

# Supporting Information

## Beaman et al. 10.1073/pnas.1200244109

### An In-Depth Look at the pH Experiments with PAA and PMA.

Detailed plots of the VSF spectra for both PAA and PMA at a variety of pH values are shown in Fig. S1. As described in the main text, clear VSF signal is shown for PAA (A), aPMA (B), and iPMA (C) at low pH values. Raising the solution pH to 4.5 triggers desorption of polymer from the interface in all cases, leaving a nearly neat H<sub>2</sub>O – CCl<sub>4</sub> (D) structure behind. In each of the three panels shown in the carbonyl vibrational stretching region, the amplitudes of the fit peaks are plotted with respect to pH, clearly showing the desorption step. The fit amplitudes (1) of Fig. S1 A–C plotted as a function of solution pH, are shown in Fig. S2 with fits to the equation,

$$\text{SFG}_A = \text{SFG}_{A_{\min}} + (\text{SFG}_{A_{\max}} - \text{SFG}_{I_{\min}})/(1 + 10^{n(\text{pH}-\text{pK}_a)}) \quad [\text{S1}]$$

where  $n$  is the Hill coefficient and is an indicator of cooperative ( $n \neq 1$ ) or noncooperative ( $n = 1$ ) processes. As shown in Fig. S2, the Hill coefficient ( $n$ ) for each of the three polymers desorbing from the interface is much greater than 1, indicating that desorption is a highly cooperative process, as one would expect. In addition, the  $\text{pK}_a$  of each of the polymers is very close to 4, which is significantly lower than what is found in the bulk in literature.

### Methods and Materials.

**Interfacial Tension.** Interfacial tension experiments were carried out on a KSV “Theta” optical tensiometer using the pendant drop method. Drop shape analysis was completed using the KSV supplied software. When acquiring data of aqueous polymer solutions, a neat CCl<sub>4</sub>–water interface was always prepared first and the interfacial tension value verified against the known value of CCl<sub>4</sub>–water, which is 44 mN/m (2, 3). Once the correct neat interfacial tension value was achieved, then the syringe was filled with the polymer solution of interest and a pendant drop was made. Data was recorded until an equilibrium interfacial tension value was achieved, or in the cases of the long time acquisitions, there was drop failure. Interfacial tension values were calculated from the acquired images using the KSV software.

**Spectroscopic Measurements.** VSFS data was acquired with an Ekspla laser and IR generation system with a sample area built to

accommodate the liquid–liquid cell and inverted beam geometries. This system has been described in detail elsewhere (4). Briefly, a YAG laser outputs 1,064-nm light with  $\approx 30$  ps pulse lengths. The 1,064-nm light is split into two lines and one line is frequency doubled to give 532 nm light. A small portion of the 532-nm line is used as the visible portion at the interface, while the remainder of the 532-nm line and the 1,064-nm line are used to generate tunable infrared light via an OPG/OPA/DFG setup. In these experiments, all data was taken with the beams at their respective TIR angles.

**Sample Preparation.** Chemicals were purchased in the highest purity possible from Sigma-Aldrich (NaOH 1.0 N solution in water, HCl 37%). PAA, also purchased from Sigma-Aldrich, was used as is and the viscosity average molecular weight from the manufacturer was 1,800, 450,000, and 1,250,000 Daltons. aPMA was purchased from Sigma-Aldrich with a viscosity average molecular weight of 31.1 kD and was used as received. iPMA was purchased from Polymer Source and had a viscosity average molecular weight of 3 kD and was used as received. Solutions were prepared using clean glassware, an analytical balance and water from a Barnstead ePure system. Solution pH was adjusted using NaOH or HCl and tested using EMD pH paper with regular verification via an Oakton 110 series pH meter.

The sample cell was designed from a solid piece of Kel-f and contains two windows set normal to the incident and outgoing 532-nm beam and are sealed with Dupont Kalrez® perfluoropolymer O-rings. The input window was CaF<sub>2</sub> and the output window was BK-7 glass. All glassware, the cell, the BK-7 window, and the O rings were soaked in concentrated sulfuric acid with No-Chromix for a minimum of 12 h and then each piece was rinsed with 18 M $\Omega$  water from a Barnstead ePure filtration system for at least 25 min. The CaF<sub>2</sub> window was allowed to soak in the same acidic solution for 15–20 min and then copiously rinsed.

Data acquisition started immediately after the interface was prepared. Each spectra shown in these experiments is an average of at least 300 laser shots per data point. Long term equilibration was checked by letting the interface sit for several hours and then retaking the spectra. Unless otherwise noted, long term equilibration was not observed.

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