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Surface Structure of Solutions of Polyvinyl Alcohol in Water

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Abstract:

We use surface-specific heterodyne-detected vibrational sum-frequency generation spectroscopy (HD-VSFG) and surface tension measurements to investigate the molecular structure of the surface of aqueous solutions of polyvinyl alcohol (PVA) polymers with average molecular weights of 10000 g/mol and 125000 g/mol. We find that the interfacial water molecules have a preferred orientation with their hydrogen-bonded O-H groups pointing away from the bulk, for both PVA_{10000} and PVA_{125000}. This observation is explained from the ongoing hydrolysis of the acetyl impurities on the PVA polymer chains. This hydrolysis yields negatively charged acetate ions that have a relatively high surface propensity. For both PVA_{10000} and PVA_{125000} the strong positive signal vanishes when the pH is decreased, due to the neutralization of the acetate ions. For solutions with a high concentration of PVA_{10000} the interfacial water signal becomes very small, indicating that the surface gets completely covered with a disordered PVA polymer film. In contrast, for high concentrations of PVA_{125000} the strong positive water signal persists at high pH, which shows that the water surface does not get completely covered. The HD-VSFG data combined with surface tension data indicate that concentrated PVA_{125000} solutions form a structured surface layer with pores containing a high density of interfacial water.

Introduction:

In the last decades synthetic polymers have gained tremendous attention since they can be fabricated in various shapes and structures and with a wide range of physical and chemical properties. Current research on synthetic polymers is strongly focused on the production of nontoxic, biodegradable polymers and their applications in biomedicine and material technologies[1,2,3]. Polyvinyl alcohol (PVA) is a well-known synthetic polymer that has a large number of desirable properties like water affinity, non-toxicity, biocompatibility, biodegradability and the flexibility to form networks[4]. It is widely used in applications ranging from membrane-based liquid and gas mixture separation to material technologies and encapsulation of bacteria via electrospinning[5,6,7]. PVA-based systems are further used for controlled drug delivery, medical imaging enhancement and cell interactions where the characteristics of the interface between PVA and the external medium plays an important role in determining the physicochemical stability and affinity toward biological systems[8]. PVA has further been reported to have remarkable properties at the ice-water interface[9]. It is a very potent compound to inhibit ice recrystallization and was proposed to be able to bind to ice, a property that was long believed to be unique for antifreeze proteins[10,11].

The behaviour of PVA at interfaces is currently poorly understood despite its high relevance for numerous technologies[4]. The reason for this lack of knowledge is the limited number of molecular probing techniques that are capable of selectively measuring the interface in aqueous solution. Up to now, surface tension measurements have been the main tool to investigate PVA at the water-air interface[12,13].

PVA has an amphiphilic nature with alternating hydrophobic methylene and hydrophilic hydroxyl groups as shown in the inset in Figure 1. In the diluted regime PVA behaves like a surfactant and decreases the surface tension γ of water with increasing polymer concentration[12]. The degree of the decrease in surface tension can be influenced by the molecular weight, the stereochemistry, and the presence of charge impurities on the PVA polymer[13,14,15]. At concentrations higher than ~4% the surface tension of PVA_{125000} solutions behaves anomalously and starts to increase with increasing PVA concentration[4]. For concentrations >10% the surface tension of the PVA solution is similar to that of pure water[4]. This anomaly was first noticed in the 1980s and has been observed in several studies of concentrated PVA solutions[13, 16].

Here we use heterodyne-detected vibrational sum-frequency generation spectroscopy (HD-VSFG) to investigate the structure and conformation of PVA at the water-air interface, and to unravel the molecular origin of the anomalous surface tension behaviour of PVA. VSFG is a highly surface-specific technique that is ideally suited for the study of molecules adsorbed at interfaces[17]. In VSFG an infrared light pulse and a visible pulse are combined to generate light at their sum-frequency. The generation is enhanced in case the infrared light is resonant with a molecular vibration. For the bulk, the generation of sum-frequency is symmetry forbidden. VSFG techniques have been successfully used to investigate polymers at interfaces and were demonstrated to provide molecular details on the conformation and solvent interactions of the molecule of interest[18,19,20]. By interfering the VSFG signal from the sample with a reference sum-frequency field, we determine the phase of the generated sum-frequency light and thereby the phase of the second-order optical susceptibility $\chi^{(2)}$. The real (Re) and imaginary (Im) parts of $\chi^{(2)}$ provide direct information on the orientation of the vibrational transition dipole moments at the surface. This heterodyne-detected VSFG thus provides unique information on the absolute molecular orientation[21].

Material & Methods:

The laser source for the vibrational sum-frequency generation experiments is a regenerative Ti:Sapphire amplifier (Coherent) producing 800 nm pulses at a 1 kHz repetition rate with a pulse duration of ~35 fs and a pulse energy of ~3.5 mJ. Approximately one third of the laser output is used to pump a home-built optical parametric amplifier and a difference-frequency mixing stage. This nonlinear frequency conversion produces broadband mid-IR pulses (tuneable from 2-10 μm, with a bandwidth of 600 cm^{-1} (FWHM), and a pulse energy of 10-20 μJ). In the current study the mid-IR pulse was centred at ~3 μm and had pulse energies of ~15 μJ. Another part of the 800 nm pulse is sent through an etalon to narrow down its bandwidth to ~15 cm^{-1}. The resulting narrow-band 800 nm pulse (VIS) and the broadband IR pulse are directed to the sample surface at angles of ~50° and ~55°, respectively, to generate light at the sum frequency. The VIS and IR beams are focused in spatial and temporal overlap on the sample surface with 200 mm and 100 mm focal length lenses, respectively. The visible focus is located ~0.5 cm above the sample surfaces.

The SFG light generated at the surface is passed to a monochromator and detected with an Electron-Multiplied Charge Coupled Device (EMCCD, Andor Technologies). Heterodyne-

detected VSFG is used to determine the imaginary and real parts of $\chi^{(2)}$. In HD-VSFG the SFG electric field generated from the sample is combined with that of a local oscillator (LO, gold) at the same frequency. The LO sum-frequency (LO-SFG) light is generated by first focusing the IR and VIS beams on a metal surface to generate a strong non-resonant $\chi^{(2)}$ SFG signal. This signal is delayed with respect to the IR and VIS beams by passing it through a silica plate (~ 1 mm). The LO-SFG and the IR and VIS beams are refocused on the sample surface using a spherical mirror. The IR and VIS beam generate the SFG signal of the sample. Subsequently, the LO-SFG and sample SFG beams are collimated, sent into a monochromator and detected with a CCD.

The detected interference pattern contains cross terms from which we extract the real and imaginary $\chi^{(2)}$ part using Fourier transformation. To obtain the Im $\chi^{(2)}$ of the sample, we compare the signal with the HD-VSFG signal of a reference sample for which the phase of the SFG light is known. For this purpose we use a z-cut quartz crystal. For HD-VSFG measurements it is crucial that the HD-VSFG signal from the reference (z-cut quartz crystal) is generated at the same height as the sample. A mismatch in height would result in a phase shift of the recorded spectra and thus in the extracted real and imaginary $\chi^{(2)}$. We control the height of the reference quartz crystal and the sample by monitoring the position of the VSFG signal on the CCD camera. This enables us to define the SFG signal on the camera with a precision of 1 pixel size (16 x 16 μm). In combination with our setup geometry this results in a phase uncertainty of ~π/10 (~20 degrees). The typical acquisition time of a HD-VSFG spectrum is 120 s.

All VSFG measurements were performed in H_2O (Millipore). The polyvinyl alcohol samples are specified in weight %. The pH value (Mettler Toledo FE20) of the samples was adjusted using hydrochloric acid or sodium hydroxide. The pH was checked before and after each measurement. The surface tension measurements (Kibron, DeltaPi) were performed at room temperature using the Wilhelmy plate method. The measurements were performed using a multiwall plate, and were repeated at least three times. Polyvinyl alcohol samples were acquired from Sigma Aldrich and were used without further purification. The PVA samples differ in their molecular weight and degree of hydrolysis. PVA is unlike most vinyl polymers not prepared by the polymerization of the corresponding monomer since the monomer, vinyl alcohol, is unstable with respect to acetaldehyde[22]. PVA is prepared by first polymerizing vinyl acetate, and the resulting polyvinyl acetate is converted to PVA via hydrolysis. This process is often incomplete and a number of

charge impurities (acetyl groups) remain. The average molecular weight of the smaller PVA (PVA_{10000}) polymer was 10,000 g/mol with a hydrolysis degree of ~80%, which means that ~20% of the acetyl groups have not been hydrolyzed to hydroxyl groups. The larger PVA (PVA_{125000}) polymer has an average molecular weight of 125,000 g/mol and a hydrolysis degree of ~98%. Solutions were prepared by dissolving PVA in ultrapure water (Millipore) at high temperature (80-90 °C). Due to the presence of the acetyl groups, the PVA can undergo spontaneous hydrolysis of the ester groups of the PVA molecules, a process that is enhanced in acidic or basic aqueous media and that is schematically shown in the Supporting Figures 1 and 2. The hydrolysis leads to the release of acetic acid in neutral or acidic solution, or acetate in basic solution. The acetic acid molecules will partly deprotonate, thus decreasing the pH and creating negative acetate ions (Fig. S3). The negative acetate ions have a strong affinity for the water surface[23].

Results and Discussion

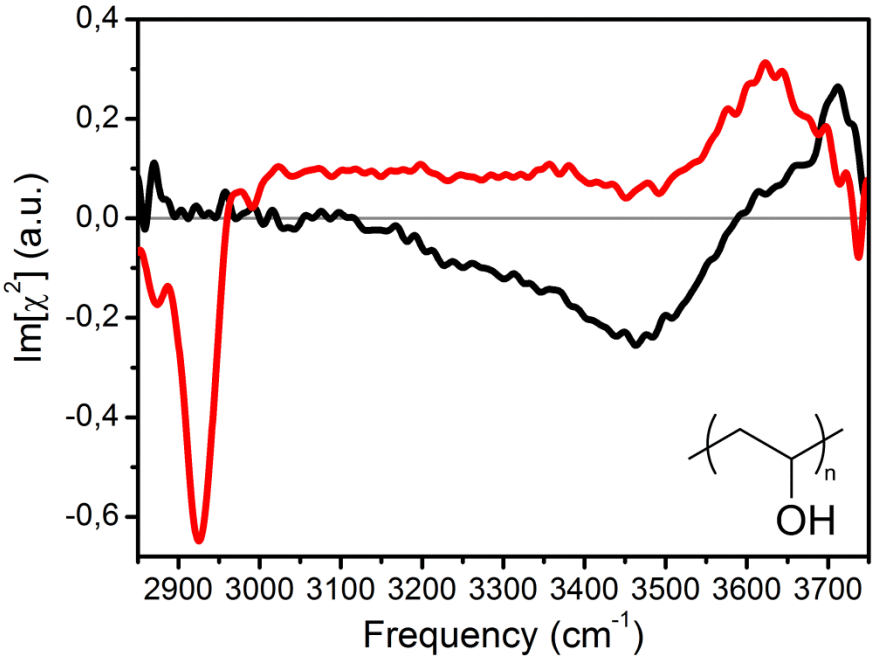

Figure 1: Imaginary [$\chi^{(2)}$] spectra of pure water (black) and PVA_{10000} (5 wt%, red) at the water-air interface, measured in SSP polarization configuration (s-SFG, s-VIS, p-IR). Inset shows the schematic molecular structure of PVA.

In Figure 1 we present HD-VSFG spectra of pure water and an aqueous 5 wt% PVA_{10000} solution at the water surface, measured with an SSP polarization configuration (s-SFG, s-VIS, p-IR). The presented Im[$\chi^{(2)}$] spectrum of pure water is in excellent agreement with results obtained in previous studies[24,25]. The Im[$\chi^{(2)}$] water spectrum shows a broad negative band between 3200 and 3500 cm^{-1} and a narrow positive band at ~3700 cm^{-1}. We assign the broad band to the O-H stretch vibrations of water molecules that form hydrogen bonds to other water molecules. The sharp feature at ~3700 cm^{-1} is assigned to the O-H stretch vibrations of non-hydrogen bonded O-H-groups that stick out of the surface. The sign of the Im[$\chi^{(2)}$] spectrum of the stretch vibration of water is directly related to the orientation of the vibrational transition dipole moment. A positive sign of Im[$\chi^{(2)}$] of the O-H stretch vibrations corresponds to a net orientation with the hydrogen atoms pointing towards the air (up), while a negative sign of Im[$\chi^{(2)}$] corresponds to hydrogen atoms pointing into the liquid (down).

The Im[$\chi^{(2)}$] spectrum of the PVA_{10000} solution strongly differs from that of pure water. In the 2800-3000 cm^{-1} region we find narrow peaks that are associated with the C-H vibrations of the polymer backbone. We assign the two negative bands centered at ~2880 cm^{-1} and ~2930 cm^{-1} to the stretch vibration of the methine group (ν_{CH}) and to the symmetric stretch of the methylene group ($\nu_{CH_2,SS}$), respectively. The positive band at ~2975 cm^{-1} is assigned to the asymmetric stretch of the methylene group ($\nu_{CH_2,AS}$). The negative sign of the $\nu_{CH_2,SS}$ and the positive sign of $\nu_{CH_2,AS}$, show that the methylene groups have a net orientation with the C-H bonds pointing towards the air phase[18, 24]. The negative sign of the ν_{CH} band suggests that the methine groups are also pointing preferentially towards air. Between 3100 and 3500 cm^{-1} we observe a broad signal that is associated with the O–H stretch vibrations of interfacial water molecules. The positive sign of the signal shows that the interfacial water molecules have a net orientation with the O-H groups pointing away from the bulk. The response that is observed at ~3600 cm^{-1} is likely due to non-hydrogen-bonded O-H groups sticking out of the surface. However, this signal cannot be due to free OH groups of interfacial water molecules, as those molecules would yield a narrow peak at ~3700 cm^{-1}, clearly blue shifted from the observed response[26]. We assign the observed signal at ~3600 cm^{-1} to the O-H stretch vibrations of non-hydrogen bonded alcohol groups of the PVA chains, in agreement with the results of a previous VSFG study of PVA[27]. Apparently, PVA is a polymer with a high concentration of hydroxyl groups of which a fraction interacts with the bulk water underneath and a fraction will stick out of the surface.

PVA_{10000} has a hydrolysis degree of ~80%, which means that ~20% of the acetyl groups have not been hydrolyzed to hydroxyl groups. The ongoing hydrolysis of PVA_{10000} leads to the production of acetic acid and negatively charged acetate ions with a relatively high surface propensity. As a result, the interfacial water molecules have a preferred orientation with their hydrogen atoms pointing towards the surface (away from the bulk), thus explaining the positive sign of the broad spectral response between 3100 and 3500 cm^{-1}. This SFG signal can also be described as a $\chi^{(3)}$ effect, where the negative charges at the surface create a static field that orients molecules close to the surface. This orientation results in an asymmetry and thus allows the generation of an SFG signal from the input infrared and visible electric fields. This surface-field induced $\chi^{(3)}$ effect has been studied in detail theoretically[28,29,30] and has been experimentally observed for surfactants, polyelectrolytes and proteins[18,24,31,32,33].

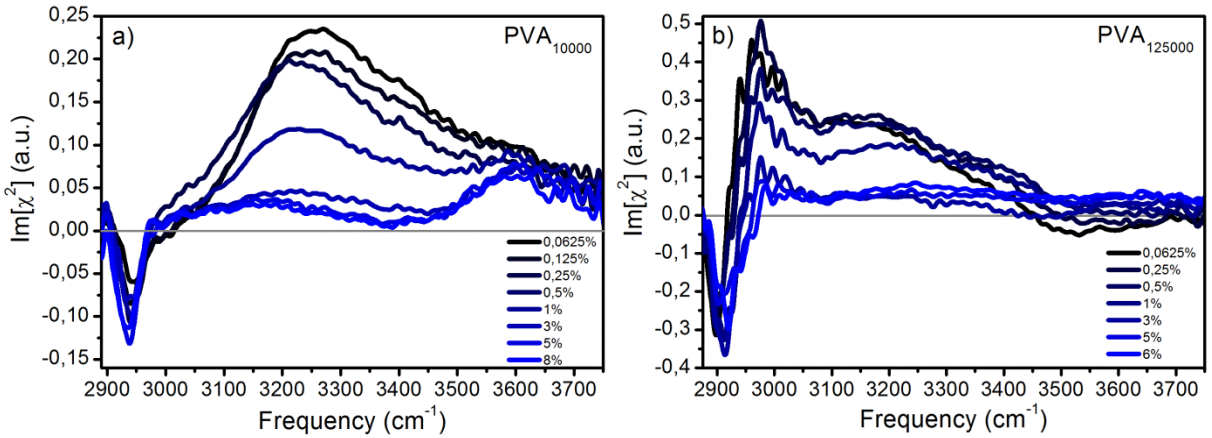

Figure 2: a) Concentration-dependent Imaginary [$\chi^{(2)}$] spectra of PVA_{10000} and PVA_{125000} at the water-air interface, measured in SSP polarization configuration (s-SFG, s-VIS, p-IR). Solution concentrations span from ~0.0625% (black) to ~8% (blue).

In Figure 2a we present Im[$\chi^{(2)}$] spectra of aqueous PVA_{10000} solutions with concentrations spanning from ~0.0625% to ~8%. At the lowest concentration of ~0.0625% we observe that the broad positive band at ~3200 cm^{-1}, attributed to interfacial water molecules, has the highest intensity. With increasing PVA_{10000} concentrations we observe that the intensity of the 3200 cm^{-1} band decreases, confirming the assignment of this band to interfacial water, and at PVA_{10000} concentrations higher than about 1 wt% we find that the intensity is not changing further. A different trend is observed in the C-H region, where the intensity of the signal at ~2970 cm^{-1} first increases and saturates at PVA concentrations higher than about 1 wt%. This last trend is consistent with surface tension measurements that show an initial decrease in γ, and a saturation of this decrease at concentrations >1 wt% (Fig. S4)[12].

The strong decrease of the positive Im[$\chi^{(2)}$] signal between 3100 and 3500 cm^{-1} with increasing concentration (Figure 2a) can be explained from the reduction of the free water surface. At low concentrations, the surface will not be completely covered with PVA_{10000}, and a significant part of the surface consists of water molecules of which the orientation is governed by the surface active acetate ions, yielding to a strong positive signal at ~3200 cm^{-1}. When the concentration is increased, the surface will become increasingly covered with a disordered PVA_{10000} polymer film, leading to a decrease of the free water surface and the orienting effect of surface-active acetate

ions. Molecular dynamics (MD) simulations indeed show that at higher concentrations, the PVA polymers occupy both the surface and the subregion of the interface[14].

The Im[$\chi^{(2)}$] spectra also show a positive peak centred at 3600 cm^{-1}. This signal can be attributed to the response of the non-hydrogen-bonded hydroxyl groups of PVA_{10000}. The positive sign means that the non-hydrogen-bonded hydroxyl groups have a preferential orientation away from the bulk solution, which is to be expected. We observe negligible spectral changes of this signal upon changing the PVA_{10000} concentration, which suggests that PVA_{10000} does not show large conformational changes when the concentration is increased. The alcohol groups of PVA_{10000} that form hydrogen bonds with water molecules will have a net orientation towards the bulk. The response of these groups likely causes the dip in the signal between 3400 and 3500 cm^{-1}.

In Figure 2b we present the Im[$\chi^{(2)}$] spectra of aqueous PVA_{125000} solutions with concentrations ranging from 0.0625% to 6%. PVA_{125000} is much larger than PVA_{10000} and has a higher hydrolysis degree of ~98% (~2% acetyl groups). The signal in the frequency range 3100-3500 cm^{-1} is positive, indicating that the interfacial water molecules have a preferential orientation with their O-H groups away from the bulk, which can again be explained from the ongoing hydrolysis and the production of negatively charged acetate ions that have a relatively high surface propensity. The signal at 3200 cm^{-1} shows the highest intensity at low PVA_{125000} concentrations, and decreases with increasing concentration, but not as strongly as was observed for the smaller PVA_{10000}. Above a concentration of 3 wt%, no further VSFG changes are observed for PVA_{125000}. The increase of the concentration of PVA_{125000} leads to a change of the spectral shape in the CH-region between 2870 and 3000 cm^{-1}. This change in shape is largely due to the fact that the broad and overlapping positive response of the OH vibrations of interfacial water centred at 3200 cm^{-1} decreases. This decrease reduces the observed total positive signal between 2950 and 3000 cm^{-1} while it hardly affects the negative signal between 2870 and 2950 cm^{-1}, thus leading to a change of the overall shape of the spectral response between 2900 and 3000 cm^{-1}.

We find that the VSFG signal between 3500 and 3600 cm^{-1} has a negative sign for low PVA_{125000} concentrations, which is quite different from the observations for the PVA_{10000} solutions. This negative signal corresponds to weakly and non-hydrogen bonded hydroxyl groups of the PVA chains. This finding suggests that PVA_{125000} polymers acquire a special folded conformation in which the alcohol groups have a net orientation towards the aqueous solution. Such a preferential

orientation towards the bulk agrees with the result of a molecular simulation study on 100% hydrolyzed PVA[14]. We observe that the 3500-3600 cm^{-1} signal becomes positive at high concentrations, which indicates that the polymer undergoes a significant conformational change in the surface region at high concentrations.

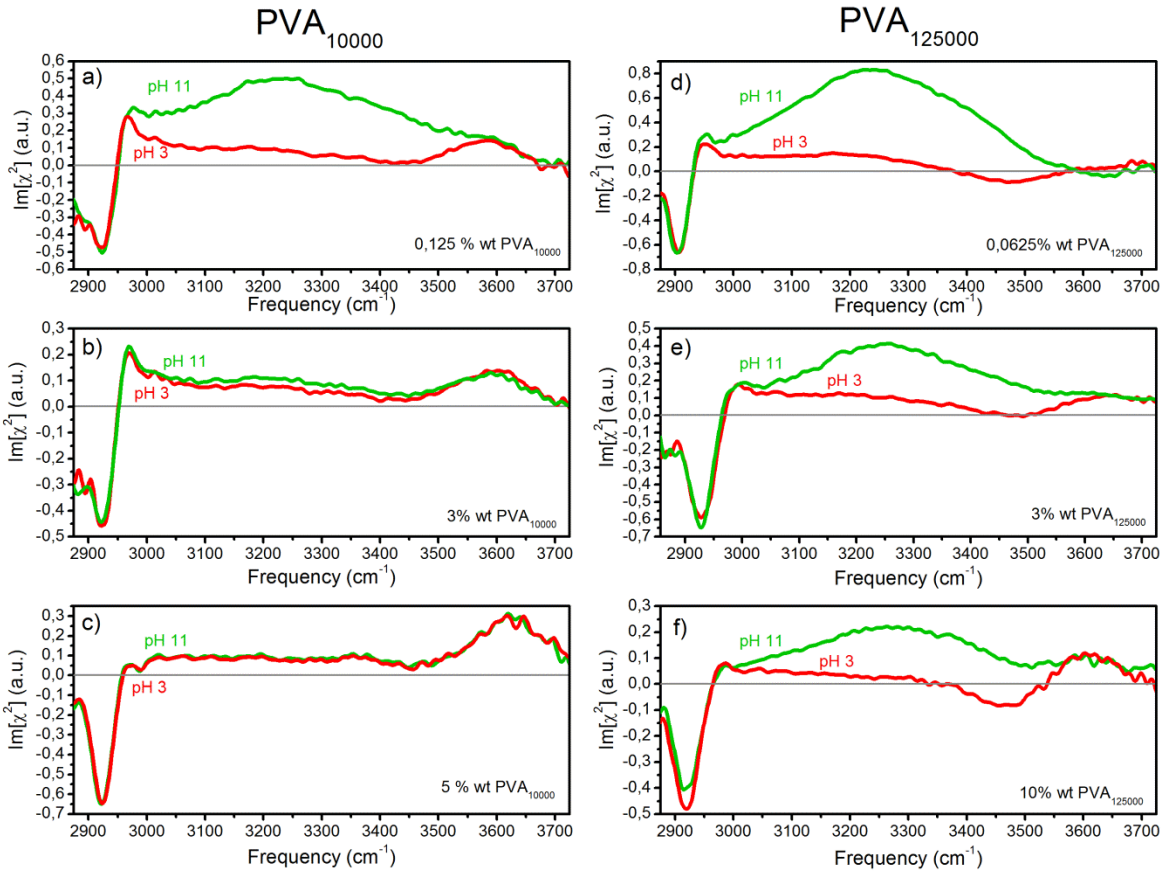

Figure 3: a) Concentration-dependent Imaginary [$\chi^{(2)}$] spectra of PVA_{125000} at the solution-air interface. Solution concentrations span from ~0.0625% (black) to ~6% (blue). b) pH-dependent Imaginary [$\chi^{(2)}$] spectra of PVA_{125000} at low concentrations. c) pH-dependent Imaginary [$\chi^{(2)}$] spectra of PVA_{125000} at high concentrations.

In Figure 3a we present PVA_{10000} spectra at a low concentration for two different pH values. Lowering the pH value causes the signal at ~3200 cm^{-1} to decrease significantly in intensity due to the neutralization of the negative acetate ions. In Figures 3b and 3c we present pH-dependent

PVA_{10000} spectra at high concentrations. In contrast to Figure 3a, we find that the solution pH has a negligible effect on the amplitude of the interfacial water signal centred at ~3200 cm^{-1}. The signal of the hydrogen-bonded water molecules remains low for an alkaline solution with pH=11. We also observe no changes for the PVA specific signals at ~2970 cm^{-1} and ~3600 cm^{-1}.

When we increase the PVA_{10000} concentration, the surface gets completely covered with a disordered polymer layer and the interfacial water signal becomes very small. In this limit, the pH has little effect on the magnitude of the signal, because there is no water surface at which negatively charged acetate ions can accumulate. Hence, also at high pH there will be no net orienting effect on the interfacial water molecules, and thus the signal remains low.

In Figure 3d we show $Im[\chi^{(2)}]$ spectra of a low concentration PVA_{125000} solution at two different pH values. When the pH is decreased we observe a strong decrease in the intensity of the broad signal centred at 3200 cm^{-1}. We explain this signal decrease again from the neutralization of the acetate ions. In Figures 3e and 3f, we present $Im[\chi^{(2)}]$ spectra of a high concentration PVA_{125000} solution at two different pH values. At high pH we observe a significantly stronger $Im[\chi^{(2)}]$ signal near 3200 cm^{-1} than at low pH. This observation is quite different from the results obtained for the smaller PVA_{10000} polymers for which very little dependence on pH was observed at high polymer concentrations. This finding shows that a concentrated PVA_{125000} polymer solution contains a relatively high density of interfacial water molecules of which the orientation depends on the pH, which indicates that the surface contains regions where water is in direct contact with air and where acetate ions can accumulate. Hence, this finding indicates that the surface of a highly concentrated solution of PVA_{125000} possesses open spaces.

Recently, Roŝic et al. reported that for PVA_{125000} concentrations above 5%, the surface tension of the PVA solution rises with increasing polymer concentration and reaches the value of pure water at concentrations higher than ~10%[4]. We observe a similar surface tension anomaly (Fig. S5). Interestingly, we can still detect VSFG signals of the C-H vibrations of PVA_{125000} even at a high concentration of 10% (Figure 3f), which shows that a significant amount of PVA remains present at the surface, despite the surface tension values becoming similar to water. The combination of the surface tension data with the VSFG data indicates that at high concentrations of PVA_{125000}, the polymers in the surface region aggregate to form pores, thus leading to a direct contact between surface water and air. The formation of such an extremely inhomogeneous interfacial solution

configuration explains why both the PVA polymer and the interfacial water signals remain to be observed, and why the surface tension shows an anomalous increase with concentration in the regime of high PVA_{125000} concentrations. In addition, a conformational transition of the PVA_{125000} polymer chains from a more stretched arrangement at low concentrations to a more compact, aggregated conformation at higher concentrations can also explain the change in sign of the 3500-3600 cm^{-1} signal when the concentration is increased (Figure 2b).

Conclusions

We studied the properties of the surface of aqueous solutions of polyvinyl alcohol polymers with average molecular weights of 10000 g/mol and 125000 g/mol using heterodyne-detected vibrational sum-frequency generation spectroscopy. This technique allows us to determine $Im[\chi^{(2)}]$ over a wide frequency range, from which we can derive information on the orientation of the interfacial water molecules and the orientation and conformation of the PVA molecules.

The $Im[\chi^{(2)}]$ spectrum of the interfacial water molecules has a positive sign for both PVA_{10000} and PVA_{125000} at all studied concentrations, which implies that the interfacial water molecules have a preferred orientation with their O-H groups pointing away from the bulk. This observation can be explained from the presence of negatively charged acetate ions that are produced by the ongoing hydrolysis of the acetyl impurities on the PVA polymer chains. We observe $Im[\chi^{(2)}]$ to be positive for the response of the non-hydrogen-bonded hydroxyl groups of PVA_{10000}, indicating that these groups are sticking out of the surface.

For solutions containing a low concentration of PVA_{10000} or PVA_{125000} the interfacial water signal strongly decreases with decreasing pH because of the neutralization of the acetate ions. For highly concentrated solutions of PVA_{10000} polymers the signal becomes very small, irrespective of the pH, indicating that the surface is completely covered with a disordered PVA_{10000} polymer film. For highly concentrated solutions of PVA_{125000} polymers, the interfacial water signal remains pH dependent, getting large at high pH values, which indicates that these concentrated polymer solutions still contain a relatively high density of interfacial water molecules. This relatively high density of interfacial water is consistent with the anomaly in the surface tension that has been observed for large molecular weight PVA polymer solutions. For these solutions, the surface tension first decreases, as is commonly observed for surfactant molecules, but beyond a certain

concentration (~3%) the surface tension re-rises. Combining this finding with the present Im[$\chi^{(2)}$] spectra we propose that large molecular weight PVA polymer solutions form aggregated pores in the interfacial region, thus allowing for a high density of interfacial water.

Supporting Information:

Figure S1: Schematic representation of ester hydrolysis on PVA polymer chains; Figure S2: Surface Tension measurements of $PVA_{10000;}$ Figure S3: Variation of pH values of PVA with concentration Figure S4: Surface Tension measurements of PVA_{125000}.

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