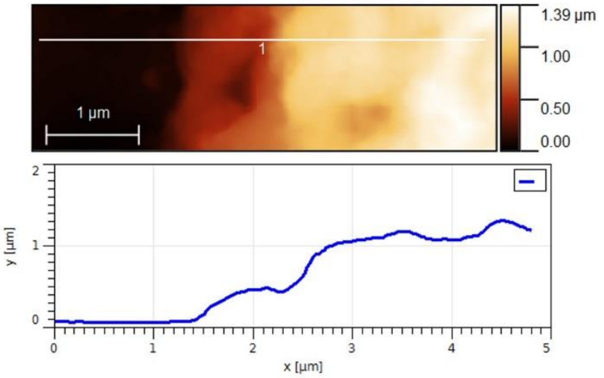


**Figure S3**: AFM topographic images (upper image in each panel) for LbL films on a gold substrate. The films were partially removed by scratching the surface with a gold wire. The lower plots in each panel show the height profiles that were used to determine the thicknesses of the films. The films correspond to those shown in Figure 3 in the main text and their thicknesses are: a. PSSA/PEO: (306 ± 15) nm, b. PAA/PEO: (535 ± 44) nm and c. Nafion/PEO: (1080 ± 80) nm.

## 6. Additional Turbidity Titration Experiments

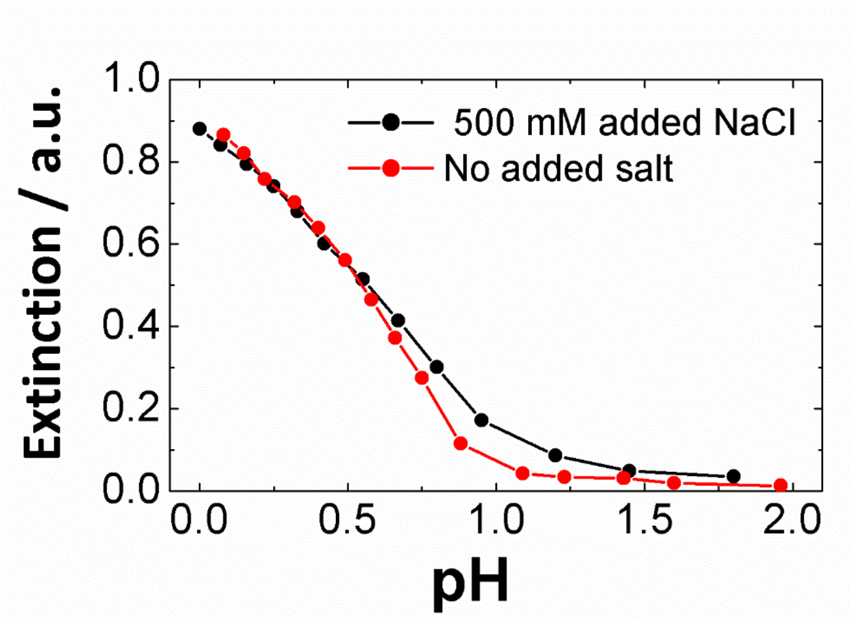


**Figure S4**: Turbidity of PEO/PSSA mixtures (1:1 mixture of 10 mM PEO and 10 mM PSSA) measured by the extinction at 400 nm as a function of the solution pH without added salt (red line) and with 500 mM added NaCl (black line). The pH was adjusted with HCl 3 M.

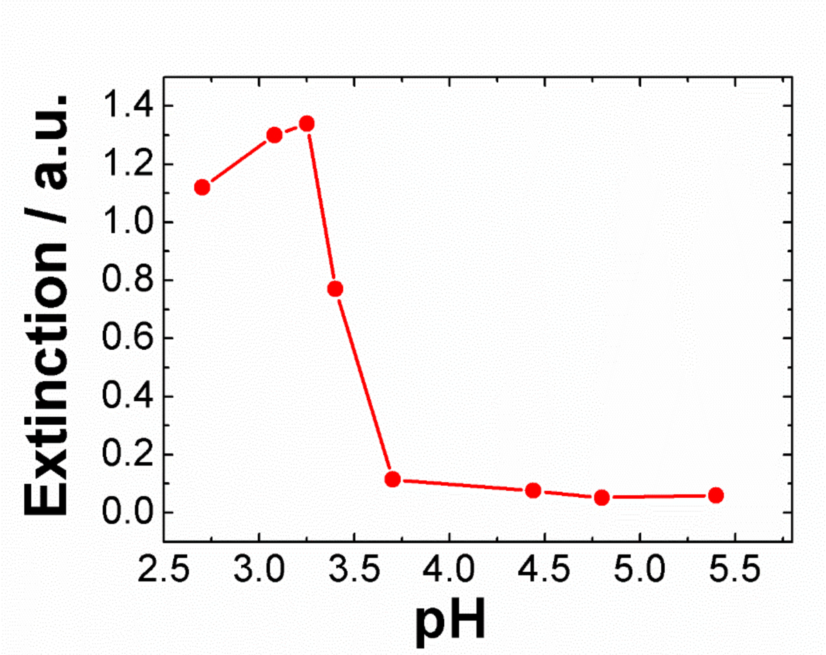


**Figure S5**: Turbidity of a PEO/PAA mixture (1:1 mixture of 10 mM PEO and 10 mM PAA) measured by the extinction at 400 nm as a function of the solution pH. The pH was adjusted with HCl 3 M. The critical pH determined from this experiment is 3.65.

# 7. References

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