Effect of Acid–Base Interactions on Conformation of Adsorbed Polymer Chains

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Supporting Information

ABSTRACT: Sum frequency generation spectroscopy (SFG) and attenuated-total-reflection IR (ATR-IR) were used to investigate polymer adsorption on solid surfaces in CCl₄ (neutral), CHCl₃ (acidic), and acetone (basic) solvents. Fowkes showed that the adsorbed amount of the polymer from acidic and basic solvents is less than that from a neutral solvent (Ind. Eng. Chem. Prod. Res. Dev. 1978, 17, 3–7). Here, we show that besides the differences in adsorbed amount, chains adsorbed from an acidic solvent adopted a flat conformation with a much smaller ratio of segments of loops and tails to trains compared to those adsorbed from a neutral solvent. Sapphire (Al₂O₃) surfaces were saturated by train segments at 1.3 × 10⁻⁵ volume fraction for both CCl₄ and CHCl₃ solutions, with a large fraction of the surface sites occupied by the PMMA segments, which was different from what was expected based on Fowkes’ experiment. In contrast, PMMA segments were not able to replace acetone molecules from the surface in a time period of 2 h. Surface interaction parameters alone were unable to predict the differences in conformation of chains adsorbed from acidic or neutral solvents.

Figure 1 summarizes the results from SFG for the adsorption of PMMA (101 kg/mol) in three solvents: acetone (basic), CHCl₃ (acidic), and CCl₄ (neutral). The adsorption process was monitored by measuring the changes in the intensity of the SFG signal from the PMMA segments.

Adsoption of macromolecules from solutions plays an important role in a wide range of applications such as the colloidal stabilization,1 adhesion,2 chromatography,3 pharmaceuticals,4 biophysics,5 and nanocomposites.6,7 An adsorbed polymer chain adopts a conformation consisting of segments in contact with the substrate (trains) and fully surrounded by solvent molecules (loops and tails).8 The conformation leads to a low energy state as a result of balancing the enthalpic and the entropic contributions. One of the most iconic contributions in this field has been the demonstration of acid–base interactions in determining polymer adsorption by Fowkes et al.9 They showed that the adsorbed amount of a basic polymer on an acidic substrate is much higher in a neutral solvent compared to basic or acidic solvents. The basic solvent molecules compete with the basic polymer for the acidic surface sites. In consequence, basic solvents reduce the adsorbed amount. In contrast, the acidic solvent molecules and the substrate compete for the basic polymer groups, resulting in a reduction of adsorption. Although the scenario of adsorbed polymer chains have been modified in recent years, such as non-equilibrium structure,10,11 the basic tenet of Fowkes’ picture of acid–base interactions has remained unshaken for almost 40 years. Even though we expect a very low adsorbed amount in acidic solvent, it is unclear what is the conformation of the chains in the acidic solvent compared to chains adsorbed from the neutral solvent. More important is the question of what is interacting with the acidic surface, acidic solvent or poly(methyl methacrylate) (PMMA), considering the fact that the adsorbed amount is so low in acidic solvent compared to neutral solvent. These conformations have a profound influence on the dynamics, exchange kinetics, stabilizing colloid particles, and separation of these chains during chromatography.

Here, we have revisited this classical experiment by Fowkes et al.1 by directly measuring the acid–base interactions (a more familiar nomenclature of hydrogen bonding is a subset of acid–base interactions) of solvents or PMMA with acidic sapphire (Al₂O₃) surfaces using surface-sensitive sum frequency generation spectroscopy (SFG). SFG is a second-order nonlinear optical technique that is sensitive to the concentration and the orientation of the molecular groups present at the surface or interface, while the contribution from the isotropic bulk to the SFG signal is negligible.12 Because the orientation of the segments in tails and loops is expected to be isotropic, the majority of the SFG signal is going to be from the molecular groups in the train segments. Here, we have taken advantage of the fact that the vibration of the surface −OH groups will be red-shifted when in contact with a base, and the magnitude of this shift depends on the strength of the acid–base interactions.12 This provides a direct approach to determine the concentration of the surface −OH group in contact with either the solvent molecules or PMMA segments. These acid–base interactions are much stronger than the shift in OH peak expected for dispersion interactions.14

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carbon tetrachloride (CCl₄, neutral), and chloroform (CHCl₃, acidic). PMMA concentrations are shown in volume fractions throughout this paper. Sapphire surfaces are terminated with −OH groups and are very similar to those of silica particles used in the experiments by Fowkes et al.⁹ For the basic solvent, acetone, the spectral peak at 2930 cm⁻¹ corresponds to the methyl groups of acetone.¹³ The broad peak at 3575 cm⁻¹ is assigned to the surface −OH groups interacting with acetone molecules. The sapphire −OH groups in contact with air were observed as a sharp peak at 3720 cm⁻¹.¹⁴ A shift to lower wavenumbers and broadening of this −OH peak in acetone signify the acid−base interactions between them.¹⁴,¹⁵ The spectral features remain unperturbed in both C−H and O−H stretching regions after the acetone solution was replaced with the PMMA−acetone solutions. Thus, PMMA molecules were not able to replace the acetone molecules, even for a volume fraction as high as 7 × 10⁻³ and an adsorption time of 2 h. For the adsorption from a neutral (this definition is based on the concept of acid or base and is not based on the interaction parameter between the polymer and the solvent molecules) solvent, CCl₄, the SFG spectra (panels C and D) show a clear adsorption of PMMA chains at a volume fraction as low as 1.3 × 10⁻⁵. The SFG peak for the adsorbed PMMA train segments was observed at 2954 cm⁻¹, assigned to the ester methyl groups,¹² with the ester carbonyl groups instead of CCl₄ molecules. As the volume fraction further increases to 1.3 × 10⁻³, the spectral features do not change in either the C−H or O−H stretching region. Because SFG is sensitive to the train segments, no further change in the SFG signals suggests that the sapphire surface is saturated by the PMMA train segments at a volume fraction of 1.3 × 10⁻⁵.

Surprisingly, PMMA adsorption was also observed from an acidic solvent, CHCl₃. Figure 1E clearly shows the PMMA peak at 2954 cm⁻¹, suggesting the adsorption of PMMA at a volume fraction as low as 1.3 × 10⁻⁵. The peak at 3028 cm⁻¹ is from the C−H vibration of chloroform.¹³ PMMA adsorption can also be confirmed by a shift of the −OH peak to lower wavenumbers due to the acid−base interactions of the ester carbonyl groups of PMMA with the surface −OH groups. CHCl₃ molecules interacted weakly with surface −OH groups represented by the −OH peak at 3662 cm⁻¹. Although CHCl₃ has been conventionally considered as an acid, it also exhibits a basic character in the presence of a stronger acid.¹⁶ The −OH peak can be modeled using a combination of two peaks. The first peak is assigned to the surface −OH groups interacting with the solvent molecules. The second peak is associated with the interaction of PMMA segments with the surface −OH groups (described in more detail in the SI). The areas of the two peaks can be used to calculate the ratio of the surface −OH groups interacting with PMMA segments to the total −OH groups on the surface (Figure 2).¹⁵ Here we have assumed that
the average orientation of OH groups did not change by interacting with PMMA segments and the solvent molecules. A considerable fraction of the surface —OH sites were occupied by the PMMA segments adsorbed from both neutral and acid solvents at saturation. The conclusion that a small fraction of acidic solvent remains in contact with surface —OH groups is also consistent with a prominent peak in the SFG spectra assigned to the C—H vibration of chloroform. However, we cannot directly use the SFG signals in the hydrocarbon region to determine the surface coverage because the SFG signals are a function of orientation, concentration, and molecular hyperpolarizability.

The above results raise the question of whether there is a discrepancy in the data presented here, and the conclusions reached by Fowkes et al. that the adsorbed amount is much higher in a neutral solvent compared to an acidic solvent. Here, we have independently confirmed Fowkes’ conclusion by measuring the PMMA adsorption on a silica layer grown on a silicon crystal using attenuated-total-reflection IR (ATR-IR; Figure 3). The surface of the silica layer also has the acidic —OH groups. Figure 3A shows the IR spectra for both CCl4 and CHCl3 solutions at a volume fraction of 1.3 × 10⁻³. The carbonyl peak is composed of two constituent peaks. For CCl4 solutions, the dominant peak at 1733 cm⁻¹ is assigned to the carbonyl groups solvated by CCl4.17 The solvated groups in CHCl3 are represented by the broad peak at 1725 cm⁻¹.18 These two peaks appear for the free segments in loops, tails, and nonadsorbed chains dangling in the solution. The other peak at 1710 cm⁻¹ in both spectra is assigned to the carbonyl of the adsorbed chains from acid or neutral solvents (Figure 4). Based on the work of Johnson and Granick,19 the solution contribution was subtracted at the volume fraction used in the ATR-IR experiments (details provided in the SI). Figure 3B shows the peak areas for the carbonyl groups interacting with surface —OH groups (1710 cm⁻¹) and the solvents CHCl3 (1725 cm⁻¹) and CCl4 (1733 cm⁻¹). Based on the work of Johnson and Granick,19 the solution contribution was subtracted at the volume fraction used in the ATR-IR experiments (details provided in the SI). The peak area ratio of the loop and tail segments to the train segments is 2.4 for the PMMA—CHCl3 solution and 10.4 for the PMMA—CCl4 solution. Data presented here are averaged over four independent sets of spectra, and error bars are plotted using the standard deviation.

solutions since the peak areas for the train segments are the same within experimental errors. The adsorbed amount indicated by the total area of the two peaks is higher for a CCl4 solution than a CHCl3 solution, which is consistent with the observations of Fowkes et al.9

Based on the IR and SFG data, we provide a physical picture of the adsorbed chains from acid or neutral solvents (Figure 4). In PMMA—acetone solutions, acetone molecules formed stronger acid—base interactions with the surface hydroxyl groups and prevented PMMA adsorption. The structure of more segments in loops and tails for adsorbed chains in a neutral solvent is surprising. Since CCl4 is a poor solvent for PMMA at room temperature,20 the interaction between PMMA segments and CCl4 molecules is not favorable. This should result in fewer segments in tails and loops. However, placing more chains at the surface is preferable due to an increased number of chain—chain interactions within the adsorbed layer, reminiscent of a phase separation. Since the SFG results suggest a surface saturation at a low concentration, it is likely that a few PMMA chains initially adsorbed tightly in a flat conformation. At higher concentrations, the chains adsorbed loosely with a higher fraction of segments in tails and loops as indicated by the ATR-IR results. Here this bimodal distribution of adsorbed PMMA chains in CCl4 was preferred over a homogeneous layer of loopy PMMA chains since this model has been previously
determined by Granick et al. based on the infrared analysis of chain conformation.\(^\text{10}\)

The observation of fewer loop and tail segments in CHCl\(_3\) compared to CCl\(_4\) also raises an intriguing question. Since the acidic solvent molecules interact favorably with the basic polymer segments, we expect the adsorbed chains to form more loops and tails. This structure would maximize the polymer–solvent interactions. However, if the PMMA chains did adsorb with extended tails and loops, then the total adsorbed amount would be high in chloroform, and this will be inconsistent with the low adsorbed amount observed in experiments. Instead, at a low volume fraction of CHCl\(_3\) solutions, a smaller number of chains saturate the sapphire surfaces by attaching in a flat conformation, similar to the low concentrated solutions of PMMA in CCl\(_4\). As we increase the concentration of PMMA in chloroform, PMMA chains prefer to remain in the solution. This lowers the overall free energy of the system (solvent, polymer, and substrate) but not necessarily minimize the free energy of the adsorbed chains. As the ATR-IR results suggested, the fewer chains adsorbed in a flat conformation resulted in a higher fraction of train segments in CHCl\(_3\) compared to CCl\(_4\).

One could also qualitatively understand the adsorption process by comparing the Silberger’s parameters \(\chi_s\) for the interactions between PMMA and the substrate in the three solvents, \(\chi_s = (U\text{solvent–substrate} - U\text{polymer–substrate})/kT\). These values are summarized in Table 1. Using acetone as the solvent, the values of \(\chi_s\) for both silica and alumina (as a reference for sapphire) are negative, which indicates no adsorption. In comparison, the values of \(\chi_s\) for both CCl\(_4\) and CHCl\(_3\) are higher than the value of 0.4 required for adsorption.\(^\text{7}\) This predicts that PMMA will adsorb on sapphire substrates from both CCl\(_4\) and CHCl\(_3\). However, the knowledge of \(\chi_s\) alone is not sufficient to explain the differences in the conformation (trains, loops, and tails) and the adsorbed amount. In addition to the Silberger’s parameter, the interactions between the polymer segments and the solvent molecules are also necessary to understand the experimental results.

In summary, we find that the PMMA chains adsorbed with a flat conformation in acidic solvent and occupied 71% of the surface –OH sites at a very low concentration \((1.3 \times 10^{-5})\). These results were surprising considering that the adsorbed amount is much smaller in acidic solvent compared to that adsorbed from neutral solvent. This is of striking importance to our understanding of the adsorption process. The SFG data showed that the interactions of surface –OH groups with a basic solvent (acetone) is much stronger than PMMA segments, and this prevents any adsorption of PMMA on acidic surfaces in a basic solvent. This is consistent with the results of Fowkes et al.\(^\text{9}\) where they showed that the adsorption was weak in basic and acidic solvents. In a neutral solvent, the SFG and IR data are consistent with the conclusion drawn from earlier studies that adsorbed chains show a bimodal distribution with a fraction of chains adsorbing strongly onto the substrate (train segments) and the other fraction adsorbing with longer tails and loops. These results bring up some intriguing questions on the differences in the dynamics of desorption of these adsorbed chains,\(^\text{19,22}\) especially in neutral, basic, and acidic solvents and the consequences of the static and dynamic conformation on the stabilization of colloidal particles, adhesion, and mechanical properties of nanocomposites.

\[ \text{Table 1. } \chi_s \text{ Values in Units of } kT \text{ for PMMA Adsorption on Silica and Alumina Surfaces} \]

<table>
<thead>
<tr>
<th>substrates</th>
<th>CCl(_4)</th>
<th>acetone</th>
<th>CHCl(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>silica</td>
<td>4.3</td>
<td>−0.7</td>
<td>3.2</td>
</tr>
<tr>
<td>alumina</td>
<td>3.6</td>
<td>−0.3</td>
<td>2.6</td>
</tr>
</tbody>
</table>

\[ \text{REFERENCES} \]

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