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On the Stability of Oligo(ethylene glycol) ($C_{11}EG_6OMe$) SAMs on Gold: Behavior at Elevated Temperature in Contact with Water

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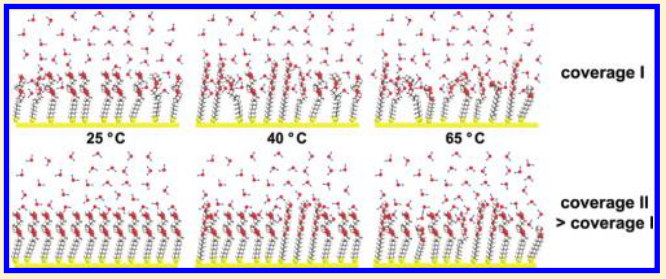
Supporting Information

ABSTRACT: In this study the temperature dependent conformation of hexa(ethylene glycol) self-assembling monolayers (SAMs) under aqueous conditions (*in situ*) is investigated. To this end characteristic absorption modes in the fingerprint region (1050−1500 cm^{-1}) were monitored with real-time polarization modulation infrared spectroscopy. We found a temperature induced conformational change from predominantly helical to helical/all-trans. The process may be divided into two temperature regimes. Up to 40 °C the process is reversible after drying the monolayers in air and successive reimmersion in water, indicating a strong binding of the water molecules to the SAM. At higher temperatures, the conformational change is irreversible. Additionally, a rapid change to a larger mode width and a shift of the mode position to higher wavenumbers (blue-shift) at about 50 °C indicates structural changes caused by decreasing crystallinity of the SAM. While the conformational changes up to 40 °C are supposed to originate from an increased conformational freedom in combination with a stronger interaction with water molecules, the irreversibility and rapid change of mode characteristics at higher temperatures indicate chemical degradation. Complementary measurements in air show a fast and virtually complete reversibility up to 40 °C underlining the effect of the interaction of the ethylene glycol moiety with water. At temperatures above 50 °C modes indicating ester and formate groups appear, supporting the idea of chemical degeneration. Moreover, the temperature behavior is coverage dependent. At incomplete coverage the structural order of the SAM starts decreasing at lower temperatures. This study shows, that the conformational and structural change of hexa(ethylene glycol) SAMs at elevated temperature is an interplay of conformational changes of the SAM, its interaction with water and at higher temperatures its chemical degradation. Our experiments also underline the importance of the *in situ* analysis on the film structure.



1. INTRODUCTION

Self-assembling monolayers (SAMs) have gained increasing importance within the last decades as a valuable tool for tailoring surface properties.[1,2] SAM coatings with protein resistant properties have a wide application in order to prevent protein adsorption on surfaces.[2−6] They can be used as coatings on ship hulls to prevent algae growth[7] as well as in biological and medical applications to prevent or localize cell growth.[5,8]

Owing to the tremendous importance of protein resistant SAMs there has been extensive work to obtain an understanding of the mechanism[9] and to produce SAMs with improved antibiofouling properties. To prevent biofouling, proteins have to be prevented to leave the hydrophilic environment they have in solution. Thus, hydrophilic surface properties as well as hydrophilic moieties of SAMs enhance their protein resistance. Additionally, it is important that the proteins are not able to penetrate into the SAM and interact with the hydrophobic spacer groups or substrate. Oligo(ethylene glycol) SAMs on gold substrates, introduced by Prime and Whitesides in 1991 represent a good model system for such investigations.[6] In order to stabilize OEG SAMs, the interaction of the OEG moiety with water and its ability to form hydrogen bonds plays an important role. Recent studies suggest, that this is strongly influenced by the conformation of the SAM molecules, the related packing density[10] and its surface coverage. It has been shown that OEG SAMs with maximum surface coverage and perfect helical conformation are not able to prevent nonspecific protein adsorption, whereas such with lower coverage and less perfect order are protein resistant.[11] Recent investigations indicate that the ability of water to penetrate the SAM is a key to the understanding of this behavior.[12]

Many applications of protein resistant SAMs, for instance in the field of medicine for implants or in the domain of biology for cell culturing require the property of protein resistance to be maintained well above ambient temperature. Thus, it is of interest

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to determine if there are any changes in SAMs structure on increasing the temperature above room temperature. Also, there are several conflicting reports in the literature on the temperature and coverage dependence, some of which may result from different degrees of intactness of the SAMs as a function of temperature, coverage and storage.[9−11,13−15] Time dependent measurements at 37 °C with tri(ethylene glycol) SAMs showed that SAMs could retain their protein resistant properties over days in a protein solution at this temperature.[14] Neutron measurements, however, show that it is also possible to switch off the protein resistance with temperature change around 37 °C with mixed OEG and alkane SAMs.[13] Structural investigations of OEG SAMs so far have only been completed under vacuum conditions. Valiokas et al.[16] showed, that for hexa(ethylene glycol) SAMs stabilized with an amide group, the conformation changes from predominant helical to all-trans with rising temperature. Thus, we were interested in the conformational and structural behavior of OEG SAMs under *in situ* conditions. Especially at temperatures above 50 °C, where the conformational transition of hexa(ethylene glycol) SAMs observed by Valiokas et al. occurs, also degradation effects may play a role as described in literature for poly(ethylene glycols) (PEGs).[7,17]

In this study the conformational and structural change of hexa(ethylene glycol) (EG_6OMe) SAMs in aqueous conditions is investigated with polarization modulation infrared spectroscopy (PMIRRAS). PMIRRAS is suitable for *in situ* "under water" studies and is an extremely sensitive tool to monitor changes in the conformation of OEG SAMs. To this end, vibrational modes in the infrared fingerprint region which indicate the conformation of the SAM molecules, were tracked as a function of temperature within a range of 22 and 65 °C. Further, the reversibility of this change was tested and the results were compared to PMIRRAS and grazing incidence X-ray diffraction measurements in air.

2. EXPERIMENTAL SECTION

2.1. Sample Preparation. As substrates gold-coated glass slides (Arrandee) were used. The slides were successively sonicated in Milli-Q 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 Milli-Q water. The cleaning treatment was done directly before each experiment. For the SAM grown inside the *in situ* cell a 1.25 mM solution of $C_{11}EG_6OMe$ thiol (ProChimia, Gdansk, Poland) in Milli-Q water was used. We added NaF (0.1 M) to the solution, to enhance the stability of the BaF_2 half cylinder of the thin liquid cell. For the SAMs grown in bulk solution a 0.01 mM solution of $C_{11}EG_6OMe$ in Milli-Q water was used with an immersion time of 150 h. We will refer to this as maximum coverage. In addition a SAM was grown in the same solution for 10 h. We will refer to this as close-to-maximum coverage, which we assume to be only a few percent below maximum coverage. Note that SPR measurements of the growth of OEG SAMs in water with comparable concentrations show no significant increase in surface coverage after a growth time of 2 h.[11]

2.2. Sample Characterization. PMIRRAS measurements were performed with a setup described recently.[18,19] In short, we used a Vertex70 Spectrometer (Bruker, Ettlingen, Germany) equipped with a PMA50 extension (Bruker) containing a photoelastic modulator (PEM), purged with dry air. We used a resolution of 4 cm^{-1}, 256 scans per measurement were recorded in air, 1024 scans under aqueous conditions.

For the measurements under *in situ* conditions a temperature regulated cell with a design very similar to an *in situ* cell used in previous studies[12,18,19] was constructed, see Figure 1. It can be temperature regulated by hot water provided by a water bath. The thermostated water bath

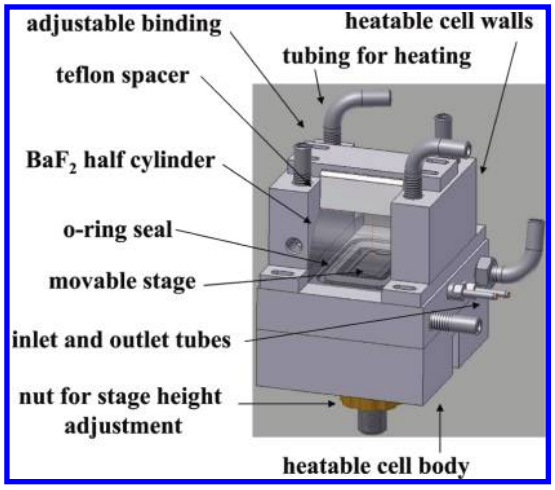

Figure 1. Sketch of the temperature controllable thin liquid layer cell. The sample is placed in between the movable stage and the barium fluoride crystal.

temperature can be controlled with an accuracy of 0.5 °C. Simultaneously to the measurement of the temperature of the reservoir of the water bath, the temperature of the water in the sample cell was measured. There was no measurable difference only a delay of about 30 s in the cell when running a temperature gradient of 0.5 °C/min. For the temperature dependent measurements the temperature of the water bath was increased in steps of 2.5 °C with a waiting time of 10 min before the IR scans to ensure an equilibrated system. The temperature range was 22 to 65 °C; in the reversibility runs the range was limited from 22 to 45 °C.

The spectra were exported from the Bruker data acquisition program OPUS and baseline corrected in Igor Pro (WaveMetrics, USA) as described elsewhere.[19] The area, amplitude, width and position of the modes in the fingerprint region were determined by fitting of Gaussian functions.[12] We approximate the C−O−C absorption band with two modes which leads to robust fits. For the purpose of our kinetic experiments we do not interpret smaller details with the same approach as explained in ref 12. To determine the statistical error bars (rms values) we measured a large number of spectra under equilibrium conditions.

As complementary characterization, in-plane grazing incidence X-ray diffraction (GIXD) experiments were performed at the beamline I07 at the Diamond synchrotron facility in air and at a photon energy of 20 keV.[20] A detailed description of GIXD can be found in refs 1 and 21.

3. RESULTS AND DISCUSSION

3.1. Temperature Range up to 40 °C. An identification of the modes of OEG SAMs in the fingerprint region under *in situ* conditions can be found in ref 12; see also Table 1 and refs 10 and 22. First, we will focus on the temperature region of 22−40 °C, as this is relevant for most applications. Figure 2 shows the spectra of a SAM grown in the sample cell as described in ref 12 and then monitored at elevated temperatures without changing the environment apart from the temperature. As can be seen, there is a gradual decrease of the modes indicating helical structure with increased temperature, while the mode indicating all-*trans* structure is increasing. The widths and positions of the helical modes are not changing, implying that there are no substantial structural changes (see Figure 3). Note that there is no splitting of the mode at 1325 cm^{-1} as would be expected for the case of strong coupling between the trans bonds in the OEG part. Instead, the

Table 1. Spectral Mode Assignment of Ordered OEG SAMs in the Fingerprint Region in Helical and All-*Trans* Conformation[10,22]

mode assignment	EG_6OMe helical (cm^{-1})	EG_6OMe all-*trans* (cm^{-1})
EG CH_2 rock (gauche)	964	
C−O−C stretch (gauche)	1116	
C−O−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	

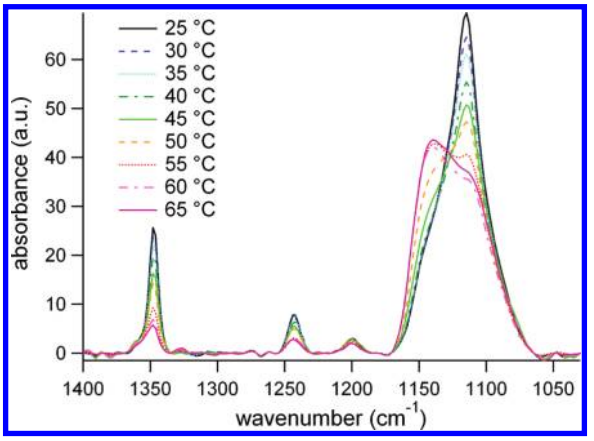

Figure 2. Spectra of an EG_6OMe SAM in aqueous environment as a function of temperature up to 65 °C. The intensity of the low frequency part of the C−O−C stretching mode, the EG CH_2 twisting mode and the EG CH_2 wagging mode decrease with temperature, while the intensity of the high frequency part of the C−O−C stretching mode increases, indicating a change from predominant helical to helical/all-*trans* conformation.

broad mode suggests the presence of gauche defects. The strong absorption mode at 1144 cm^{-1} and the absence of a significant mode at 1128 cm^{-1} support, however, that there is a conformational rather than a structural change (see ref 10). As discussed in ref 23, also a reorientation of OEG segments perpendicular to the surface normal can give rise to an absorption mode at 1149 cm^{-1}. In ref 16, however, it is shown that under vacuum conditions the evolution of the C−O−C stretching mode at 75 °C from a position of 1114 to 1144 cm^{-1} is nearly complete and reversible. Since there is not enough space for a reorientation of the complete OEG moiety at maximum coverage, reorientation is believed to be of minor importance (see also ref 12). The conformational change may be due to a change of the intra- and intermolecular interaction of the OEG molecules or a change of the interaction with water. Valiokas et al.[16] measured the conformational changes of hexa(ethylene glycol)thiol SAMs on gold, which contained amide groups, under vacuum conditions. At elevated temperatures, they observed a change from helical to all-*trans* conformation. However, the transition occurred at higher temperatures (around 60 °C) compared to our experiments. A reason for this behavior may be due to the different molecules used, those containing an amide group in between the alkane spacer and the OEG moiety of the molecules, may be able

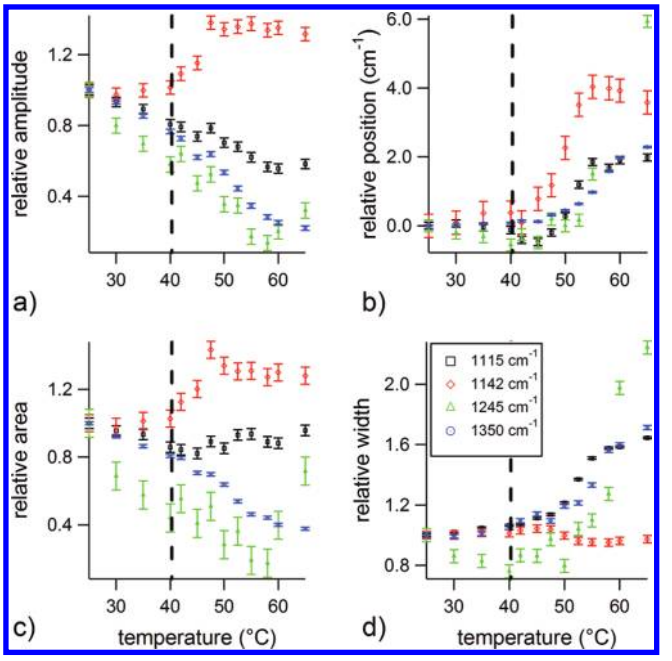

Figure 3. Spectral characteristics as a function of temperature up to 65 °C. For visualization in one graph, the values are normalized to the magnitudes at 25 °C. The error bars show the combined uncertainties related to the measurement and fitting. In A and C, one can see that the Gaussian fits of area and amplitude of the modes, indicating a helical conformation, are decreasing, whereas the values of the high frequency mode of the C−O−C peak are increasing slightly indicating a decrease in helical structure. In B and D, it becomes obvious that there are two temperature regimes—below and above 45 °C. It can be seen that there is an increase in width and a shift in mode position starting at about 45 °C, indicating structural changes.

to form intermolecular hydrogen bridges and stabilize the structure.

Another argument may be the interaction between the SAM and water molecules in our experiment. Considering a higher degree of freedom of the ethylene glycol moiety at elevated temperature, it might be easier for water to penetrate the SAM. Its interaction with the lone-pairs of the oxygen atoms in the ethylene−glycol moiety may ease conformational changes. Additionally, further gauche defects could be introduced due to hydrogen bridging of water molecules.

It is hard to distinguish the destabilizing effects caused by the lack of amide groups on the one hand and water at the other hand, since both exhibit a quite similar result—a decrease in order and a decrease of the fraction of molecules in helical conformation.

To shed light into this issue, the reversibility of this conformational change was investigated. The transition monitored by Valiokas et al.[24] was completely reversible and the reordering occurred on a 5 min time scale. In Figure 4, *in situ* spectra of a EG_6OMe SAM being heated up from 25 to 40 °C and cooled down to 25 °C again are shown. Our measurements show that the transition from helical to helical/all-*trans* conformation takes place on a similar time scale as described in Valiokas et al.;[24] however, the changes were not reversible within minutes when cooling down the system. After decreasing the temperature again to room temperature, the molecules stayed in the conformation they adopted at higher temperature and even after several hours there was no substantial change. Drying the SAMs in an argon stream after the *in situ* temperature scans and monitoring under

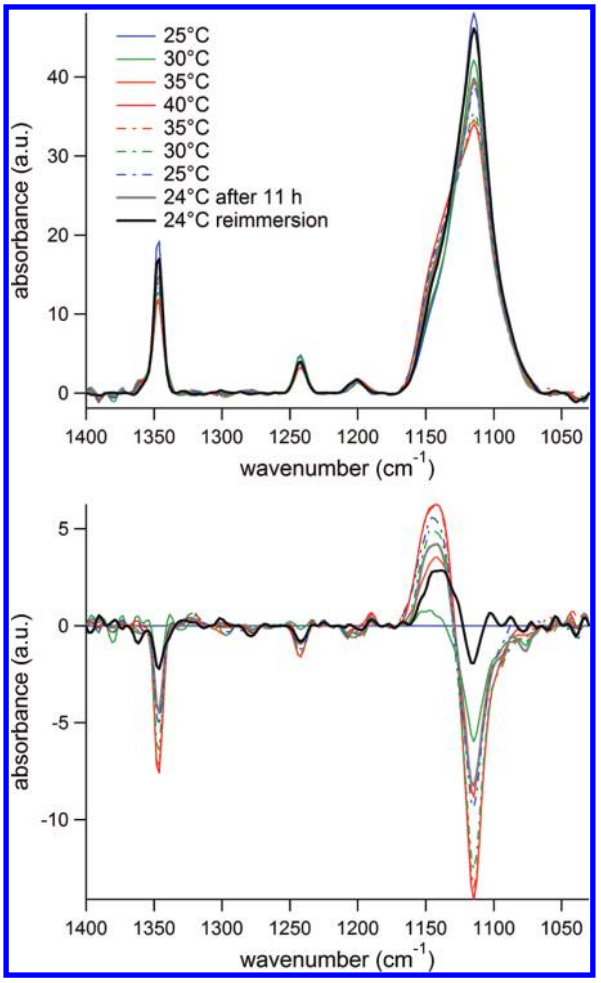

Figure 4. Evolution of the spectral modes and difference spectra with respect to the first run at room temperature of an EG_6OMe SAM in aqueous environment during heating from 25 °C up to 40 °C and cooling down to 25 °C. The conformational changes are not reversible in solution, even after 11 h. However, after drying and reimmersion, the predominantly helical conformation is virtually restored.

water after reimmersion led to a return to a conformation close to the initial conformation; see Figure 4. The reversibility is virtually complete, although degeneration effects hinder complete reversibility. This leads to the conclusion that more water molecules were able to penetrate into the SAM at elevated temperature which induces a conformational change of the OEG moiety. Further, this may support the idea that these water molecules are tightly bound to the OEG-layer.[25] Only drying in air is able to release the water, enabling the OEG molecules to adopt their original conformation. This is another indication of the relatively strong binding of water molecules to the ethylene glycol moiety and its importance for OEGs biofouling properties.

This result is only in apparent conflict with the observations during SAM growth in our previous work.[12] There, an increase of the fraction of the OEG moiety in helical conformation and an improved crystallinity over time were observed. Drying and reimmersion of the OEG SAMs after *in situ* growth did not lead to an additional increase in order. However, there is an important difference between these experiments. During SAM growth, the binding of more thiol molecules to the surface is a driving force for a structural change and may press water out of the OEG moiety. When decreasing the temperature, there is no such driving force, being able to disrupt the water-SAM interaction in the OEG moiety once the water molecules have penetrated the SAM. In addition to energetic effects, also entropic aspects may be considered. In ref 26, the change in entropy due to the binding of water molecules to the ethylene glycol moiety and their relation to the change in energy is discussed. Since the entropy gain due to water molecules leaving the SAM in the bulk solution is partly compensated by the loss of entropy of the SAM due to higher crystallinity, energetic effects are believed to play a more prominent role.[26]

3.2. Temperature Range above 40 °C. In a next step, the behavior of OEG SAMs at temperatures up to 65 °C was investigated. As can be seen in Figure 2, there is a change in the ratio of the absorbance of the modes indicating a helical structure and the mode indicating an all-*trans* structure. In addition, there is a change in mode position and width, starting at a temperature between 40 and 50 °C, see Figure 3. This suggests an increase of disorder within the OEG moiety and therefore an increase in amorphous structure. Further, those changes of the SAM conformation and structure are no longer reversible. Neither cooling the SAMs down to room temperature nor drying and successive reimmersion were able to restore their initial conformation. This strongly implies that parts of the OEG moiety are changed irreversibly. It is known from the literature[14] that OEG SAMs are very stable in solution at temperatures up to 37 °C. Qin et al. reported that OEG SAMs stored for 4 weeks in PBS solution at 37 °C were still protein resistant.[14] However, bulk phase experiments monitoring the stability of *poly*(ethylene glycols) in solution at elevated temperatures revealed that at 50 °C, the molecules are oxidized.[17] Therefore, the irreversible change in structure of the OEG moiety at temperatures above 50 °C may be attributed to oxidation. A spectrum of the SAM after cooling down can be found in the Supporting Information of this article. Therein, absorption modes at 1740 and 1264 cm^{-1} are indicating the presence of oxidation products. For the mechanism of the oxidation of PEG, see ref 17.

3.3. Temperature Dependence for Different Coverages. It has been shown previously in ref 12 that the OEG SAM conformation in aqueous conditions strongly depends on coverage. Even at close-to-maximum coverage small changes in coverage have a strong influence on the SAM conformation.[12] In this section, the influence of SAM coverage on the conformational transition behavior at rising temperature will be considered in this close-to-maximum coverage regime. To this end, SAMs of different coverage, apparent in a different ratio of the intensities of the high- and low-frequency mode of the C−O−C band, were grown and monitored at elevated temperatures afterward. As can be seen by comparing Figure 2 and Figure 5, at room temperature, SAMs have different fractions of helical structure depending on the surface coverage. For all SAMs, the modes indicating a helical structure decrease with rising temperature, starting at 30 °C. For close-to-maximum coverage SAMs (grown for 10 h in 0.01 mM EG_6OMe solution in water), however, the conformational change starts at lower temperatures and the structure becomes amorphous at 40 °C, whereas the structure remains crystalline and only the conformation is changing up to a temperature of 40 °C for maximum coverage SAMs. This suggests that the higher the SAMs surface coverage, the higher its stability toward temperature-induced changes in conformation. The reasons for this behavior may be an interplay of the interaction of SAM molecules with each other and its change with increasing temperature.

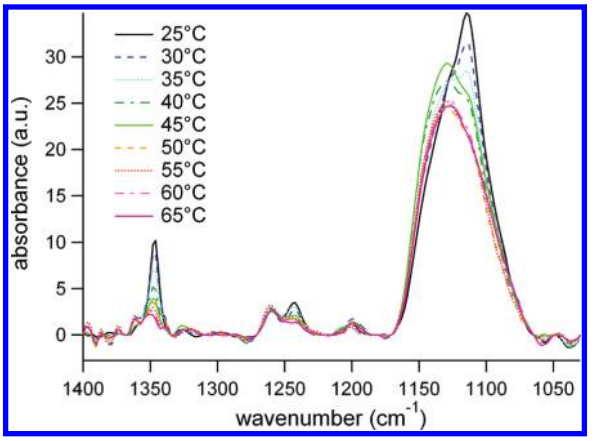

Figure 5. Spectra of an EG_6OMe SAM in aqueous environment as a function of temperature up to 65 °C. Because of a slightly lower coverage (grown for 10 h in 0.01 mM EG_6OMe solution in water) compared to the SAM in Figure 2, the conformational and structural change takes place in a lower temperature regime, the spectrum at 65 °C indicates an amorphous structure.

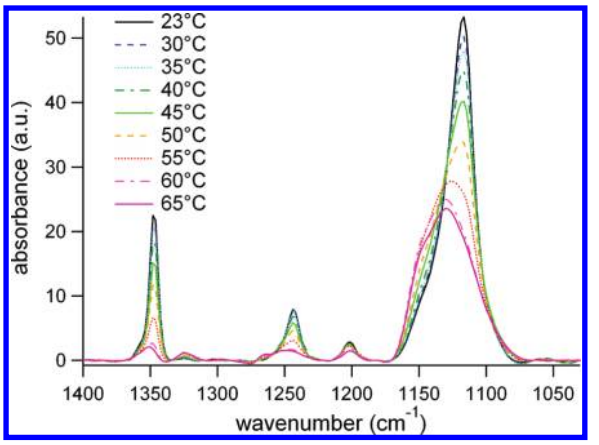

Figure 6. Spectra of an EG_6OMe SAM in air as a function of temperature up to 65 °C. The conformational change occurs at higher temperature than in aqueous environment, indicating that the change is induced by the penetration of water molecules into the OEG moiety of the SAM. At about 65 °C, the SAM adopts an amorphous structure, additionally the CH_3 rocking mode is decreasing indicating degeneration effects, possibly by thermal oxidation.

Water may have easier access to the OEG moiety at higher temperatures due to an enhanced conformational freedom. The effect of decreasing crystallinity especially for not maximum coverage SAMs may be based on a deeper penetration of water molecules and their stronger interaction with the SAM; compare to Figure 8.

3.4. Measurements in Air. To learn more about the influence of water, information about the structural change in air is needed. Since a direct comparison with literature concerning the behavior of EG_6OMe in air is not possible, reference measurements in air were performed. In order to exclude effects of different surface coverage, measurements in air and water using SAMs grown for the same time in bulk solution (10 h in 0.01 mM EG_6OMe solution in water) were compared. Figure 5 shows the temperature dependent behavior of EG_6OMe SAMs grown in bulk solution overnight under aqueous conditions, Figure 6 shows the corresponding spectra of a SAM grown at the same conditions in air. There are two findings: First, when comparing the SAMs in aqueous environment and in air, it is obvious that there is an interaction between SAM and water in aqueous environment, resulting in a decrease in the SAMs order at room temperature, compare to ref 12. Second, it can be seen that the conformational change of the SAM in aqueous environment is starting at a lower temperature than the one of the SAM in air. At 40 °C, the SAMs vibrational modes under water indicate a virtually amorphous structure while the spectra in air still show a predominantly crystalline structure in helical conformation. This is further evidence for the enhancing influence of water molecules penetrating the SAM on the transition process.

3.5. Reversibility of Conformational Change in Air. To test whether the conformational transition of the OEG moiety in air is reversible disregarding oxidation effects, an experiment involving a very short time period at high temperatures was performed. The temperature was increased in the water bath to 65 °C and then pumped into the sample cell, resulting in a heating from 25 to 62 °C within 5 min. The temperature was kept constant for 5 min, to attain an equilibrium and then another 7 min for the measurement. Afterward, the cell was cooled down to 25 °C with cold water within 10 min. A comparison of the spectra before and after heating showed a conformational change in the SAM from predominantly helical to mixed all-*trans* and helical (data not shown). The successive cooling led to a reordering to a predominantly helical conformation. The intensity of the modes indicating a helical conformation was only slightly weaker after the temperature step, than before the heating. This indicates only minor degradation effects, likely to occur during the short period at elevated temperature. It further suggests that disregarding degeneration effects, the conformational changes on EG_6OMe SAMs in air are reversible within a few minutes, similar to the findings of Valiokas et al.[16]

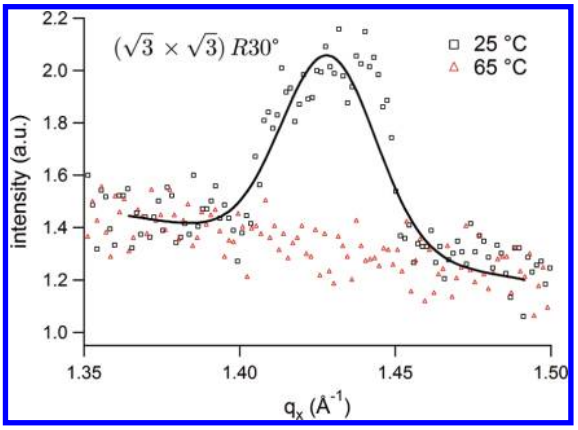

Figure 7. Bragg peak of an EG_6OMe thiol SAM grown on top of a thin polycrystalline Au layer measured with GIXD. At a temperature of 25 °C, the (1,1) peak of the thiol SAM can be seen, indicating a crystalline structure. After increasing the temperature to 65 °C the (1,1) thiol peak disappears, indicating a loss in crystalline structure.

3.6. In Plane Structure Measured with Grazing Incidence X-ray Scattering. Complementary to the infrared experiments in-plane grazing incidence X-ray diffraction measurements were performed to monitor the influence of rising temperature on the crystalline structure of EG_6OMe thiol SAMs. As substrates, silicon wafers coated with a 20 nm thick polycrystalline but (111) textured Au layer on top of a 5 nm thick Cr adhesion layer were used. The SAM was grown in a 500 μm ethanolic solution of EG_6OMe thiol overnight. The scattering profile was measured

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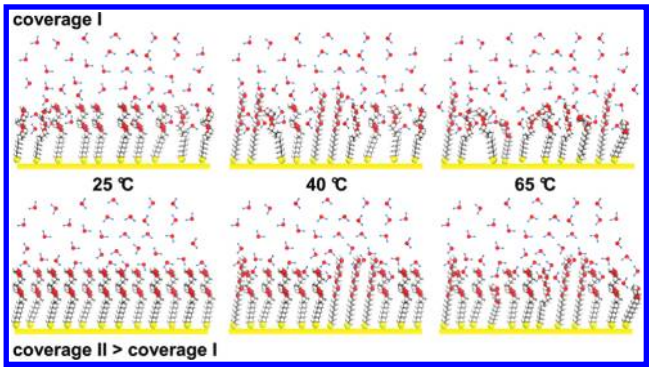

Figure 8. Schematic of the temperature behavior of EG_6OMe SAMs in aqueous environment for different surface coverage. Coverage I refers to close-to-maximum coverage, coverage II to maximum coverage. At 25 °C, the OEG moiety of a close-to-maximum coverage SAM is interacting with water molecules, whereas for maximum surface coverage water molecules are not able to penetrate the SAM, because of a higher crystalline order of the latter at 25 °C. At 40 °C the OEG moiety of a close-to-maximum coverage SAM strongly interacts with water molecules giving rise to an increasing amorphization of the SAM, in addition to a transformation in a helical/all-*trans* conformation, the structure of a SAM with maximum surface coverage remains crystalline and the interaction with water is rather weak. Above temperatures of 50 °C in addition to the change in structure an irreversible degradation is observed and an increasing amorphization occurs.

along the q_x (i.e., in-plane) coordinate with an area detector. First, a measurement was performed at 25 °C. The measurements were performed at an incidence angle θ of 0.17°, well below the total reflectivity edge of Au which for 20 keV is at 0.228°. Apart from the substrate in-plane reflection at q_x = 2.51 $Å^{-1}$ we observed a reflection at q_x = 1.44 $Å^{-1}$ consistent with the $(\sqrt{3} \times \sqrt{3})R30°$ structural motif known for alkanethiols,[1,27] see Figure 7. EG_6OMe has an alkane linker segment between the thiol group and the OEG moiety. Additionally, there is a nearly perfect match between the cross-section area of the OEG helix and the thiol packing density.[28]

After measuring the in-plane structure at 25 °C the temperature was increased to 65 °C which led to the disappearance of the Bragg reflection peak, indicating a loss of crystallinity at 65 °C (or below) for this SAM. Note, though, that the temperature stability is expected to depend on the coverage[1] and therefore these data should not be taken as an intrinsic equilibrium melting curve as in ref 29. For alkanethiol SAMs, the loss of hexagonal order occurs at temperatures, which depend on chain length and on surface coverage. For a full coverage C_{10} alkanethiol SAM this loss in crystalline structure occurs at about 100 °C. The alkane spacer of EG_6OMe SAMs contains 11 carbon atoms, so a loss in hexagonal order at a temperature of 65 °C (well below the melting point of a full coverage decanethiol SAM) may indicate an incomplete surface coverage. A loss in crystalline structure of the EG_6OMe SAM at 65 °C has also been observed in the infrared studies (Figure 8).

4. CONCLUSION

We investigated the conformational change of EG_6OMe in aqueous environment at elevated temperatures. A conformational change, indicated by a decrease of modes arising from helical structure and an increase of the high frequency C−O−C stretching mode suggesting all-*trans* structure could be observed. Under aqueous conditions, the process is not reversible even after several hours. However, after a drying and reimmersion of the SAM, the conformational change was almost fully reversible for $T \leq 40$ °C. At $T > 40$ °C the conformational changes proceed and a broadening and shifting of the vibrational modes indicating structural changes could also be monitored. It is assumed, that oxidative degeneration is responsible for this behavior. Indeed, the conformational change is not reversible for $T > 40$ °C, neither under aqueous conditions nor after drying and reimmersion. The conformational change depends on the surface coverage. For maximum coverage the SAM remains in crystalline order and only changes its conformation, for close-to-maximum coverage structural changes could also be observed at high temperatures, as revealed by an amorphization of the SAM. Our results give important clues about the stability of SAMs and the strength of their interaction with water. Further, they help to explain the behavior of SAMs regarding structural integrity at elevated temperatures.

■ ASSOCIATED CONTENT

Supporting Information. Spectra of an EG_6OMe SAM. This material is available free of charge via the Internet at http://pubs.acs.org.

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