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# Infrared spectroscopic study of a γ-mercaptopropyltrimethoxysilane monolayer on a gold surface

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Reflectance–absorption infrared spectra of γ-mercaptopropyltrimethoxysilane (γ-MPT) adsorbed on Au (111)-oriented films are analyzed on the basis of the calculated vibrational modes of a monomer, a dimer and *n*-membered rings of $SiO_3R$ ($R = CH_2CH_2CH_2SAu$). The results show that the γ-MPT molecules adsorbed on the Au surface are partially hydrolyzed and that the orientation of the methyl groups and propyl chains are near perpendicular to the surface. After a hydrolysis procedure, the $SiO_3$ groups in γ-MPT form a quasi two-dimensional system built predominantly of 6-membered puckered Si–O rings. Additional treatment of the γ-MPT monolayer with a surface-charge-reversing cationic polymer disrupts the connectivity and increases the topological disorder in the silicate system.

## 1 Introduction

It is well established that thiol groups have a strong affinity for noble metal surfaces, permitting the formation of self-assembled monolayers in the presence of a number of other functional groups.[1–4] Due to this affinity, thiol-functionalized organic compounds can be utilized as coupling agents to obtain surfaces with various properties, which are mainly determined by the choice of functional tail-group in the thiol-functionalized molecule. The interest in this type of chemistry derives from the possibilities of preparing model systems for various types of fundamental studies, for the preparation of sensors and as a means to attach small particles or thin films of other materials to a gold surface.[5–7]

Molecular sieve films on noble metal surfaces have a potential application as essential components of piezoelectric devices with high selectivity and sensitivity.[8,9] The preparation of such films often involves modification of the metal surface through a silane coupling agent adsorption which may be followed by a treatment with a surface-charge-reversing cationic polymer. The resulting surface is then used for the attachment of colloidal molecular sieve seeds which subsequently are grown into a continuous film.[10–12] γ-Mercaptopropyltrimethoxysilane (γ-MPT) is one of the compounds used for silanisation of the gold electrode of quartz crystal microbalances.[13,14] To gain greater understanding of the phenomena which take place in the interface between zeolite seeds and the modified gold surface it is important to investigate the state of the γ-MPT monolayer on the Au surface. Several studies have shown that sulfur-containing organic compounds are chemically adsorbed on the surface and that the S–Au bonds are oriented normal to the surface.[15–17] Adsorbed γ-MPT on metal surfaces has been characterized by ellipsometry and infrared (IR) spectroscopic data on C–H vibrations.[13,18] A self-assembled γ-MPT monolayer on a gold surface has been investigated by scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy.[19]

The objective of the work presented here was to further study the adsorption and hydrolysis of γ-MPT on gold surfaces using IR spectroscopy. Experimental spectra recorded below 1300 $cm^{-1}$ were used for structural modeling of the surface silicate species.

## 2 Experimental

Gold films evaporated on (100) silicon wafers were used. According to the X-ray diffraction data (Siemens D5000 powder diffractometer), the crystalline gold was oriented with the (111)-planes parallel to the silicon wafer surface. The Au surfaces were cleaned with acetone under ultrasonic action for 5 min at room temperature and rinsed with $CH_3OH$ (Merck). The silanisation was performed at room temperature for 3 h using 20 mM γ-MPT (Osi specialities) dissolved in $CH_3OH$. The silanised substrate was rinsed with distilled $H_2O$, put in 0.1 M HCl(aq) for 15 h at room temperature to hydrolyze the adsorbed γ-MPT molecules and rinsed with 0.1 M $NH_3$(aq). Reversal of the surface charge was carried out using a cationic polymer, Redifloc 4150 (Eka Nobel AB, Sweden), repeating unit $[CH_2CHOHCH_2N(CH_3)_2]^+_n$. The samples were kept for 5 min at room temperature in a 0.4 wt% aqueous solution of Redifloc adjusted to pH 8 with $NH_3$ and rinsed with 0.1 M $NH_3$(aq).

Reflectance–absorption infrared (RAIR) spectra were recorded in the range 400–4000 $cm^{-1}$ at room temperature under vacuum using a Bruker FT-IR spectrometer equipped with a DTGS detector and a SPECAC reflection accessory. The light beam was incident at an angle of 84° to the normal of the sample surface and masked with a 4 mm wide iris. The spectra were taken by averaging 1500 scans, with a scanning velocity of 6.25 Hz and a spectral resolution of 4 $cm^{-1}$. A cleaned gold surface was used for collecting the background signal. The measured spectra were baseline corrected and smoothed through the Savitzky–Golay algorithm with a degree of smoothing equal to 37.

The spectrum of the unhydrolyzed γ-MPT layer was measured immediately after silanisation of the Au surface. In this case anhydrous $CH_3OH$ (Aldrich, 99.8%) was used for preparing the γ-MPT solution and the silanised Au surfaces were rinsed with the dry methanol, instead of distilled water, and subsequently dried in a stream of nitrogen gas at room temperature.

## 3 Results and discussion

Fig. 1 presents experimental RAIR spectra of γ-MPT adsorbed on Au before hydrolysis (curve a), after hydrolysis (curve b) and after treatment with the cationic polymer (curve c) in the spectral range 500–1350 $cm^{-1}$. The insert shows the RAIR

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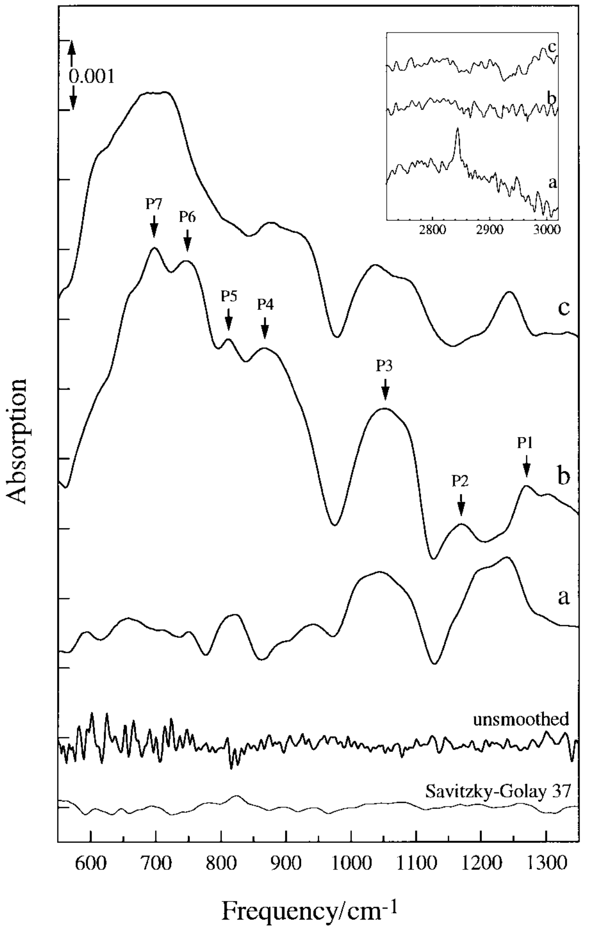

**Fig. 1** Experimental RAIR spectra of the unhydrolyzed γ-MPT layer on a Au surface (curve a), the hydrolyzed γ-MPT layer on a Au surface before (curve b) and after (curve c) treatment with a cationic polymer. The two traces at the bottom represent the level of the noise and the degree of smoothing. The spectra in the insert are not smoothed in order to better reveal the signal-to-noise ratio in this spectral range. The assignment of the marked peaks is given in Table 2.

spectra of the same samples in the spectral range typical of C–H bond stretching modes. Because of the poor signal-to-noise ratio we will not discuss the spectral range 1350–1900 $\mathrm{cm}^{-1}$. As can be seen, no peaks arising from C–H stretching modes were detected in the spectra of the hydrolyzed samples, while a weak peak at 2844 $\mathrm{cm}^{-1}$ was observed in the spectrum of the unhydrolyzed sample. In RAIR spectra of layers on metal surfaces, only those vibrational modes which have a non-vanishing component of the induced dipole moment normal to the surface give rise to peaks. The C–H stretching vibrations of $CH_3$ groups give rise to IR absorption peaks at *ca.* 2845 and *ca.* 2965 $\mathrm{cm}^{-1}$ corresponding to the symmetric and the anti-symmetric modes.[20] If the methyl group is oriented with its $C_3$-axis perpendicular to the surface, the normal component of the dipole moment of the anti-symmetric stretching mode will be zero, while that of the symmetric stretching mode will be non-zero (Fig. 2). The fact that only the peak resulting from the symmetric $CH_3$ stretching mode is present in the RAIR spectrum favors the methyl groups being predominantly oriented with their $C_3$-axes perpendicular to the surface. The absence of a peak at *ca.* 2844 $\mathrm{cm}^{-1}$ in the spectra of hydrolyzed samples shows that no detectable amount of unhydrolyzed methoxy groups remains in the adsorbed γ-MPT layer after 15 h of treatment in 0.1 M HCl(aq). Peaks arising from methylene symmetric and anti-symmetric stretching modes (at *ca.* 2860 and 2925 $\mathrm{cm}^{-1}$, respectively[21]) are not observed in the RAIR spectra of either unhydrolyzed or hydrolyzed samples which shows that the $CH_2$ groups in the propyl chain are approximately parallel to the surface, *i.e.* the γ-MPT molecules are upright oriented. Thiol-containing molecules are considered to form S–Au bonds when adsorbed on Au surfaces. Evidence for this is provided by the observation of Au–S vibrations by surface-enhanced Raman spectroscopy.[15] Thus we assume that each adsorbed γ-MPT molecule is bonded to one Au atom only. Besides, two upright-oriented γ-MPT molecules, which are linked to each other, cannot be adsorbed to the next nearest Au atoms. Comparing the interatomic distances between γ-MPT molecules with perpendicularly-oriented methyl groups which are adsorbed on two neighboring Au atom positions, one can see that there is not enough room to adjust the molecules to the Au–Au distance. Therefore, the nearest adsorbed γ-MPT molecules cannot retain all three methyl groups and, probably, most of the γ-MPT molecules are forced to hydrolyze partially in order to bind on the gold surface. This need for prehydrolysis could explain the long time period necessary to cover the gold surface with sufficient silane for successful seeding of the zeolite colloidal crystals after surface modification.

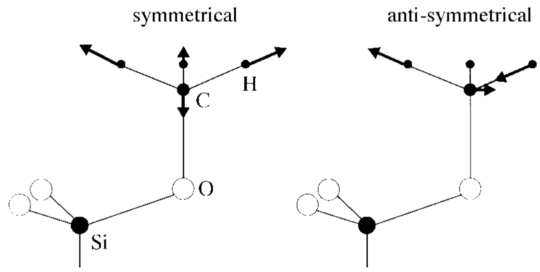

**Fig. 2** Atom vector displacements in the stretching modes of the $CH_3$ groups in γ-MPT molecules adsorbed on a Au surface.

The $SiO_3$ groups of fully hydrolyzed upright-oriented γ-MPT molecules should link to each other and form a continuous quasi-two dimensional silicon–oxygen sheet. It is therefore important to consider the two idealized conformations of γ-MPT molecules differing in the tilting of the $SiO_3$ groups: A, when all the oxygen atoms in the $SiO_3$ group lie in one plane parallel to the surface and B, when the silicon and two oxygen atoms are in a plane parallel to the surface (Fig. 3). In the former case all the oxygens in the hydrolyzed γ-MPT molecule will form Si–O–Si bridges, whereas in the latter one of the oxygens will be non-bridging. Assuming that the Au–S bonds are normal to the surface and that all the C–C–C bond angles are equal to the tetrahedral value $\varphi_T = 109.47°$, the two conformations of the γ-MPT molecule can be interconverted by changing the Si–C–C angle whose value is 144° in the A conformation and $\varphi_T$ in the B conformation.

Irrespective of the conformation of the hydrolyzed γ-MPT molecules, the silicon atoms have to more or less follow the

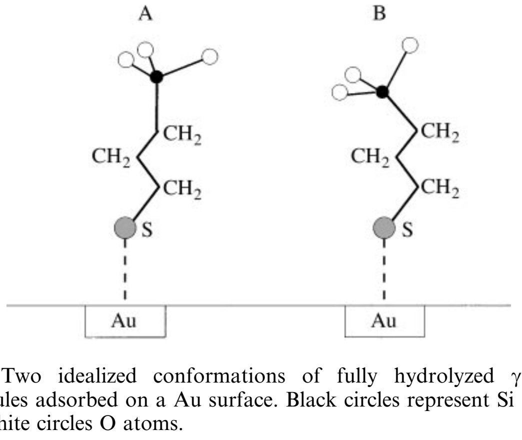

**Fig. 3** Two idealized conformations of fully hydrolyzed γ-MPT molecules adsorbed on a Au surface. Black circles represent Si atoms and white circles O atoms.

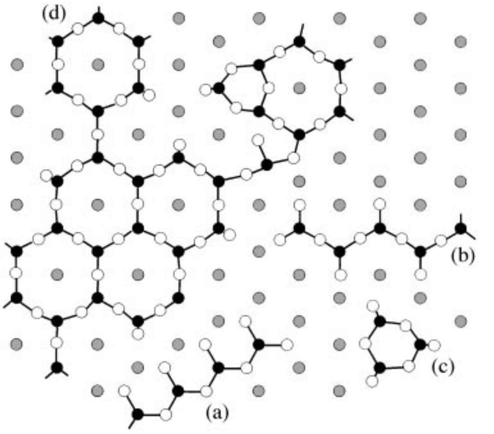

**Fig. 4** Top view of possible clusters of $SiO_3R$ units on a Au (111) surface: (a) a chain of monomers; (b) a chain of dimers; (c) an isolated 3-membered ring; (d) a defected sheet of rings. Black circles represent Si atoms, white circles O atoms and grey circles vacant sites in the hexagonal close packing.

arrangement of Au atoms. In the (111) projection, the Au atoms follow a hexagonal close packing arrangement with an interatomic distance of 2.88 Å. The possible structural units in the γ-MPT monolayer are chains and sheets of monomers, dimers or *n*-membered rings of $SiO_3R$ groups, $R = CH_2CH_2CH_2SAu$ (Fig. 4). The rings which best fit the hexagonal arrangement of the Au atoms are 3- and 6-membered, but according to STM data, a reconstruction or annealing of the Au surface may occur after the adsorption of γ-MPT.[19] Accordingly, rings composed of 3, 4, 5, 6, 7 and 8 atoms, with different topologies depending on the conformation of the building $SiO_3R$ groups, were investigated.

The vibrational modes of the clusters considered were calculated in a bond approximation.[22,23] The dynamic matrix of the cluster was calculated using a Keating-type potential. The frequencies and the atom vector displacements were derived from the eigenvalues and eigenvectors of the cluster dynamic matrix. The dipole moment was determined from the atom vector displacements and charges. The vibrational modes of quasi-1*D* (chain-like) or quasi-2*D* (sheet-like) systems were modeled by polymerizing the cluster to form a shell of first and second neighbors of cluster peripheral atoms, and then including interactions between cluster and shell atoms in the corresponding dynamic matrix elements.

In order to estimate the predominant type of oligomer in the layer, we calculated the vibrational modes of possible arrangements of $SiO_3R$ groups and compared the calculated frequencies for the different oligomers with the experimental RAIR spectrum of the hydrolyzed γ-MPT layer on a Au surface. In the analysis we took into account only those vibrational modes which have a large component of their dipole moments normal to the gold surface. For all the types of oligomers, we used a single common set of force constant values which are listed in Table 1. The values of the force constants describing the interactions between the silicon and oxygen atoms are nearly the same as those used for silica.[23,24] The values of the force constants responsible for interactions between carbon and hydrogen atoms were specified by fitting the experimental C–H vibration frequencies for $C_nH_{2n+2}$ and $C_nH_{2n+1}OH$, and are also similar to those already reported in the literature.[20,25] The values of the Si–C and S–C force constants are in agreement with the data on the bond vibration frequencies of molecules containing Si–C or S–C bonds. The results show that the experimental IR spectrum of an adsorbed γ-MPT layer can be best modeled using a 2*D*-polymerized 6-membered ring in which two of the $SiO_3R$ groups have the B conformation. The experimental frequencies of the peaks marked by arrows in Fig. 1, the calculated vibrational mode frequencies for such a ring and the types of modes which give rise to the peaks are given in Table 2. For comparison, the calculated bond vibration frequencies for some other oligomers are given in Table 3. It is worth noting the following:

**Table 1** Values of the force constants used in the calculations

| Force constant | Value/N $m^{-1}$ |
|---|---|
| Si–O bond stretching | 400 |
| O–Si–O bond bending | 50 |
| Si–O–Si bond bending | 10 |
| C–H bond stretching | 461 |
| C–C bond stretching | 440 |
| H–C–H bond bending | 43 |
| C–C–H bond bending | 35 |
| C–C–C bond bending | 52 |
| Si–C bond stretching | 300 |
| Si–C–C bond bending | 52 |
| O–Si–C bond bending | 40 |
| S–C bond stretching | 220 |
| C–C–S bond bending | 52 |
| S–Au bond stretching | 50 |

(i) the modes generating the peaks P1, P2 and P3 also exist in the spectra of the monomers and dimers, but on the basis of their spectra one cannot explain the spectral range below 900 $cm^{-1}$;

(ii) the mode giving rise to the peak P2 only exists in the spectra of polymerized clusters, *i.e.* this mode is typical of a continuous network of $SiO_3R$ groups. The infrared absorption intensity of this mode for rings is larger than for monomers and dimers;

(iii) the P4-, P5-, P6- and P7-modes are typical ring modes and their frequencies depend on the ring order;

(iv) the participation ratio of non-bridging oxygens from $SiO_3R$ groups with B conformations in the mode giving rise to P4 is very high. The mode generating the peak P5 is of a similar type to that generating P4, but is present only in the spectra of rings containing $SiO_3R$ groups in both A and B conformations;

(v) the peak P6 arises from a mode localised on Si atoms and is typical of a framework of rings. The mode frequency and intensity depend on the degree of Si–O ring puckering.

The large half-width and the asymmetric shape of the peaks in the recorded spectra are caused by several factors: conformational disorder of the Si–O system implying the existence of small amounts of other oligomers with a distribution of Si–O–Si bond angles, conformational disorder of the methylene groups and additional dipole–dipole long range interactions. The quality of the experimental spectra was not sufficient to perform more precise analysis of the influence of these factors on the spectra.

**Table 2** Experimental IR frequencies of the hydrolyzed γ-MPT layer adsorbed on a Au surface; the calculated frequencies and the type of vibrational modes generating the peaks

| | Frequency/$cm^{-1}$ | | |
|---|---|---|---|
| Mode | exp. | calc. | Type of vibration |
| P1 | 1266 | 1249 | $CH_2$ wagging |
| P2 | 1169 | 1160 | Si–$O_{br}$ stretching, Si–C rocking and $CH_2$ twisting[a] |
| P3 | 1053 | 1050 | Si–$O_{br}$ stretching, C–C stretching and $CH_2$ wagging[a] |
| P4 | 863 | 861 | Si–$O_{non}$, Si–C stretching and in-plane $O_{br}$ vibrations[a] |
| P5 | 812 | 816 | |
| P6 | 745 | 750 | Si–O stretching and Si–O–Si bending |
| P7 | 695 | 690 | Si and $O_{br}$ out-of-plane vibrations and $CH_2$ wagging[a] |
| | | 660 | S–C stretching |

[a] $O_{br}$, bridging oxygen atoms; $O_{non}$, non-bridging oxygen atoms.

**Table 3** Calculated frequencies (cm$^{-1}$) of the vibrational modes, having a large normal component of the dipole moment, of different arrangements of $SiO_3R$ groups. The labeling of the modes is the same as in Table 2

| Mode | 1*D* monomer[a] | 1*D* dimer | 2*D* dimer | 1*D* ring AAB[b] | 1*D* ring ABABB | 2*D* ring AAAAB | Isolated ring AAABAB | Isolated ring AAAAAA |
|---|---|---|---|---|---|---|---|---|
| P1 | 1249 | 1249 | 1249 | 1249 | 1249 | 1249 | 1249 | 1249 |
| P2 | 1178 | 1177 | 1178 | 1147 | 1116 | 1155 | — | — |
| P3 | 1073 | 1075 | 1064 | 1009 | 1021 | 1090 | 1032 | 1089 |
| P4 | 952 | 895 | — | 887 | 870 | 853 | 878 | 881 |
| P5 | 862 | 867 | 845 | 805 | 855 | 802 | 845 | — |
| P6 | — | 727 | 733 | 726 | 725 | 755 | 744 | 753 |
| P7 | 688 | 641 | 638 | 594 | 688 | 679 | 695 | 525 |
| | 660 | 660 | 660 | 660 | 660 | 660 | 660 | 660 |

[a] 1*D*, one-dimensionally polymerised; 2*D*, two-dimensionally polymerised. [b] A and B represent the conformations of the $SiO_3P$ groups which form the ring.

The peak P2, characteristic of polymerized clusters, is not observed in the spectrum of the unhydrolyzed silanised Au surface. In addition, the peaks below 900 cm$^{-1}$ which result from ring modes are not well-pronounced in this spectrum. Both these facts indicate that in the initial stage the adsorbed γ-MPT molecules are linked in small isolated units. In the spectrum of the γ-MPT layer treated with the cationic polymer the peaks P2 and P6 do not appear. A broadening of the other peaks arising from Si–O modes is observed which can be explained by an enlargement of the $SiO_3$ tilt angle distribution. The shoulder at about 940 cm$^{-1}$ is most probably due to Si–O···H interactions between the silane layer and the cationic polymer. Therefore, covering the silanised Au surface with a cationic polymer disrupts the connectivity of the Si–O sheet and increases the topological disorder. No peaks originating from internal vibrational modes of the cationic polymer were detected in the whole spectral range considered. We believe that this is due to the low concentration and to the absence of any arrangement of the cationic polymer on the surface.

## 4 Conclusion

On the basis of RAIR spectra one can conclude that the γ-MPT molecules adsorbed on the Au surface are partially hydrolyzed and that their methyl groups and propyl chains are near perpendicularly oriented to the surface. After the hydrolysis procedure, the $SiO_3$ groups in the γ-MPT molecules form a quasi two-dimensional system built predominantly from 6-membered puckered Si–O rings in which a significant number of the oxygen atoms are non-bridging. Treatment with the cationic polymer increases the structural disorder in the silane layer. No evidence was obtained for the existence of covalent bonds between atoms from the Si–O system and from the cationic polymer to give a specific orientation of the bonds between silicon and non-bridging oxygen atoms before the attachment of the zeolite seeds.

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## References

1 R. G. Nuzzo and D. L. Allara, *J. Am. Chem. Soc.*, 1983, **105**, 4481.
2 C. D. Bain, E. B. Troughton, Y.-T. Tao, J. Evall and G. M. Whitesides, *J. Am. Chem. Soc.*, 1989, **111**, 321.
3 R. G. Nuzzo, B. R. Zegarski and L. H. Dubois, *J. Am. Chem. Soc.*, 1987, **109**, 733.
4 R. I. Carey, J. P. Folkers and G. M. Whitesides, *Langmuir*, 1994, **10**, 2228.
5 J. Lukkari, K. Kleemola, M. Meretoja, T. Ollonqvist and J. Kankare, *Langmuir*, 1998, **14**, 1705.
6 A. Saitoh, T. Nomura, S. Munoz and T. Moriizumi, *Jpn. J. Appl. Phys.*, 1998, **37**, 2849.
7 M. S. Yang, H. S. M. Yau and H. L. Chan, *Langmuir*, 1998, **14**, 6121.
8 M. D. Ward and D. A. Buttry, *Science*, 1990, **249**, 1000.
9 S. Feng and T. Bein, *Science*, 1994, **265**, 1839.
10 J. Sterte, S. Mintova, G. Zhang and B. J. Schoeman, *Zeolites*, 1997, **18**, 387.
11 S. Mintova, J. Hedlund, B. J. Schoeman, V. Valtchev and J. Sterte, *Chem. Commun.*, 1997, 15.
12 S. Mintova, V. Valtchev, V. Engström, B. J. Schoeman and J. Sterte, *Microporous Mater.*, 1997, **11**, 149.
13 Y. Yan and T. Bein, *J. Phys. Chem.*, 1992, **96**, 9387.
14 S. Mintova, B. Schoeman, V. Valtchev, J. Sterte, S. Mo and T. Bein, *Adv. Mater.*, 1997, **9**, 585.
15 K. V. G. K. Murfty, M. Venkataramanan and T. Pradeep, *Langmuir*, 1998, **14**, 5446.
16 F. K. Huang, R. C. Horton, Jr., D.C. Myles and R. L. Garrell, *Langmuir*, 1998, **14**, 4802.
17 L. A. Godinez, J. Lin, M. Munoz, A. W. Coleman, S. Rubin, A. Parikh, T. A. Zawodzinski, Jr., D. Loveday, J. P. Ferraris and A. E. Kaifer, *Langmuir*, 1998, **14**, 137.
18 D. G. Kurth and T. Bein, *Langmuir*, 1993, **9**, 2965.
19 A. Morneau, A. Manivannan and C. R. Cabrera, *Langmuir*, 1994, **10**, 3940.
20 A. Serrallach, R. Meyer and Hs. H. Gunthard, *J. Mol. Spectrosc.*, 1974, **52**, 94.
21 J. Koenig, *Spectroscopy of Polymers*, American Chemical Society, Washington DC, 1992, p. 22.
22 B. Mihailova and L. Konstantinov, *Phys. Chem. Glasses*, 1997, **38**, 27.
23 T. Furukawa, K. Fox and W. White, *J. Chem. Phys.*, 1981, **75**, 3226.
24 J. Bock and G.-J. Su, *J. Am. Ceram. Soc.*, 1970, **53**, 69.
25 M. Urban, *Vibrational Spectroscopy of Molecules and Macromolecules on Surfaces*, John Wiley & Sons, Inc., New York•Chichester•Brisbane•Toronto•Singapore, 1993, p. 32.

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