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Stability of hexa(ethylene glycol) SAMs towards the exposure to natural light and repeated reimmersion

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ABSTRACT

We investigate the stability of HS—$(CH_2)_{11}$—$(OCH_2CH_2)_6$—CH_3 self assembling monolayers (hexa(ethylene glycol) SAMs) on gold regarding reimmersion and exposure to natural light over long periods of time up to several months. With polarisation modulation infrared spectroscopy we were able to monitor significant changes in the fingerprint region (900–1800 cm^{-1}) of the absorption modes of the SAMs, starting after a few days of exposure to natural light. We observed an exponential intensity decrease of modes indicating helical conformation of the SAM, as well as an exponential increase of modes indicating esters and formates suggesting a degradation of the SAM. X-ray photoelectron spectra of carbon C1s and sulphur S2p confirm the chemical nature of those changes. SAMs stored without light exposure show a drastically decreased change in the infrared spectra. In addition, we could find substantial conformational changes upon repeated drying and reimmersion in EtOH, manifesting in an intensity decrease of the absorption modes indicating hexa(ethylene glycol) molecules in helical conformation. Since the XPS data do not show changes in the chemical structure, we assume disordering effects and dissolution of molecules in solution. Our results suggest that SAMs can be stored over long periods of time in air without major changes if light exposure is avoided.

1. Introduction

Self assembling monolayers (SAMs) are widely utilized to customize surface properties. They are used as lubricants, elements in molecular electronics [1,2] as well as in biological and medical applications [3–6]. SAMs with protein resistant properties have become especially valuable. They can be applied for coatings of ship hulls hindering algae growth [7], in tissue engineering controlling cell adhesion [8], and in combination with attached molecules with specific binding properties in biosensors based on surface plasmon resonance or quartz crystal micro balance systems [9].

Because of their great importance protein resistant SAMs have been subject of extensive studies concerning the mechanism of their ability to prevent biofouling [5,6,4]. Oligo (ethylene glycol) SAMs (OEG SAMs), introduced by Prime and Whitesides [10] have become a model system for those studies [11,12,6]. However, a full understanding of the process has yet to be reached. In addition to the mechanism of protein resistance, the long-term stability of SAMs is an important issue for their application. Despite its obvious relevance, however, it has not been completely characterized so far. It is known that poly(ethylene glycol) can be oxidized by heat or light, which can trigger a radical reaction resulting in ester and formate products and chain scission [13–15]. It was reported that this degeneration can be slowed down in solution by diffusion which transports the radicals formed during the degradation away from the surface, resulting in OEG SAMs which are protein resistant in solution for more than a week [16,17]. The stability of SAMs over long times also depends on the storage medium. Jans et al. [18] for instance discuss the stability of tri(ethylene glycol) SAMs for biosensing applications under different conditions. It turned out the SAMs stored in air and nitrogen atmosphere as well as in water and phosphate buffer are stable over weeks in contrast to SAMs stored in ethanol which showed degeneration effects after a week [18]. There has been no long time study over the course of weeks and month so far showing degradation kinetics. In an earlier study, we described the conformational and structural effects of heat on hexa(ethylene glycol) SAMs and observed reversible effects up to a temperature of 40 °C and irreversible effects at higher temperature [19]. In addition, thiol

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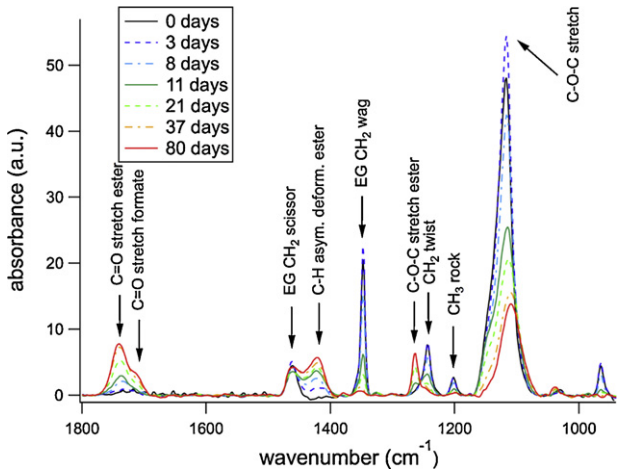

Fig. 1. PMIRRAS spectra of an hexa(ethylene glycol) SAM in air as a function of exposure time to natural light. The modes indicating crystalline OEG molecules in helical conformation, as well as the CH_3 rocking mode indicating the presence of the CH_3 end group and the part of the C—O—C mode indicating amorphous structure decreased in intensity. This indicates a degeneration of the OEG moiety of the SAM. Spectral modes at 1264 cm^{-1}, 1460 cm^{-1}, 1712 cm^{-1} and 1740 cm^{-1} which can be assigned to ester and formate groups increased, indicating that these compounds are end products of the degeneration of the SAM. Note that the modes indicating helical conformation increased in intensity in between the first and the second measurement. Since the SAM was grown in water and the first measurement was made immediately after the growth, the helical part is believed to be distorted by residual water for this first measurement.

bonds can be oxidized by UV light in combination with oxygen [20].

In this study, the structural and conformational implications of this degeneration are addressed. Using polarisation modulation infrared spectroscopy (PMIRRAS) and X-ray photoelectron spectroscopy we have studied the influence of exposure to natural light under ambient conditions on the structure and conformation of hexa(ethylene glycol) SAMs on gold. This is to our knowledge the first publication about the long term stability of protein resistant thiol SAMs which combines infrared spectroscopy and XPS. These complementary methods enable to relate conformational and structural changes to chemical alteration of the SAMs. The results are compared with the long-term behaviour of SAMs in solution. Further, we performed a systematic study of the structural changes in SAMs, which were repeatedly dried and re-immersed into aqueous media.

2. Experimental

2.1. Sample preparation

As substrates gold coated glass slides (www.arrandee.com) were used. The slides were successively sonicated in MilliQ water (18.2 MΩ cm, Millipore) and EtOH (99.9%, Riedel de Haën), then dried in an argon stream, treated with an ozone producing UV-light for 20 min and rinsed with MilliQ water. The cleaning treatment was done directly before each experiment. The SAMs were grown in a 0.5 mM solution of HS—$(CH_2)_{11}$—$(OCH_2CH_2)_6$—CH_3 (hexa(ethylene glycol)) (Prochimia, Gdansk, Poland) in MilliQ water, if other thiol concentrations are used it is indicated in the results part.

Samples were freshly prepared prior to each measurement. For long-term measurements, they were stored in transparent petri dishes under ambient conditions, i.e. room temperature (22 °C) and exposure to natural light, or stored in the dark as indicated. For reimmersion experiments, samples were rinsed with EtOH for 3 s and blow dried directly prior to each measurement.

2.2. Measurements and data analysis

The PMIRRAS setup used was described recently, see Ref. [21]. In short, PMIRRAS data were recorded with a Vertex 70 spectrometer (Bruker, Etlingen, Germany) with an PMA 50 extension unit for reflectivity measurements (Bruker) containing a photoelastic modulator (PEM). The spectral resolution was set to 4 cm^{-1}, 512 scans were co-added.

The data were recorded with the Bruker OPUS software and exported to Igor Pro (Wavemetrics Inc., Lake Oswaego, USA) for baseline correction and Gaussian fitting of spectral modes in the fingerprint region [17]. The error bars reported below represent the standard deviation of the Gaussian fits of 16 spectra of an hexa(ethylene glycol) SAM. The sample was remounted in the spectrometer after each measurement.

X-ray photoemission spectroscopy (XPS) of the SAMs was performed in a multi-chamber UHV-system (base pressure below 1×10^{-9} mbar) equipped with an EA 125 cylindrical hemispherical analyzer (Omicron) and a Mg Kα X-ray source. The energy scale of all spectra was calibrated to reproduce the binding energy (BE) of Au4f$_{7/2}$ (84.0 eV). The raw data were fitted using a numerical routine [22], assuming identical peak shapes for different chemical components.

3. Results and discussion

3.1. Stability in air

Recent studies showed that the infrared spectrum of hexa(ethylene glycol) SAMs on Au is a very sensitive indicator for conformational and structural changes [17,19]. This makes it a good model system for the investigation of the long-term stability of alkanethiol SAMs. Hexa(ethylene glycol) SAMs grown over night in a 500 μM ethanolic hexa(ethylene glycol) solution were stored under different conditions and measured at increasing time intervals. First, a series of SAMs stored in transparent containers was investigated. Fig. 1 shows the evolution of the spectrum of a hexa(ethylene glycol) SAM in air as a function of exposure time to natural light. Already after three days, there are significant changes in the SAM structure, notably a decrease in the intensity of vibrational modes indicating a helical structure and the emergence of modes corresponding to degradation products. After two weeks the spectrum has changed dramatically, implying a notable degradation of the SAM.

The relevant modes are described below: Highly ordered hexa(ethylene glycol) SAMs adopt a predominantly helical conformation, giving rise to characteristic modes: the low frequency component of the C—O—C stretching vibration at 1114 cm^{-1}, the EG CH_2 twisting vibration at 1244 cm^{-1}, the EG CH_2 wagging vibration at 1348 cm^{-1}, and the EG CH_2 scissoring vibration at 1463 cm^{-1}. In addition, a CH_3 rocking vibration at 1200 cm^{-1} verifies the existence of the CH_3 end group of hexa(ethylene glycol) (compare to Table 1 and Ref. [11]).

On the other hand, spectra of SAMs exposed to natural light over long times show modes, which can be attributed to esters and formates. These are the absorption modes at 1740 cm^{-1} and 1712 cm^{-1} which can be assigned to the C=O stretching vibration of ester and formate groups respectively [14,13,23]. The mode at 1460 cm^{-1} can be assigned to the C—H asymmetrical deformation vibration of esters [23] and the mode at 1264 cm^{-1} can be assigned to the C—O—C stretching vibration if one of the C atoms is esterified to C=O [23,24].

To obtain a more quantitative understanding of the underlying conversion process a Gaussian fitting of the spectral modes

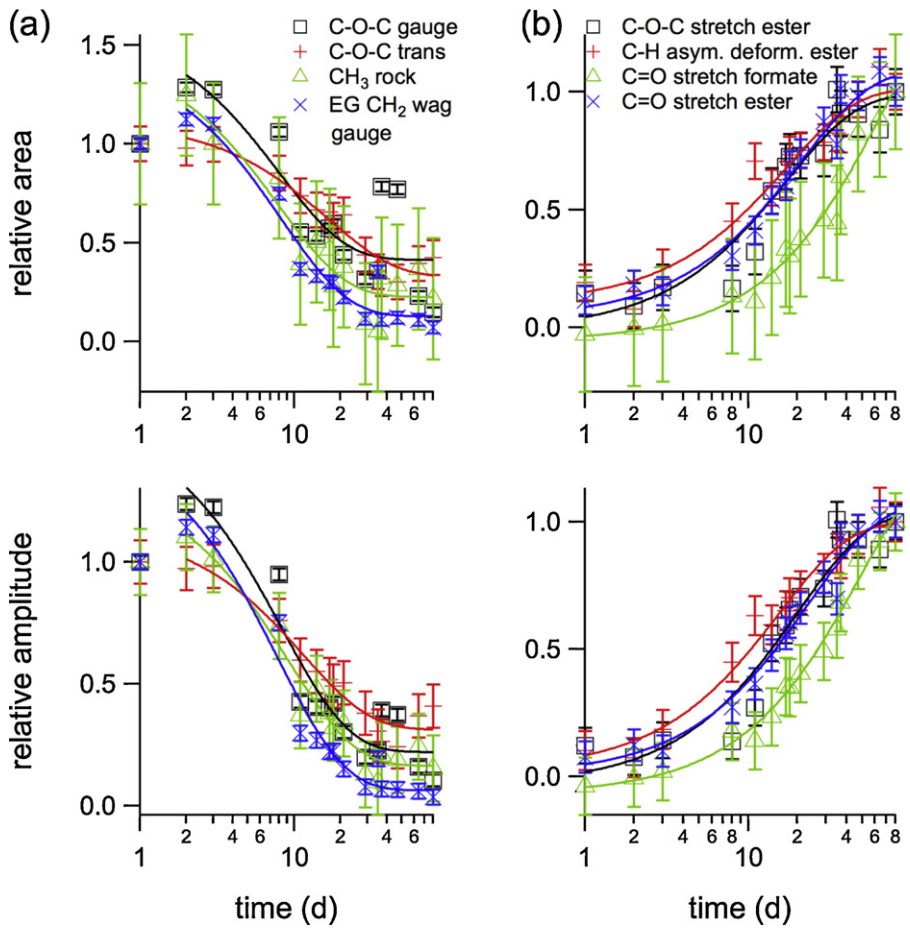

Fig. 2. Gaussian fit of the spectral characteristics, from the spectra shown in Fig. 1 as a function of exposure time to natural light. For visualisation in one graph the values are normalized to the magnitudes at the start for the modes arising from the intact OEG moiety and long time for the modes indicating the degeneration products. The amplitude and area of the Gaussian fits of the modes follow an exponential behaviour, the solid lines represent a fit with a single exponential function. The modes indicating a helical conformation of the OEG moiety, as well as the CH_3 rocking mode indicating the presence of the CH_3 end group and the part of the C—O—C mode indicating amorphous structure decreased in area and intensity. The time constants for the decrease of the area and amplitude of modes indicating amorphous structure are bigger, than the ones for the modes indicating helical structure. The values of the spectral modes which can be assigned to ester and formate groups increased. The time constants of the of the modes indicating ester groups are smaller than the time constants of the mode indicating formate groups.

was performed following the procedure described in Ref. [17]. In Fig. 2a the amplitude and area of the modes of the helical part of the OEG SAM and the CH_3 rocking mode indicating the presence of the CH_3 end group are plotted as a function of time. The amplitude and the area of all four modes decreased following a single exponential, indicating a first order degradation process. The time constants of the modes associated with the helical structure and the CH_3 rocking mode are similar suggesting a real degradation of the molecules rather than a conformational change, see Table 2. Also, the intensity of the absorption modes of the alkane linker between the sulphur atom and the OEG moiety, which can be found in the CH_2 stretching region of the spectra decreased (data not shown), indicating a degradation of the complete SAM rather than only the OEG part. However, the decrease of the modes of the OEG part was more pronounced, indicating a higher stability of the alkane part. Fig. 2b shows the time evolution of the amplitude and the area of the modes corresponding to the ester and formate degradation products. The time constants of the increase of the amplitude and the area of the modes are similar for all four modes and also to the time constants of the decrease of the modes of hexa(ethylene

Table 1
Spectral mode assignment of ordered hexa(ethylene glycol) SAMs in the fingerprint region in helical and all-trans conformation respectively [11,31].

Mode assignment	Helical (cm^{-1})	All-trans (cm^{-1})	Ester (cm^{-1})	Formate (cm^{-1})
EG CH_2 rock (gauche)	964			
C—O, C—C stretch (gauche)	1116			
C—O, C—C stretch (trans)		1144		
CH_3 rock	1200	1200		
EG CH_2 twist	1244			
EG CH_2 wag (trans)		1325		
EG CH_2 wag (gauche)	1348			
EG CH_2 scissor (gauche)	1461			
C—O—C stretch (ester)			1264	
C—H asym. deform. (ester)			1427	
C=O stretch (formate)				1712
C=O stretch (ester)			1740	

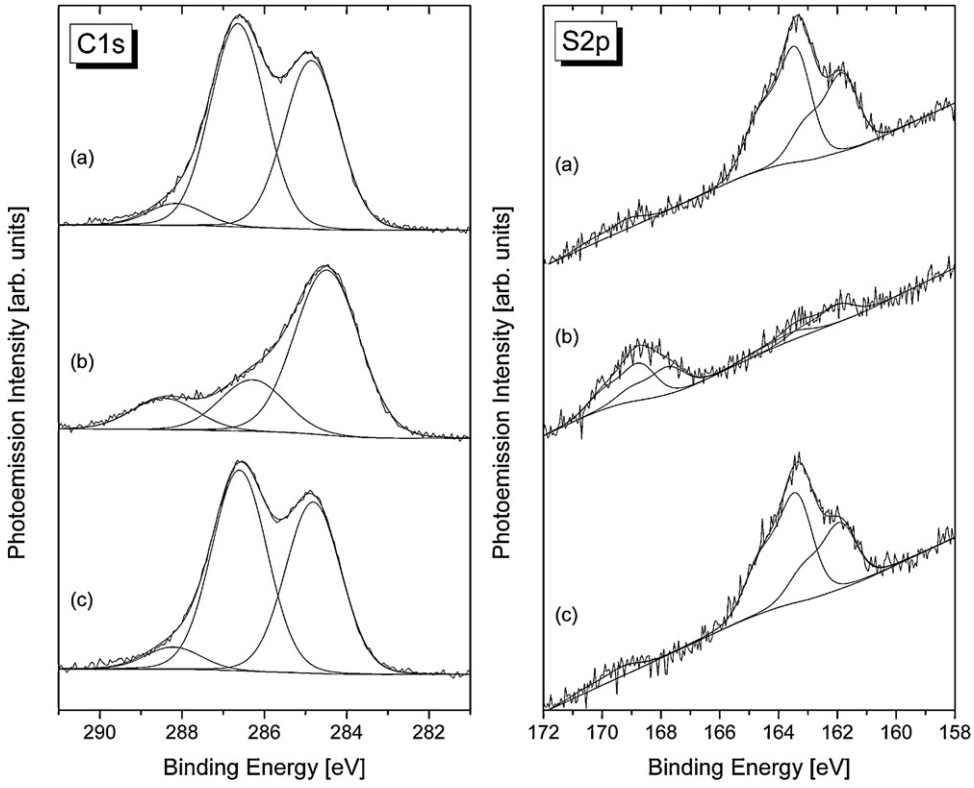

Fig. 3. (Left panel) C1s core-level spectra of hexa(ethylene glycol) SAMs. (a) Spectrum of a freshly prepared sample, used to compare to (b), the spectrum of hexa(ethylene glycol) SAMs, stored under natural light illumination, which shows features that can be assigned to photo-degradation products. And (c), the spectrum of hexa(ethylene glycol) SAMs, treated with repeated immersions, for which no significant variation of the chemical structure is detectable. (Right panel) S2p core-level spectra of hexa(ethylene glycol) SAMs. (a) Spectrum of freshly prepared sample, used to compare to (b), the spectrum of hexa(ethylene glycol) SAMs, stored under natural light illumination, showing oxidation of the majority of the sulphur atoms. And (c), the spectrum of hexa(ethylene glycol) SAMs, treated with repeated immersions. No changes in the chemical structure of the sulphur are visible.

glycol) molecules in helical conformation and the CH_3 end group, see Table 2.

Esters and formates are the two main products of the degeneration of poly(ethylene glycol) exposed to light with $\lambda \geq 300$ nm [14]. Qin and Cai [16] also found formates and esters as the main products, studying the degradation of OEG molecules with 3 EG units. Based on these results, we expected to find these products on our substrates after the exposure of OEG SAMs to natural light. Morlat and Gardette [14] concluded that for photo-oxidation formates are the main products rather than esters. In our experiments, however, esters are the main products. One explanation may be the following. Morlat and Gardette [14] were investigating the degradation of long poly(ethylene glycol) molecules in the bulk phase. There, the scission products are still relatively long chains remaining in solution. In our case the molecules are much shorter, so a number of the formate products after β-scission (compare to Ref. [14]) are short-chained. If an alkoxy radical is formed, attacking the first available carbon atom from top, methyl formate and a

Table 2
Time constants of change of selected spectral modes during light exposure.

Position (cm^{-1})	Amplitude time constant (d)	Area time constant (d)
1116 x	8.3375 ± 1.74	8.0047 ± 3.46
1144 x	11.517 ± 1.84	16.755 ± 3.28
1200 x	9.1322 ± 1.36	7.9658 ± 1.97
1348 x	8.2869 ± 1.34	7.8696 ± 1.03
1264 o	18.301 ± 3.8	15.582 ± 3.48
1427 o	14.998 ± 1.88	15.797 ± 3.34
1712 o	49.85 ± 8.6	67.506 ± 21.3
1740 o	22.763 ± 3.24	20.384 ± 3.22

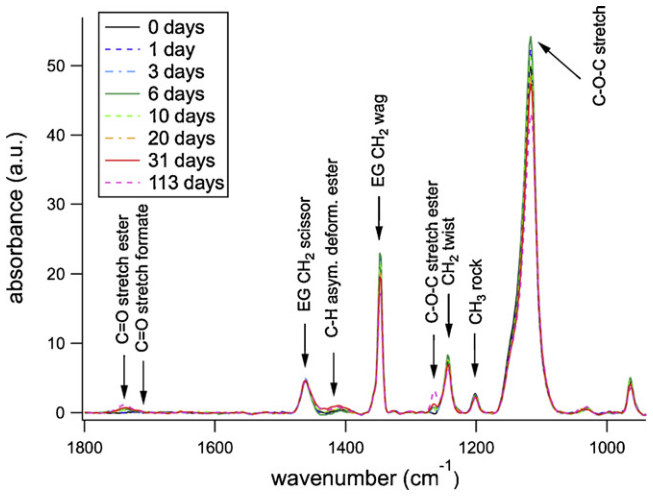

Fig. 4. PMIRRAS spectra of an hexa(ethylene glycol) SAM in air as a function of storage time in the dark. The intensity of the modes indicating crystalline ordered OEG molecules in helical conformation, as well as the CH_3 rocking mode indicating the presence of the CH_3 end group and the part of the C—O—C mode indicating amorphous structure decreased. This indicates a degeneration of the OEG moiety of the SAM. However, the decrease of the modes is significantly slower than in the case of a SAM under light exposure. The intensity of the spectral modes which can be assigned to ester and formate groups increased, indicating that these compounds are end products of the degeneration of the SAM. Note that the intensity of the modes indicating helical conformation increased in between the first and the second measurement. Since the SAM was grown in water and the first measurement was made immediately after the growth, the helical part is distorted by residual water for this first measurement.

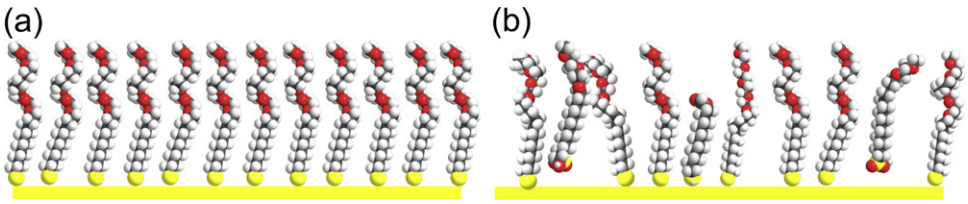

Fig. 5. Degeneration effects during the long-term storage of hexa(ethylene glycol) in air under exposure to natural light are shown, starting with a very high coverage SAM (a), after two weeks significant changes in the absorption spectra can be seen (b). Due to formation of esters and formates a big fraction of molecules is no longer stabilized in the helical conformation. The chains of molecules reacting to formats are truncated [14,15]. Additionally, the UV part in the natural light is inducing a oxidation of sulphur atoms. Therefore, a significant fraction of the SAM molecules is only physisorbed on the surface and can be removed by rinsing with solvent.

macroradical comprising the remaining part of the hexa(ethylene glycol) molecule are formed. Methyl formate has a boiling point of 32 °C and it is likely that it evaporates shortly after formation at room temperature. This evaporation of short chained formates may explain that the modes indicating formates in the infrared spectra measured during degradation are rather weak. In addition to the kinetics of degradation, we investigated whether the degradation products are still chemisorbed on the surface or just physisorbed. To this end the samples being exposed to light for 80 days were rinsed with EtOH and and the resulting spectra were compared to measurements before rinsing. Results showed a further decrease in the intensity of modes attributed to the OEG moiety of the SAM and alkane spacers and a decrease in the modes indicating the degradation products, esters and formates. This shows that many molecules were not longer chemisorbed and washed away during rinsing. Reasons for this behaviour may be the scission of the OEG chains during oxidation (compare to Ref. [14,15]) as well as the oxidation of the sulphur atoms due to the UV part of the light [20].In order to gain information about oxidation products, freshly prepared hexa(ethylene glycol) SAMs and samples stored under illumination of natural light were characterized using XPS. The C1s photoemission core-level spectrum of the freshly prepared sample in the left panel of Fig. 3 shows features at 284.8 eV binding energy (BE) which can be attributed to the alkane linker, at 286.6 eV BE arising from the OEG part of the molecule and at 288.1 eV BE due to a slight oxidation of the *ex-situ* prepared sample. The intensity ratio of the two main carbon species, i.e. alkane linker:OEG moiety, is 1:1.20 which is in good agreement with the ratio expected from the number of atoms per molecule (1:1.27). This demonstrates that the molecules, measured as reference samples, were neither fragmented nor degraded. The spectrum of the illuminated sample shows the respective features at slightly lower binding energies due to the changed chemical environments of the carbon atoms after illumination. The feature of the alkane linker appears at 284.5 eV BE and the feature of the OEG moiety at 286.3 eV BE. Furthermore, an additional crucial feature at higher BE is present in the spectrum of the illuminated sample. Its binding energy of 288.4 eV is pointing to the presence of higher oxidized carbon species, like esters or formates which is in good agreement with the results obtained by infrared spectroscopy (see above). Here, the feature of the alkane linker dominates the spectrum in contrast to the spectrum of the freshly prepared sample which is dominated by the feature of the OEG moiety, which also manifests in the decrease of the O1s peak of the illuminated sample (not shown), corresponding to the OEG moiety of the molecule. The S2p spectrum of the freshly prepared sample, shown in the right panel of Fig. 3b (top), can essentially be described by three S2p doublets with binding energies of the $S2p_{3/2}$ peaks of 161.8 eV, 163.4 eV and 169.1 eV. The doublet at 161.8 eV BE corresponds to the sulphur atom of the chemisorbed hexa(ethylene glycol) SAM molecule. The origin of the feature at 163.4 eV BE is X-ray induced damage of the SAM caused by extended exposure to irradiation [1], all samples were exposed to X-rays for the same time. The shift of the S2p peak in relation to the S2p peak of the chemisorbed hexa(ethylene glycol) at 161.8 eV may indicate the formation of —S—S— bonding or detaching thiol with protonation of sulphur. Whereas the feature at 169.1 eV BE represents an amount of about 4% of highly oxidized sulphur, due to a slight oxidation of the *ex-situ* prepared samples. The spectrum of the illuminated sample in the right panel of Fig. 3b (middle) on the other hand has its main features in the region of high binding energies (~169 eV), indicating that the majority of the sulphur atoms of the SAMs were highly oxidized after storage under natural light illumination. The spectrum of this sample shows a small amount of unoxidized sulphur at 161.8 eV and again, a feature related to X-ray damage, which is recognizable by a doublet at 163.4 eV [25]. In summary, the sample stored under natural light illumination shows an oxidation of all parts of the molecule. Judging from relative intensity changes in the C1s and S2p spectra, the oxidation of the OEG- and the thiol-groups are more pronounced than the oxidation of the alkane linker.

In addition, a series of SAMs stored in the same containers, but in the dark, was measured by PMIRRAS (Fig. 4). Even after long storage times (weeks) there was only little change in the spectra, the decrease of the modes which can be assigned to the not oxidized part of the SAM and the modes assigned to the oxidation products are significantly smaller than for a similar SAM exposed to natural light. The degree of degradation is significantly lower, compared to the measurements under illumination. The results are indicating a much higher stability of the SAMs in the dark compared to those exposed to natural light, which is consistent with the literature [15] considering photo-oxidation of the ethylene glycol part as the major process of SAM degradation at room temperature, see also Fig. 5.

3.2. Stability during repeated drying and reimmersion

While OEG SAMs are applied in an aqueous environment, they are mainly characterized in ambient atmosphere or in vacuum [26]. Since OEG SAMs undergo a conformational change when exposed to an aqueous environment [17,27–29], it is crucial to compare the SAM structure and conformation with and without surrounding solvent. Due to SAM–water-interactions the OEG moiety in helical conformation becomes amorphous if water molecules are able to penetrate the SAM. For comparison of the spectra of SAMs in different environments and for an evaluation of their long-term stability in changing environment, it is important to check if OEG SAMs partly dissolve, degrade or change their structure during repeated immersion in solvents. To investigate this behaviour, again the model system of an hexa(ethylene glycol) SAM grown in a 500 μM ethanolic hexa(ethylene glycol) solution over night is used. First, we measured a series of infrared spectra, each of them after a cycle of rinsing the SAM with EtOH for 3 s and blow drying afterwards. Comparing of the intensity of the absorption modes reveals that the helical structure of the SAM gradually vanishes, Fig. 6. Fig. 6e and f shows the area and amplitude as a function of the number of reimmersions in EtOH. The decrease of the area and the amplitude of the modes follows an exponential behaviour. Importantly,

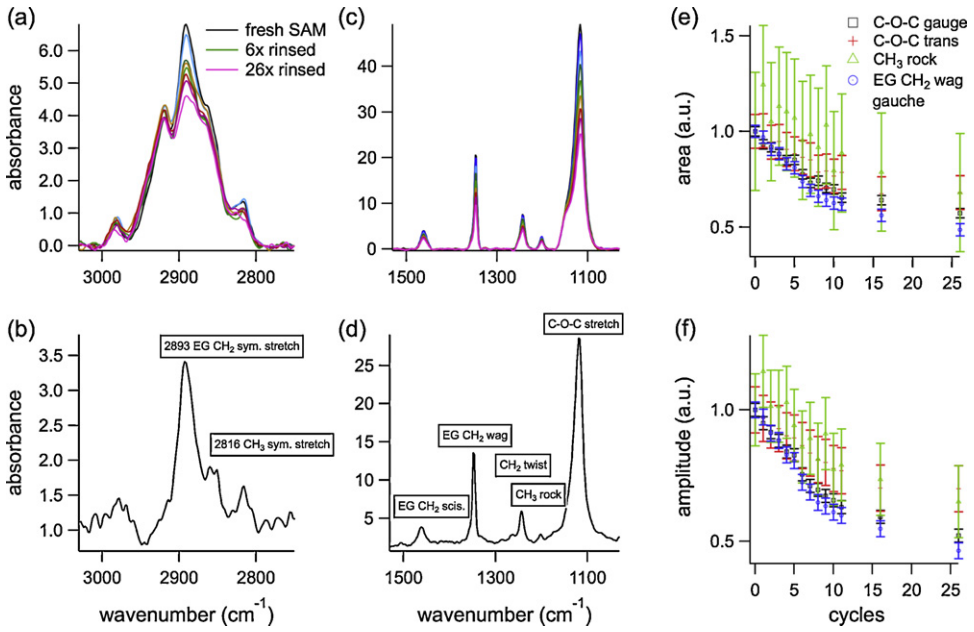

Fig. 6. PMIRRAS spectra of an hexa(ethylene glycol) SAM measured in air after repeated reimmersion in EtOH and successive drying. (a, c) Evolution of the spectra in the CH region and the fingerprint region, respectively. With the increasing number of immersion cycles the modes indicating a crystalline OEG moiety decreased gradually, indicating an increasing disorder. (b, d) Difference spectra of the spectrum of the fresh SAM and the SAM after 26 reimmersion cycles. Note especially, that the absorption bands indicating a helical structure and indicating the presence of the CH_3 head group decreased in intensity, whereas the absorption modes indicating an ordered alkane spacer are not affected. This is suggesting, that mainly the OEG moiety is becoming disordered during repeated reimmersion. (e, f) Area and amplitude of characteristic modes of the spectra of the hexa(ethylene glycol) SAM measured in air after repeated reimmersion in EtOH and successive drying. The modes indicating a ordered OEG moiety decrease exponentially, suggesting a decreasing order of this part of the SAM.

the decrease in intensity is the same for the modes associated with the helical conformation and the CH_3 rocking mode. The intensity of the part of the C—O—C peak indicating an amorphous structure does not decrease, which is discussed in the next paragraph. The width and peak position are not changing significantly suggesting no substantial structural and conformational change in the remaining OEG molecules. In Fig. 6b, d the difference spectrum of the hexa(ethylene glycol) SAM prior to the rinsing process and that after 25 rinsing steps is shown. It reveals in the C—O—C region changes of the modes indicating helical conformation and the CH_3 rocking mode, however not the part of the C—O—C peak indicating an amorphous structure. This supports our results from the spectral mode fit: the number of OEG molecules adopting a crystalline structure and a helical conformation decreases continuously with each reimmersion and drying step. The difference spectrum in the CH_3 region shows virtually only modes of the OEG moiety and of the CH_3 rocking vibration. This indicates that the conformation and orientation of the alkane linkers of the OEG molecules is not significantly changed due to the reimmersion cycles. From the literature it is known that there are desorption effects from thiol SAMs in solution [5,30]. The desorption rate depends on the crystallinity of the SAM: the higher the crystallinity the slower the desorption rate. This suggests that the desorption starts at defect sites of the SAM. It may also comprise the washing out of SAM molecules which are only physisorbed to the SAM without the formation of a thiol bond, compare to Ref. [26]. Since the amount of time required for a significant desorption is hours rather than seconds [30], there is only a tiny change in surface coverage after short immersion times as applied in this study.

Comparison of the XPS spectra recorded of the freshly prepared samples and the samples treated with repeated immersions does not show changes in the chemical structures of the hexa(ethylene glycol) SAMs. Neither the carbon spectra (Fig. 3a) nor the sulphur spectra (Fig. 3b) exhibit any significant variation. The ratio of the C1s intensities of the carbon components assigned to the alkane linker and the OEG moiety of the re-immersed sample is 1:1.17, which is again in good accordance to the ratio expected from the number of atoms per molecule, mentioned in the previous part. The S2p spectra also do not show significant differences between the freshly prepared sample and the sample after re-immersion. The particular features can be explained analogously to the ones in (a) in the left panel of Fig. 3 (see above). In summary, both C1s and S2p spectra show no indication for a chemically different composition of the SAM.

Overall, we derive the following picture: the small change of the vibrational modes related to the alkane chains implies that there is only a tiny change in surface coverage and further that the

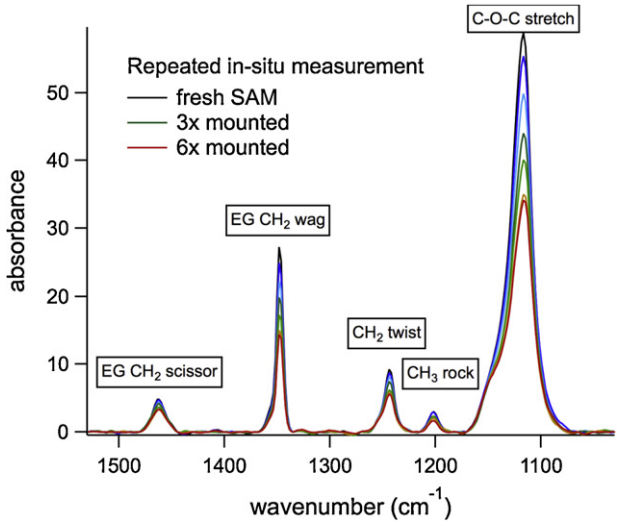

Fig. 7. Spectra of hexa(ethylene glycol) SAM measured in air after repeated measurements in an aqueous environment in our thin liquid cell. The change of the intensity of the spectral modes is qualitatively very similar to the change for repeated rinsing with EtOH, suggesting a similar degeneration mechanism.

conformation of this part of the SAM is not significantly affected. In contrast, there is a substantial change in the conformation of the OEG part of the SAM manifesting itself in a decreasing intensity of the modes related to a helical structure and the rocking mode originating from the CH_3 endgroup of the SAM molecules. This shows that the conformation of the OEG part is much more sensitive to small changes of the surface coverage, which is supported by recent experiments [17,19].

Additionally, alternating measurements in air and in water, using our thin liquid layer cell were performed (Fig. 7). The results are comparable with our findings for the experiments where SAMs were rinsed briefly with EtOH, if one estimates two reimmersion events per *in-situ* measurement (immersion of the sample with water during the start of the experiment and a washing step with water after the experiment). These results indicate that the reasons for the changing infrared signal in subsequent *in-situ* measurements are the same as for repeated drying and reimmersion steps, rather than being due to other effects, such as mechanical abrasion.

4. Conclusion

Our experiments show that OEG SAMs can be stable over months if they are stored and treated under appropriate conditions (no light exposure and reimmersion). OEG SAMs degrade predominantly *via* exposure to light, and by repeated drying and reimmersion. By avoiding the exposure of OEG SAMs to such conditions they can be stabilized over weeks without serious structural degradation. These findings underline the importance of *in-situ* measurements for dynamical processes such as SAM growth in solution and may help to understand long-term biofouling properties of OEG SAMs.

Acknowledgements

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