

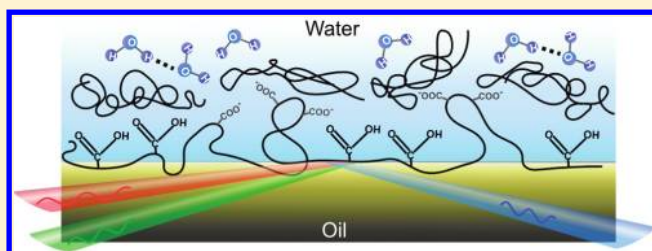
## Unique Assembly of Charged Polymers at the Oil–Water Interface

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Supporting Information

**ABSTRACT:** Understanding the interfacial adsorption of polymers has become increasingly important because a wide range of scientific disciplines utilize these macromolecular structures to facilitate processes such as nanoparticle assembly, environmental remediation, electrical multilayer assembly, and surfactant adsorption. Structure and adsorption characteristics for poly(acrylic acid) at the oil–water interface have been studied using vibrational sum frequency spectroscopy and interfacial tension to increase the comprehension of polyelectrolyte structure at interfaces. The adsorption of poly(acrylic acid) to the oil–water interface from the aqueous phase is found to be highly pH dependent and occurs in a multistep process, with the initial polymer adsorption displaying a high degree of conformational ordering.



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## INTRODUCTION

Polyelectrolytes (PE) are widely used in both industry and consumer applications. They are found in areas such as water remediation,<sup>1</sup> absorbing materials in baby diapers, electrical multilayer assemblies on solid substrates<sup>2,3</sup> and models for biological systems.<sup>4–6</sup> In addition, polyelectrolytes have long been an avenue of study as facilitators of surfactant adsorption<sup>7,8</sup> and nanoparticle flocculation.<sup>9</sup> Although many studies have focused on polyelectrolytes in bulk solution and in the presence of other additives such as surfactants and salts, little information exists regarding their propensity to adsorb from aqueous solution to a surface or their molecular structuring and conformation upon surface adsorption.

In bulk solution, a PE with a majority of its functional groups in the charged state will adopt an extended configuration because of charge–charge repulsion.<sup>10</sup> When these charges are neutralized via a proton or counterion, the PE adopts a randomly coiled configuration.<sup>11</sup> Although some structures have been proposed for PEs at charged solid interfaces,<sup>12,13</sup> at “soft” interfaces, such as an oil–water interface where PEs exist in many practical applications, few such proposals exist. In this letter, we report the first molecular-level measurement of the adsorption of a common carboxylate containing PE, poly(acrylic acid) (PAA), to the oil–water interface. We find that the adsorption of PAA is strongest under acidic conditions with desorption occurring sharply at  $\sim$ pH 4.5. The adsorption itself is found to occur as a multistep process, with a fast initial adsorption to form a highly oriented polymer layer, followed by a slower accumulation of disordered polymer at the interface.

This study has combined spectroscopic and thermodynamic methods to obtain a complete picture of the interfacial region under a variety of conditions. As in previous studies from this

laboratory, vibrational sum frequency spectroscopy (VSFS) has been used to measure the vibrational spectrum of the interfacial species at the liquid–liquid interface because of its inherent surface selectivity and sensitivity to molecular orientation.<sup>14,15</sup> The VSFS system used in these studies has been described elsewhere and will not be detailed here.<sup>16</sup> Interfacial tension measurements using the pendant drop method complement the spectral data and allow conclusions to be drawn on the basis of the distinct sensitivities of the two different methods. Although interfacial tension is sensitive to the number density of the adsorbed molecules at the interface, VSFS has the additional requirement that the adsorbed molecules have a net orientation.

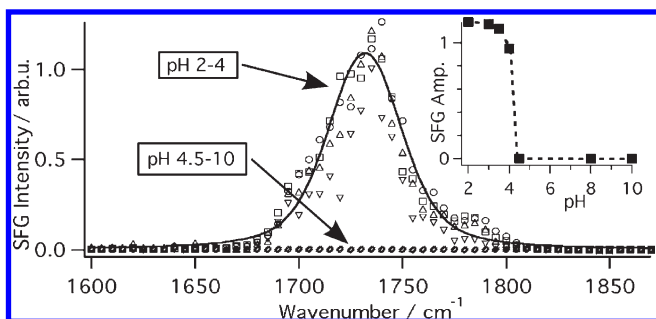
## RESULTS AND DISCUSSION

VSF spectra of PAA (Aldrich, 5 ppm, 450 kD) adsorbed to the  $\text{CCl}_4$ –water interface are shown in Figure 1 for aqueous solutions of pH 2–10. From pH 2–4, a single peak is observed at  $1730\text{ cm}^{-1}$  and is assigned to the carbonyl stretch of the carboxylic acid groups on PAA. Its appearance indicates that PAA has adsorbed to the interface with its carboxylic acid groups having a net orientation relative to the surface normal, pointing into the water phase to maximize hydrophilic interactions, whereas the backbone lies in the plane of the interface to maximize its hydrophobic interactions with the oil phase. At pH 4.5, there is an abrupt and complete loss of signal in the carbonyl region (Figure 1 inset), indicating either complete desorption of the polymer or a net loss of oriented carboxylic

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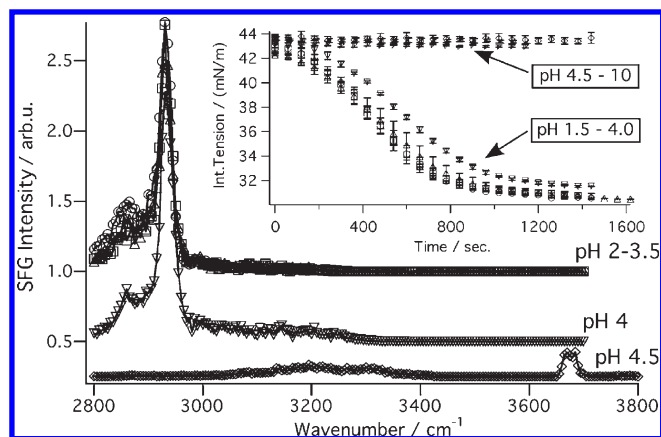
**Figure 1.** VSFS data (ssp polarization) of the PAA C=O vibrational stretch at  $1730\text{ cm}^{-1}$  from pH 2 to 10. The solid line is a fit to the pH 3 data and is taken from the global fitting results where each set of data is simultaneously fit to a single peak using global parameters. The inset shows the amplitudes of the fits to the data as a function of pH. The dashed line is a guide for the eye.

acid moieties at the interface. No VSF signal is measured at any pH from ionized carboxylate ions near  $1400\text{ cm}^{-1}$ .

Evidence that the observed sharp drop in VSF signal is due to polymer desorption can be obtained from VSF data in the CH and OH stretching regions (Figure 2). At low pH, a dominant mode at  $2930\text{ cm}^{-1}$  and a small shoulder at  $2850\text{ cm}^{-1}$  are observed, assigned respectively to the asymmetric and symmetric stretches of the  $\text{CH}_2$  groups on the backbone of the polymer. Their presence further confirms polymer adsorption at the interface and also shows the oriented nature of the interfacial polymer backbone. The pH dependence of the VSF response from the CH modes mirrors that of the carbonyl mode. The pH behavior of interfacial water, as measured by the OH stretching modes in the  $3000\text{--}3700\text{ cm}^{-1}$  window, gives a corresponding picture. At pH 4, the spectra in Figure 2 are dominated by CH modes of PAA with a very small signal from highly coordinated interfacial water molecules near  $3200\text{ cm}^{-1}$ . At a solution pH of 4.5 or higher, the CH modes disappear and the VSF spectrum resembles the “neat”  $\text{CCl}_4$ –water interface with the free OH mode appearing near  $3700\text{ cm}^{-1}$ ,<sup>17</sup> confirming that the interface is now polymer-free.

The interfacial tension measurements of PAA at the  $\text{CCl}_4$ –water interface (Figure 2 inset) confirm the conclusions from the spectral data while providing additional thermodynamic and temporal information. As shown for solutions with a pH of 1.5–4, the observed decrease in interfacial tension corresponding to polymer adsorption occurs over a time frame of  $\sim 20$  min, reaching a final equilibrium value of  $31\text{ mN/m}$ . At higher pH, a constant value of  $\sim 44\text{ mN/m}$ , the value for an undisturbed  $\text{CCl}_4$ –water interface,<sup>18</sup> is measured and confirms the absence of adsorbed PAA.

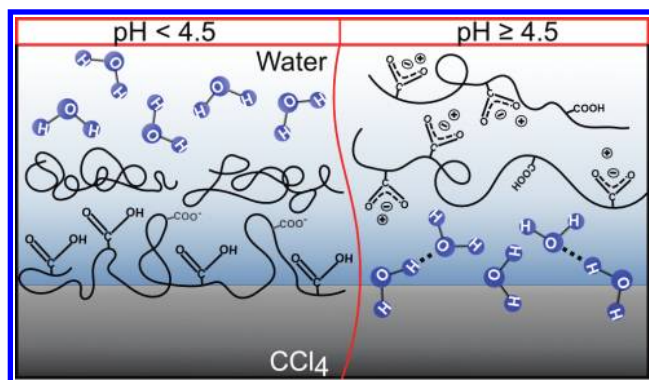
Bulk titrations of the PAA used in these experiments gave a  $\text{p}K_a$  value of  $\sim 6$ , which agrees well with literature values.<sup>19–21</sup> In our studies, the complete desorption of PAA occurs at a far lower pH (4–4.5) value than the  $\text{p}K_a$ , indicating that little accumulation of charge ( $\sim 20\%$  of COOH groups according to bulk titrations) along the backbone is required to desorb the polymer from the interface. However, surface  $\text{p}K_a$  values are known to be  $\sim 1\text{--}3$  units more alkaline than the bulk  $\text{p}K_a$  for weak acids at the interface.<sup>22,23</sup> This means that much less than 20% of the sites along the PAA backbone are deprotonated when desorption becomes energetically favorable. However, it is likely that cooperative processes facilitate desorption by concentrating charge in regions of the polymer. As charge accumulates along the length



**Figure 2.** VSFS data (ssp polarization) of PAA at the  $\text{CCl}_4$ –water interface in the CH and water vibrational region for pH 2–4.5 solutions. The inset shows the interfacial tension of these same solutions at the  $\text{CCl}_4$ –water interface.

of the polymer, carboxylic acid groups near a charge can deprotonate more readily than an acid group that has very little charge surrounding it.<sup>24</sup> Such cooperative processes would lead to a decrease in the size of the neutral sections of the polymer adsorbed to the interface, whereas the charged sections of the polymer increase in size until desorption becomes energetically favorable for the entire polymer.

One of the most intriguing results from these studies is the difference in the time evolution of the interface, as measured by VSF and tensiometry. The SF spectra shown in Figures 1 and 2 are taken immediately following the placement of the polymer solution onto the organic phase (at  $t = 0$ ). No change in the spectral amplitude or width is observed beyond the first few seconds of interface formation. However, the tensiometry measurements show a continual adsorption of polymer over a 20 min period. PAA at 5 ppm with a MW of 1.8 kD was also studied using both interfacial tension and VSFS. With the tensiometry, it was found that the adsorption of 450 kD PAA occurs over a longer time frame, reflecting the slower diffusion of the polymer to the interface relative to that of the smaller-MW polymer. However, the final interfacial tension achieved by both the low- and high-MW polymers is the same ( $31\text{ mN/m}$ ), indicating that the final surface coverage and structure are also the same. These results are consistent with previous tensiometry measurements of concentration ranges of low- and high-MW polymers at an air–water interface, where it was found that neither concentration nor MW affected the final surface structure.<sup>25–27</sup> The contrasting VSF and tensiometry results are a consequence of the different properties measured by these two methods. The surface tension data measures the total amount of polymer adsorbing to the interface over time. In contrast, the VSF spectral measurements are sensitive only to the polymers that take on a net orientation upon arrival at the interface. The fact that the VSF response is apparent almost immediately and is invariant over the longer time frame for both the 1.8 and 450 kD PAA shows that the first polymer layers take on a net orientation upon arrival at the interface whereas the polymer layers arriving at a later time do not. The results lead to the interesting conclusion that PAA adsorption at this liquid–liquid interface occurs in a multistep process with initial portions of the polymer adsorbing and orienting quickly at the neat interface, followed by a slower adsorption of more randomly coiled polymer in the subinterfacial region.



**Figure 3.** Representation of PAA at the  $\text{CCl}_4$ –water interface for the two pH regimes. In the low-pH regime (left), polymer adsorbs strongly to the interface with highly oriented carbonyl and CH groups. In the high-pH regime (right), there is a deficit of polymer from the interface, which leaves water molecules close to their normal neat interfacial structure.

Figure 3 provides a visual image of the nature of adsorption of PAA to the oil–water interface found in these studies. When the polymer adsorbs at lower pH, it is primarily in its protonated (neutral) state. The polymer units in the innermost interfacial region adsorb in a conformation that results in the ordering of both the side carboxylic acid groups as well as the backbone of the polymer. We propose that the polymer has organized sections adsorbed along the interfacial plane where the carbonyl groups are well-oriented, interrupted by sections protruding into the water region containing the charged carboxyl groups. Later arriving polymer units organize randomly in the subinterfacial region until the polymer reaches its full coverage. As the pH is increased, the charged carboxylates do not orient at the interface. Upon reaching a critical pH and thus a critical number of charged carboxylates, the entire polymeric system desorbs from the interface.

In summary, these studies provide the first detailed molecular-level measurement of a polyelectrolyte, PAA, at a liquid–liquid interface and the pH factors that contribute to its adsorption and desorption. At low pH, the ionizable polyelectrolyte PAA contains few charged groups and minimal repulsive interactions, permitting a dense packing arrangement with high net orientation at the interface. At high pH, high numbers of charged carboxyl groups make repulsive interactions significant and do not allow ordered packing or adsorption to occur. The unique interfacial environment of this fluid interface, its high degree of interfacial solvent orientation, and its ability to attract ions and charged species clearly play a role in the unique manner in which PAA behaves when it adsorbs at an oil–water interface relative to other surfaces.<sup>28,29</sup> Such results have important implications for the many applications of PAA in liquid interfacial systems such as emulsifiers and dispersants.

## ■ ASSOCIATED CONTENT

**S** Supporting Information. Experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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