Silsesquioxanes

Synthesis of an Open-Cage Structure POSS Containing Various Functional Groups and Their Effect on the Formation and Properties of Langmuir Monolayers**

Michał Dutkiewicz,^[b, c] Joanna Karasiewicz,^[a] Monika Rojewska,^[d] Marta Skrzypiec,^[d] Katarzyna Dopierała,^[d] Krystyna Prochaska,^[d] and Hieronim Maciejewski^{*[a, c]}

Abstract: Recently, silsesquioxanes have been recognized as a new group of film-forming materials. This study has been aimed at determining the effect of the kind of functional groups present in two different open-cage structure POSS molecules on the possibility of the formation of Langmuir monolayers and their properties. To achieve this goal, two new POSS derivatives (of open-cage structures) containing polyether and fluoroalkyl functional groups have been synthesized on the basis of a hydrosilylation process. An optimization of the process was performed, which makes it possible to obtain the above-mentioned derivatives with high yields. In the next step, the Langmuir technique was applied to measurements of the surface pressure (π) – the mean molecular area (A) isotherms during the compression of monolayers formed by molecules of the two POSS derivatives considered. Subsequently, the monolayers were transferred onto quartz plates according to the Langmuir–Blodgett technique. Both derivatives are able to form insoluble Langmuir films at the air–water interface, which can be transferred onto a solid substrate and effectively change its wetting properties.

Introduction

Silsesquioxanes make a large group of organosilicon derivatives of the general formula $(RSiO_{1.5})_n$ that attracts a constant interest of researchers from many areas, such as chemistry, physics, and even biology and medicine.^[1] Predominant among them are cage silsesquioxanes (POSS), which due to their strictly defined structure (of nanometric dimensions) as well as the presence of organic substituents, provide the possibility for further modification and creation of new derivatives or formation of durable bonding to other materials, for exam-

-	
[a]	Dr. J. Karasiewicz, Prof. Dr. H. Maciejewski Faculty of Chemistry Adam Mickiewicz University in Poznań Umultowska 89 B, 61-614 Poznań (Poland) E-mail: maciej@amu.edu.pl
[b]	Dr. M. Dutkiewicz Centre for Advanced Technologies Adam Mickiewicz University in Poznań Umultowska 89 C, 61-614 Poznań (Poland)
[c]	Dr. M. Dutkiewicz, Prof. Dr. H. Maciejewski Poznań Science and Technology Park Adam Mickiewicz University Foundation Rubież 46, 61-612 Poznań (Poland)
[d]	Dr. M. Rojewska, M. Skrzypiec, Dr. K. Dopierała, Prof. Dr. K. Prochaska Institute of Chemical Technology and Engineering Poznań University of Technology Berdychowo 4, 60-965 Poznań (Poland)
[**]	POSS = polyhedral oliaomeric silsesauioxane.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201602456. ple, polymers, thus creating organic-inorganic hybrid and nanocomposite materials of specific and unprecedented properties.^[1-4] In the group of cage derivatives one can additionally name fully condensed silsesquioxanes, not fully condensed silsesquioxane (open cage with one of the corner silicon atoms missing), and heterosilsesquioxanes. Much less attention has been paid to the application of POSS with open cage structures. Most of the published studies concern their application to synthesis of fully condensed derivatives in the process of corner capping, being in fact, the process of hydrolytic condensation of the respective trisilanol with trichloro- or trialkoxysilane. In this way, monofunctional derivatives containing seven identical chemically passive groups (most frequently isobutyl or phenyl ones) and one reactive functional group are formed.^[1-3] Trisilanol-POSS derivatives have also been employed for the synthesis of complexes in the capacity of chelating ligands and for the synthesis of heterosilsesquioxanes containing an atom of another element in one of the siliconoxygen core corners.^[1, 5-7] The reaction of hydrolytic condensation provides not only the possibility of end capping in trisilanols but also of attaching three reactive groups. For instance, the condensation of trisilanol with three molecules of dimethylchlorosilane or vinyldimethylchlorosilane enables to obtain derivatives with an open-cage structure having three substituents that contain terminal hydrogen atoms or vinyl groups, respectively. Derivatives of this type can be applied as agents for hydrophobization of plastic surfaces or printed surfaces after their introduction into polymers or paint just by means of mixing.^[8,9] Also known are examples of the application of di-

Chem. Eur. J. **2016**, 22, 1–13

Wiley Online Library

These are not the final page numbers! **77**



methylsiloxy group-containing derivatives as modifiers for polymethacrylates produced by means of free-radical polymerization^[10] or after their functionalization with dithiocarbamyl groups as initiators of methacrylate polymerization.^[11] The derivatives containing dimethylsiloxy and dimethylvinylsiloxy groups can also be used for the synthesis of materials with low dielectric constants, applied, for example, in the process of the manufacture of liquid-crystal displays by means of hydrosilylation of dienes or chain and cyclic derivatives of polysiloxanes.^[12,13] By using the process of hydrosilylation, it is possible to perform functionalization with a large group of organic derivatives and obtain silsesquioxanes with open-cage structures having three reactive groups. Unfortunately, the open-literature reports on this subject are still very scarce and the most of the available information is contained in patents, which describe the way of the synthesis and the direction of applications. For instance, the derivatives containing amino or polyether groups are employed in the manufacture of liquid-crystal displays, where they play the role of modifiers for protective varnishes on the basis of polyimide or polyamine resins.^[14] The derivatives with 3-isocyanatepropyl groups can be used as cross-linking agents in binders and hot-melt adhesives.^[15] They have also found an application in optical fibers and optical materials^[16,17] as well as in the manufacture of photosensitive materials.^[18-20] Compounds of this type having three functional groups in the form of derivatives of succinic acid modified by ethylenediamine and seven 2,2,4-trimethylhexyl groups play the role of a stabilizer of quantum-dot binding ligands in nanocrystalline electroluminescent materials.[21]

Despite more and more numerous examples of applications, this group of derivatives (and particularly their properties) is still little known. In the last few years, polyhedral oligomeric silsesquioxanes (POSS) have been recognized as a new group of materials forming stable Langmuir monolayers, which could be transferred onto the solid substrate as Langmuir-Blodgett (LB) or Langmuir-Schaefer (LS) thin films and modify the substrate properties.^[22-25] However, it is obvious that the modification effect as well as the character of the monolayer formed by POSS molecules strongly depend on the type of POSS compound.^[26] Therefore, it is interesting to know the effect of the type and the structure of different substituents present in POSS molecules on their ordering, and the tendency to form self-aggregates in monolayers at the air-water and air-solid substrate interfaces. This is why our study was aimed at synthesizing two new silsesquioxane derivatives with an opencage structure, containing polyether or fluoroalkyl groups and determining their properties including the possibility of forming stable Langmuir monolayers and their further use for producing coatings and hybrid materials.

Results and Discussion

At the initial stage of the study, syntheses of two new organosilicon compounds that were derivatives of cage silsesquioxanes with one open corner were performed. They contained polyether and fluoroalkyl groups (that are mutually opposite) as substituents. First, compound **1** was obtained in the reaction of a hydrolytic condensation between trisilanolisobutyl-POSS and dimethylchlorosilane, that was later employed in hydrosilylation. The synthesis of compounds **2** and **3** was based on the process of hydrosilylation of olefins (allyl polyether with a terminal hydroxyl group and a 5-(allyloxy)-1,1,2,2,3,3,4,4-octafluoropentane), respectively, by using 3,7,14-tris[dimethylsiloxy]-1,3,5,7,9,11,14-heptaisobutyltricyclo[7.3.3.^{15,11}]heptasiloxane (**1**) (as a hydrosilylating agent) in the presence of a catalyst (Karstedt's catalyst—[Pt₂{O[Si(CH₃)₂CH=CH₂]₂}] or hexachloroplatinic acid) according to Scheme 1.



Scheme 1. Synthesis of products 2 and 3 based on hydrosilylation of allyl polyether or 5-(allyloxy)-1,1,2,2,3,3,4,4-octafluoropentane with 3,7,14-tris[di-methylsiloxy]-1,3,5,7,9,11,14-heptaisobutylotricyclo[7.3.3.^{15,11}]heptasiloxane.

The hydrosilylation process was monitored with the use of real-time infrared spectroscopy. The reaction progress was quantified by observing changes in the area of the band at $\tilde{\nu} = 904 \text{ cm}^{-1}$ (ascribed to the stretching vibrations of the Si–H bond) with time. The obtained results have clearly shown a significant effect of the employed catalyst on the course of the hydrosilylation reaction.

Figure 1 presents the dependence of the change in the intensity of the studied band (i.e., $\tilde{v} = 904 \text{ cm}^{-1}$) during the hydrosilylation of 5-(allyloxy)-1,1,2,2,3,3,4,4-octafluoropentane in the presence of hexachloroplatinic acid and Karstedt's catalyst (Figures 1 a and b, respectively) and allyl polyether in the presence of the same catalysts (Figures 1 c and d, respectively). To emphasize changes occurring in the first step of the process, only the first two hours of the process duration are presented in Figure 1.

To more precisely present the effect of the catalyst and the kind of the parent compound on the course of the hydrosilylation, changes in Si–H bond conversion with time for various reaction systems are shown in the Supporting Information.

In the case of both reactions, the activity of the Karstedt's catalyst considerably surpasses that of hexachloroplatinic acid.

The obtained products, after their isolation from the post-reaction mixture, have been subjected to spectroscopic analyses, namely nuclear magnetic resonance (¹H, ¹³C, and ²⁹Si NMR spectroscopy) (see the Supporting Information). The formation of the products of the desired structures has also been confirmed by the analysis of the FTIR spectra of the products **2** and **3** and the parent compounds employed for their synthesis (Figures 2 and 3).

Chem. Eur. J. 2016, 22, 1 – 13 www.che

www.chemeurj.org

2

© 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim







Figure 1. Analysis of real-time FTIR measurements showing changes in the intensity of the band at $\tilde{v} = 904 \text{ cm}^{-1}$ with time during the hydrosilylation of 5-(allyloxy)-1,1,2,2,3,3,4,4-octafluoropentane in the presence of a) hexachlor-oplatinic acid and b) Karstedt's catalyst as well as allyl polyether catalyzed by c) hexachloroplatinic acid and d) Karstedt's catalyst.



Figure 2. FTIR spectra of the parent compounds and the product 2.



Figure 3. FTIR spectra of the parent compounds and the product 3.

Chem. Eur. J. **2016**, 22, 1–13

1–13 www.chemeurj.org

These are not the final page numbers! 77

3

In the spectrum of product **2** a band is visible at $\tilde{v} =$ 3500 cm⁻¹, which can be ascribed to stretching vibrations of the hydroxyl group. The presence of this band in the product spectrum and the decay of the bands at $\tilde{\nu} = 2100$ and 903 cm⁻¹, originating from stretching vibrations of the Si-H group (present in the parent compound spectrum), testify the formation of the hydrosilylation product and not to the occurrence of a condensation reaction between the Si-H and OH groups. The structure of the product has also been confirmed by the presence of bands attributed to symmetric and asymmetric stretching vibrations characteristic of C-H bonds of methyl and methylenic groups in the region $\tilde{\nu} = 2700-$ 3000 cm⁻¹, as well as bands ascribed to stretching vibrations of C-O-C bonds present in the polyether chains and asymmetric stretching vibrations of Si-O-Si groups in the region $\tilde{\nu}\!=\!$ 1000–1200 cm⁻¹.

The spectrum of the product **3**, which is shown in Figure 3, although somewhat poorer in signals, also makes it possible to correctly verify the structure of the obtained product. Similarly, as it was in the case of the spectrum of product **2** presented in Figure 2, also in this case one can notice the absence of bands at $\tilde{v} = 2100$ and 903 cm⁻¹, originating from stretching vibrations of the Si–H group, which were present in the spectrum of the parent compound. Also present are bands attributed to symmetric and asymmetric vibrations of C–H bonds of methyl and methylenic groups in the region $\tilde{v} = 2700$ –3000 cm⁻¹, as well as bands originating from stretching vibrations of C–F bonds present in the chains of the fluoroalkyl groups and asymmetric stretching vibrations of Si-O-Si groups in the region $\tilde{v} = 1000-1200$ cm⁻¹.

To shed light on the relation between the chemical structure of the obtained POSS derivatives and their potential ability to modify solid substrates, we have performed a multi-step investigation. In the first step, we have applied the Langmuir technique to measure the surface pressure (π) – the mean molecular area (*A*) isotherms during the compression of monolayers formed by molecules of the two POSS derivatives considered. Subsequently, the monolayers were transferred onto a quartz plate by using the Langmuir–Blodgett technique (this method provides the best control over the parameters of thin films formation) and finally the water contact angle (WCA) on the modified substrates was measured.

π -A isotherms

The PEG-POSS (**2**, PEG = [ω -(hydroxy)(polyethoxy)propyl]dimethylsiloxy) and OFP-POSS (**3**, OFP = [3-(2,2,3,3,4,4,5,5-octafluoropentyloxy)propyl]dimethylsiloxy) molecules formed insoluble Langmuir films at the air-water interface. The monolayers formed by molecules of these two POSS derivatives were spread on pure water (pH 6.5, subphase temperature = ($25 \pm$ 0.1) °C) and the π -A isotherms were recorded. The obtained results are plotted in Figure 4, which also presents the dependence of the compression modulus (C_s^{-1}) on the surface pressure (π) (insert of Figure 4a). The compression modulus C_s^{-1} , which is the reciprocal of the compressibility, is defined as given in Equation (1):^[29]



Figure 4. a) π -A isotherms of PEG-POSS (**2**) and OFP-POSS (**3**). The inset shows the compression modulus as a function of the surface pressure. b,c) Surface pressure-area and electric surface potential (ΔV)-area isotherms of PEG-POSS (**2**) and OFP-POSS (**3**), respectively.

$$C_{\rm s}^{-1} = -A(\frac{{\rm d}\pi}{{\rm d}A})_t \tag{1}$$

where C_s^{-1} is a rheological quantity related to the monolayer rigidity and it is a measure of the elastic energy stored in the monolayer upon compressive deformation of the surface. The inflexion points in the plot of C_s^{-1} versus π indicate the surface pressure at which significant reorganization of the surface film takes place in the course of the film compression. The magnitude of C_s^{-1} provides information about the elasticity of the monolayers and indirectly about their physical state as well as about the phase transition. For $C_s^{-1} < 50 \text{ mNm}^{-1}$, the state of a given monolayer is classified as liquid expanded (LE, isotropic liquid), for $50 < C_s^{-1} < 250 \text{ mNm}^{-1}$, the state is liquid condensed (LC, liquid crystalline; monolayer often diffracts X-ray radiation), and for $C_s^{-1} > 250 \text{ mNm}^{-1}$, the monolayer is described as solid, according to the criterion given by Davies and Rideal.^[30]

Table 1 presents the values of characteristic parameters of Langmuir monolayers estimated on the basis of the π -

A isotherms recorded for both POSS derivatives: A_o = average area occupied by closely packed molecules in the monolayer state determined by extrapolating the linear part of the condensed state in the π -A isotherms to zero pressure; $\pi_{collapse}$ = value of the surface pressure at which the inflection of the monolayer takes place; $A_{collapse}$ = value of the area per molecule corresponding to the film collapse, and max C_s^{-1} = maximum value of the compression modulus.

As one can note, the type of substituents R attached to the silica cage in the POSS molecules has a dramatic influence on the behavior of the silsesquioxane molecules at the air-water interface during compression. Therefore, the results should be analyzed separately for each POSS compound studied.

PEG-POSS (2)

As one can see, the isotherm of PEG-POSS starts to rise at approximately 550 Å²molecule⁻¹. This area value, named $A_{\text{lift-offr}}$ corresponds to the end of the submonolayer regime ($\pi = 0 \text{ mNm}^{-1}$) at which the film is likely to be biphasic with the co-existence of gaseous- and liquid-like domains. The further course of the isotherm indicates the liquid state of the mono-layer. Upon compression, the surface pressure raises monotonically until the film collapses, which occurs slightly above 46 mNm⁻¹.

The collapse area determined from the π -A isotherm is approximately 132 Å². It can be assumed that this value corresponds to monolayer disruption and formation of 3D structures.

According to optimization of the molecular geometry made with the Vega ZZ 3.0.1 software^[36] and shown in Figure 5a, it was found that the initial area occupied by PEG-POSS molecules is determined by three hydrophilic PEG chains and it is equal to 580 Å^{2.} This value is close to the A_{lift-off} value of PEG-POSS. It seems that at the beginning of monolayer formation the PEG chains are spaced widely at the interface with the hydroxyl groups immersed into the aqueous subphase, whereas the silsesquioxane cage is oriented toward the air. Upon compression, the PEG moieties approach each other and in the condensed monolayer the molecules reach the limiting area equal to 232 Å². The initial area could also be decreased due to partial dissolution of the PEG chains in the water subphase. However, the results of a relaxation experiment shown in Figure 7 did not reveal a significant area loss with time. Thus, the loss in area caused by the interaction of the PEG moieties with the water subphase can be probably neglected.

As mentioned above, the state of the monolayer can be quantified with the compression modulus values. As the maxi-

Table 1. Characteristic parameters of the Langmuir monolayers of the PEG-POSS (2) and OFP-POSS (3) derivatives.										
Compound	A ₀	$\pi_{ m collapse}$	$A_{collapse}$	$Max C_{s}^{-1}$	$A_{(maxCS-1)}$					
	[Å ² molecule ⁻¹]	[mN m ⁻¹]	[Å ² molecule ⁻¹]	[mN m ⁻¹]	[Å ² molecule ⁻¹]					
2	232	46.1	131.7	130.5	164.8					
3	311	11.8	216.6	34.1	229					

© 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

KK These are not the final page numbers!



Figure 5. Graphical representation of a) PEG-POSS (2) and b) OFP-POSS (3) molecules at the interface according to the space-filling model (a colored version of this graphic is given in the Supporting Information).

mum value C_s^{-1} can take is 131 mNm⁻¹, the monolayer characterized by this value of C_s^{-1} can be regarded as condensed liquid.

On the other hand, the compression modulus reaches its maximum value for $\pi \approx 32.5 \text{ mNm}^{-1}$. It is worth mentioning that this value is the best for Langmuir–Blodgett film deposition.

Moreover, the molecular area at the max $C_{\rm s}^{-1}$ value is equal to 164.8 Å² and it corresponds to the most compact arrangement of PEG-POSS molecules at the interface. Comparing this value with the calculated cross-sectional area, one can conclude that PEG-POSS shows larger compressibility in comparison with trisilanolisobutyl-POSS reported by Yin et al.^[32] This effect will be discussed later, together with the dilational viscoelasticity of the PEG-POSS monolayer.

The chemical structure of the PEG-POSS molecules should be analyzed, taking into account that the three substituents, that is, the PEG moieties, show hydrophilic character, which counter-balances the hydrophobicity of the silica cage with seven corners substituted with isobutyl groups and makes the whole molecule amphiphilic. Such a design corresponds to the classical amphiphiles having a hydrophilic head and a hydrophobic tail. It can be supposed that the PEG-POSS molecules behave like typical amphiphiles and assume the orientation with the hydrophobic tails (i.e., the cage) towards air and the hydrophilic head groups (i.e., the PEG moieties) anchored to the water subphase.

Moreover, the formation of hydrogen bonds between the PEG moieties and water molecules seems to be very likely. Upon monolayer compression, the PEG-POSS molecules assume an orientation tending to perpendicular to the interface, which is reflected by their molecular area decrease to A equal to approximately 232 Å². The shorter the distance be-

tween the molecules present at the subphase, the stronger is the intermolecular interaction between the PEG moieties. On the other hand, the stronger the interactions of PEG moieties with water, the deeper the shift of molecules into the water subphase. In consequence, a slight increase in the measured value of the surface potentials up to approximately 0.2 V can be observed (Figure 4b). On the other hand, the plot of ΔV versus the molecular area (Figure 4b) indicates that the PEG-POSS molecules increase the surface potential of water. The measured values of ΔV are positive in the whole range of monolayer compression.

The extrapolated cross-sectional area obtained from the π -A isotherm (limiting area A_o) indicates that closely packed PEG-POSS molecules occupy about 230 Å² of the interface. Taking into account that the cubic structure of the POSS cage is about 5 Å in size,^[31] it seems that the value of A_0 suggests such an orientation of the PEG-POSS molecules in which the hydrophilic moieties (i.e., the PEG groups) lie on the water surface, whereas the silica cage is located above, without direct contact with the subphase. Thus, the limiting area of the PEG-POSS molecules is determined by the dimensions of the hydrophilic PEG moieties. Besides, the value of A₀ seems to be reasonable, if one compares it with the cross-sectional area estimated for a molecule of trisilanolisobutyl POSS ($A_0 = (177 \pm$ 4) $Å^2$) or trisilanol-cyclohexyl POSS ($A_0 = 181 Å^2$), that is, the derivatives possessing much shorter moieties attached to the silicon-oxygen partially condensed open cage.^[23,24]

OFP-POSS (3)

According to the C_s^{-1} criterion, the OFP-POSS molecules form a liquid expanded Langmuir monolayer at the air–water interface because of the max C_s^{-1} value, which is equal to 34 mNm^{-1} . The limiting area A_o of the OFP-POSS π -A isotherm is approximately 311 Å² and the monolayer collapses at about 12 mNm^{-1} and an area of 216 Å² molecule⁻¹. After the collapse point, the OFP-POSS exhibits a long plateau at π of approximately 12 mNm^{-1} . The collapse of the monolayer causes a transfer from a 2D to a 3D structure and the formation of a multilayer at the air–water interface.

The three fluorinated moieties present in the structure of the OFP-POSS molecules show hydrophobic character, the same as a partly open silica cage. Thus, the OFP-POSS molecules are built of hydrophobic fragments only and do not contain any polar group. So, the orientation of these molecules at the air-water interface is not limited by any tendency to interaction with the subphase of any of the groups. Admittedly, usually it is assumed that the molecules (existing in the monolayer state), which include perfluorinated moieties have their strongly hydrophobic moieties in contact with air.^[33] However, the OFP-POSS seem highly probable to have a mosaic structure of the monolayer with domains containing alternately directed molecules. Such a mosaic structure has been proposed^[34,35] for semi-fluorinated *n*-alkane molecules. Additionally, this assumption of a mosaic model seems to be supported by the measured values of the surface potential for the OFP-POSS, which are negative but very close to zero (Figure 4c). It

```
These are not the final page numbers! 77
```

www.chemeurj.org

Chem. Eur. J. 2016, 22, 1-13



is noteworthy that, for the monolayer formed by the molecules with their perfluorinated substituents exposed towards air, the values of the surface potential should be clearly negative, much smaller than zero,^[35] whereas in the mosaic model, the values of the surface potential should be around zero because of the cancellation of oppositely directed dipole vector moments.

The optimization of the molecular structure made for the OFP-POSS by using the VEGA ZZ software^[36] (shown in Figure 5b) revealed that the cross-sectional area of the single molecule is equal to approximately 343 Å², which is in agreement with the A_{lift-off} value and it is only a little larger than the limiting area determined from the π -A isotherm (Figure 4a). However, for the OFP-POSS, the more informative parameters are the value of A at $\max C_s^{-1}$ and the area at collapse, which are equal to 229 and 216.6 Å², respectively. Both values are much lower than the calculated cross-sectional area (343 Å²) suggesting that the OFP-POSS changes the orientation of the fluorinated chains from a vertical to a titled one (the perpendicular orientation of the molecules at the interface was excluded during the calculations). It must also be emphasized that larger volume and cross-section area values for fluorocarbon chains in comparison with those for hydrocarbon chains are crucial for the explanation of their behavior at the interface. Here, the titling of the OFP-POSS may be governed by the repulsive interactions between the fluorinated chains and the isobutyl substituents attached to the Si-O cage. However, usually the variation in the orientation causes noticeable response of the surface potential. As mentioned above, for OFP-POSS we observed a ΔV value, which is surprisingly small in comparison with the values for typical fluorinated amphiphiles. This decrease was observed mainly in the gas phase and results from an increasing number of molecules under the measuring sensor.^[50] Upon further compression, the surface potential is almost constant. The key factor leading to the collapse of OFP-POSS is a weak interaction of the isobutyl groups with the water subphase in the expanded film.

The strongly hydrophobic character of the OFP-POSS molecules is the reason for their very weak interaction with the subphase. In consequence, the removal of OFP-POSS molecules from the air-water interface required much lower π values than for the PEG-POSS molecules. As one can see, the PEG-POSS (with PEG moieties anchored probably to the water subphase) has a much higher (near four-fold) dynamic collapse surface pressure ($\pi_{collapse} \approx 46 \text{ mNm}^{-1}$) at a smaller $A_{collapse}$ value of approximately 131.7 Å² molecule⁻¹ than OFP-POSS ($\pi_{collapse} \approx 12 \text{ mNm}^{-1}$ and $A_{collapse} \approx 216.6 \text{ Å}^2 \text{ molecule}^{-1}$). Moreover, their π -A isotherms reveal a vastly different behavior in the collapsing regime.

For comparison and more detailed explanation of the morphology of OFP-POSS and PEG-POSS, the monolayers were visualized with Brewster angle microscopy (BAM) and the representative images are presented in Figure 6. The PEG-POSS film remains homogeneous throughout the whole compression. The changes in the morphology of this monolayer are clearly visible only for values of the surface pressure corresponding to the collapse, whereas for OFP-POSS a gradual formation of bi-



Figure 6. BAM images recorded upon compression of a) OFP-POSS and b) PEG-POSS monolayers at room temperature.

layer takes place. Upon collapse, a multilayer is formed, which is manifested by the appearance of bright rod-like domains in the background.^[51,52] Thus, the BAM images show significant differences in the morphology of the monolayers formed at the air-water interface by the two investigated POSS derivatives, stemming from the nature of these molecules, that is, of strong hydrophobicity of OFP-POSS and an amphiphilic character of PEG-POSS.

The evidently different course of the π -A and ΔV -A isotherms (Figures 4a and c) as well as the different BAM images (Figures 6a and b) obtained for the PEG-POSS and OFP POSS derivatives indicate a quite different behavior as well as orientation of the molecules of these two compounds at the airwater interface upon monolayer compression, but does not give any information about the time stability of these two Langmuir monolayers.

To get information about the stability of the monolayer formed by PEG-POSS and OFP-POSS molecules an additional experiment was performed, in which the monolayers were first compressed until a desired surface pressure value (i.e., 10 mN m^{-1}), which was afterwards kept constant, and a decrease in the area was monitored with time (Figure 7). As can be seen, in both systems no area loss was observed with time. Thus, the obtained results can be a proof of the stability of both films.

To test the stability of the PEG-POSS and OFP-POSS monolayers under dynamic conditions, area deformation was induced by means of the oscillating barriers method.^[37,38] According to this method, it is possible to evaluate the modulus

6





Figure 7. Static stability experiments of PEG-POSS and OFP-POSS monolayers—a description is given in the text.

of the complex dilatational viscoelasticity (*E*), which is derived from the change in the surface pressure (dilatational stress) $d\pi$, resulting from a small change in the surface area (dilatational strain) dA. The modulus *E* can be calculated from the relation given in Equation (2).

$$E = -(\frac{\mathrm{d}\pi}{\mathrm{d}\ln A})_{\mathrm{T}} \tag{2}$$

The dilatational modulus obtained in the oscillating barrier experiment is a complex quantity and is composed of the real component, that is, the elastic modulus (E'), and the imaginary component, that is, the viscous modulus (E''). For a perfectly viscous monolayer, the real part is equal to zero, whereas for a perfectly elastic one, the imaginary part is zero. The ratio of E'' to E' is defined as the tangent of the loss angle, $\tan \theta$, where θ is the phase shift between the imaginary component and the real component of the dilatational modulus. A value of $\tan \theta$ lower than 1 implies elastic properties of the monolayer, whereas a value of $\tan \theta$ greater than 1 reveals a more viscous character.^[37,39]

The surface viscoelastic properties of the POSS monolayers spread on the air–water interface, as a function of the frequency of oscillations, were investigated at different surface states characterized by given values of the surface pressure. The changes in the surface elastic modulus (*E'*) and the viscous modulus (*E''*) as a function of the deformation rate (i.e., the frequency of oscillations) are presented in Figure 8. For the OFP-POSS monolayer (Figure 8a) the experiments were conducted at 5 and 10 mN m⁻¹, which corresponded to the LE state and the onset of collapse, respectively, whereas for the PEG-POSS monolayer (Figure 8b) the experiments were conducted at 5, 10, and 25 mN m⁻¹, that is, before and after the LE–LC phase transition region and at the maximal static elasticity, respectively.

The dilatational elasticity (E') depended very weakly on the frequency of oscillations in the studied range, in all considered monolayers states, whereas the dilatational viscosity (E'') increased with increasing of the frequency in an almost linear way. The results presented show that the values of E' exceed the values of the viscous modulus E'', which indicates forma-



European Journal

Full Paper

Figure 8. Dilatation rheological parameters for a) PEG-POSS and b) OFP-POSS monolayers as a function of the frequency at different surface pressures, that is, 5, 10, and 25 mN m⁻¹.

tion of elastic films by the two studied monolayers. Thus, although for both OFP-POSS and PEG-POSS films the viscoelastic response appeared, nevertheless these films have more elastic character. In the more compressed monolayer the stronger intermolecular interactions should exist, which is consistent with the results obtained. As shown for the PEG-POSS monolayer, the value of elastic modulus E' significantly increases with an increasing surface pressure, which may be caused by the formation a more stable monolayer upon compression. As mentioned above, we can conclude that the three PEG moieties present in the PEG-POSS molecules, were anchored in the water subphase and enhanced the stability of the monolayer formed at the air-water interface but did not impact the intermolecular interactions between the POSS molecules. A similar behavior was reported for closed-cage 1,2-propanediolisobutyl POSS.^[25]

In the case of the OFP-POSS monolayer, the rheological characteristics were considered only for low surface pressures that is, 5 and 10 mNm⁻¹, due to its low value of collapse of approximately 11.8 mNm⁻¹. It should be noted that the values of the elastic modulus E' determined for the OFP-POSS monolayer are higher when compared with the values of E' characterizing the PEG-POSS film under the same conditions of study. This may be due to a strongly hydrophobic nature of the OFP-POSS molecules forming a more insoluble monolayer in the LE phase at the air–water interface.

As shown in Figure 9, the tangent of the loss angle for both monolayers (under all studied conditions) assumed low values, which did not exceed 0.4 for the highest deformation rate at the highest surface pressure studied. The obtained results permit concluding that the monolayers formed by molecules of both POSS derivatives revealed rheological behavior (under dilatational conditions) that are essentially elastic.

To conclude, the oscillating barrier experiment has shown that irrespectively of the dynamic conditions resulting both from high and low deformation rates, both PEG-POSS as well as OFP-POSS monolayer behave like elastic material.

www.chemeurj.org

Chem. Eur. J. 2016, 22, 1-13

ChemPubSoc Europe



Figure 9. Frequency dependence of the tangent of the loss angle for PEG-POSS and OFP-POSS at different surface pressures. Amplitude of deformation = 1%.

Thin films of POSS at the solid substrates

The Langmuir monolayers formed by molecules of the two POSS studied were deposited onto quartz surfaces according to the Langmuir–Blodgett technique (LB) to form a layer structure and then (after drying the quartz plate) the wettability of the modified substrates was determined. Table 2 details the results obtained for the water contact angle. The wetting angle measurements of such prepared materials confirmed the successful deposition of the POSS monolayers. In both cases a significant increase in the water contact angle was observed (measured values varied from around 70 to 101° for the different POSS) when compared to quartz (i.e., $(15 \pm 0.1)^{\circ}$).

As follows from the above data, the wettability of the solid substrate modified by deposition of the PEG-POSS monolayer is significantly lower than that of the quartz covered by a thin film of the OFP-POSS. This result reflects the differences in the orientation of these two types of POSS molecules forming films on the solid substrate. It confirms that within the PEG-POSS film the hydrophilic head (i.e., the PEG moieties) was in contact with water and, after the film transfer, with the solid substrate, whereas the hydrophobic tail (i.e., the POSS cage) was exposed towards air. The measured value of the water contact angle for the quartz substrate modified with the PEG-POSS film is in good agreement with the data reported for 1,2-propanediolisobutyl POSS, that is, a POSS derivative with a silica cage substituted with seven isobutyl group similarly as the PEG-POSS molecule.^[25]

Table 2. Values of the water contact angle (WCA) on the modified quartz substrate.							
Compound	Transfer surface pressure [mNm ⁻¹]	Water contact angle [°]					
2	30	(70.4±0.1)					
3	10	(101.1 ± 0.1)					

In the case of OFP-POSS, the mosaic structure of the monolayer produced at the air-water interface remained in the same form after the deposition of this film onto the solid substrate. The presence of domains with oppositely directed OFP-POSS molecules, which are aligned at the surface, that is, direct contact of both the hydrophobic cores and the hydrophobic fluorinated groups with the molecules of wetting water results in the higher hydrophobicity of this layer than that of the PEG-POSS monolayer. Moreover, it is worth mentioning that the measured value of the contact angle for the substrate modified by deposition of the OFP-POSS film is clearly lower (by about 20°) in comparison with the wettability of the material modified by typical fluorinated polyhedral oligomeric silsesquioxanes (F-POSS).^[48,49] Thus, the results obtained seem to confirm the proposed mosaic structure and simultaneously exclude the orientation of the OFP-POSS molecules forming a LB film with the fluorinated moieties exposed towards the air.

Deposited Langmuir–Blodgett monolayers of both substances were also investigated by using an atomic force microscope in order visualize them the in nanometric scale. Representative images are presented in Figures 10a–d.

Both films cover the quartz substrates almost completely despite the fact that there are defects in the substrates visible as lines (polishing grooves) and black areas (point defects), which are typical of these type of substrates.^[41] In the images of the PEG-POSS (Figures 10a and b) many small 3D aggregates, visible as bright spots against the homogenous monolayer, can be seen. The aggregate lateral dimensions do not exceed 100 nm, protruding typically 2–5 nm above the monolayer. Emergence of these forms can be explained by the tendency to aggregation of the PEG-POSS molecules described in the literature.^[25,42] In addition to that, the PEG-POSS include highly polar groups, which, we concluded, lie on the water surface oriented parallel to each other. In close proximity, dipolar interactions between them also contribute to repellence of the molecules out of the contact with the water surface.



Figure 10. Topography AFM images of a,b) PEG-POSS and c,d) OFP-POSS Langmuir–Blodgett films deposited on quartz substrates. The image scale is a,c) $5 \times 5 \ \mu m^2$ and b,d) $1 \times 1 \ \mu m^2$.

www.chemeurj.org

8

© 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim **K** These are not the final page numbers!



In contrast to a large number of aggregates in the PEG-POSS image (56 μ m²) covering about 2% of the total substrate surface, only single spots (<1 μ m²) can be seen for the OFP-POSS monolayer (Figures 10c and d) with a negligible total coverage (0,04%). Inhibited aggregation of OFP-POSS stems from the above-mentioned smaller molecular packing (C_s^{-1} = 34.1 mNm⁻¹) when compared to that of PEG-POSS (C_s^{-1} = 130.5 mNm⁻¹). Longer intermolecular distances in the perfluorinated OFP-POSS are a result of the substitution of the silica cage with groups containing strongly electronegative atoms. In this way, fluorination (substitution with strongly electronegative atoms in general) prevents aggregation into 3D forms.^[43]

As is well known, the geometry of the surface can have a great impact on wettability.^[44,45] Roughness, represented by the root-mean-square (S_q), is identical for both investigated films (Table 3); however, its value results from imperfection of the substrate rather than from the character of the surfaces of the monolayer. On the other hand, the values of the Wenzel factor^[46,47] for both PEG-POSS as well as for OFP-POSS are very close to unity. This is due to the fact that in both cases the apparent surface area of the monolayers is almost equal to the projected surface area. Therefore, considering the difference in the hydrophobicity of these two sample surfaces we can conclude that it derives entirely from its chemical nature and is not a geometric effect.

Table 3. Values of the root-mean-square roughness (S_q), number of 3D aggregates per 1 μ m ² (N_{AGG}), percentage area covered by aggregates (\mathcal{H}_{AGG}), and Wenzel factor (r) calculated for the investigated monolayers.									
Compound	<i>S</i> _q [nm]	$N_{AGG} \ [\mu m^{-2}]$	% _{AGG}	<i>r</i> [a.u.]					
2 3	0.49 0.49	56 <1	2.23 0.04	1.0006 1.0009					

Conclusion

Two new silsesquioxane derivatives with open-cage structures, containing three fluoroalkyl groups (OFP-POSS) or hydroxy terminated polyether functional groups (PEG-POSS), have been synthesized on the basis of a hydrosilylation process. While synthesizing the above-mentioned derivatives, the effects of the kind of olefin and catalyst employed on the course of the hydrosilylation process have been determined. The reaction proceeds more effectively in the case of olefins with strongly hydrophobic properties (i.e., fluoroalkyl-allyl ether) and in the presence of the Karstedt's catalyst. The obtained derivatives were isolated and characterized spectroscopically. The mentioned POSS derivatives were subsequently subjected to an analysis of their surface properties followed by a study of the interfacial behavior of both derivatives at the air-water interface. The obtained results indicate that the PEG-POSS molecules as well as the OFP-POSS molecules are able to form insoluble Langmuir films at the air-water interface, which can be transferred onto a solid substrate and effectively change its wetting properties. It has been shown that the properties of the Langmuir monolayers formed on the water surface (i.e., packing density, orientation of the molecules, stability, electric surface potential) depend strongly on the chemical structure of the POSS compound.

The successful preparation of LB films by using the PEG-POSS and OFP-POSS suggests that these two types of silsesquioxanes can be good candidates for obtaining nanostructured hybrid materials and coatings and can be applied to other types of thin film technology.

Experimental Section

Materials: All commercially available (Sigma–Aldrich) chemicals were used as received without any further purification. 5-(Allyloxy)-1,1,2,2,3,3,4,4-octafluoropentane was synthesized by a Williamson reaction.^[27] 1,3,5,7,9,11,14-Heptaisobutyltricyclo[7.3.3.^{15,11}]hepta-siloxane-*endo*-3,7,14-triol was synthesized by hydrolytic condensation of isobutyltrimethoxysilane under basic conditions according to a procedure described elsewhere.^[28]

Synthesis of 3,7,14-tris[dimethylsiloxy]-1,3,5,7,9,11,14-heptaisobutyltricyclo[7.3.3.^{15,11}]heptasiloxane—SiH-POSS (1): The synthesis was based on the hydrolytic condensation of 1,3,5,7,9,11,14heptaisobutyltricyclo[7.3.3.^{15,11}]heptasiloxane-endo-3,7,14-triol with chlorodimethylsilane carried out in the presence of trimethylamine under an argon atmosphere. To a Schlenk flask, placed on an ice bath, were introduced dry hexane (50 mL), 1,3,5,7,9,11,14-heptaisobutyltricyclo[7.3.3.15,11]heptasiloxane-endo-3,7,14-triol (10 g, 0.0126 mol), chlorodimethylsilane (3.7 g, 0.0388 mol) followed by dropping trimethylamine (4 g, 0.0395 mol) to the obtained solution. The reaction mixture became cloudy as a result of hydrochloride formation. After one hour, the mixture was warmed to room temperature while stirring for two more hours. Then the post-reaction mixture was subjected to filtration in order to remove the formed triethylamine hydrochloride and the filtrate was evaporated under reduced pressure. The raw product was washed three times with methanol to remove any possible hydrochloride residue. The obtained 3,7,14-tris[dimethylsiloxy]-1,3,5,7,9,11,14-heptaisobutyltricyclo[7.3.3.15,11]heptasiloxane (11.8 g, 97%) was subjected to spectroscopic analysis, which confirmed its structure. ¹H NMR (400 MHz, C_6D_6 , 25 °C, TMS): $\delta = 0.40$ (d, J = 2.8 Hz, 18H; Si(CH₃)₂), 0.86-0.80 (m, 14H; SiCH₂), 1.09 (d, J=3.3 Hz, 42H; CH₃), 2.16-1.98 (m, 7H; CH), 5.18–5.13 ppm (m, 3H; SiH); ¹³C NMR (75.5 MHz, C₆D₆, 25 °C, TMS): $\delta = 0.41$ (Si(CH₃)₂), 22.90 (SiCH₂), 24.45 (CH), 26.18 ppm (CH₃); ²⁹Si NMR (59.6 MHz, C₆D₆, 25 °C, TMS): $\delta = -67.53$, -67.33, -66.58, -5.06 ppm.

Synthesis of 3,7,14-tris{[ω-(hydroxy)(polyethoxy)propyl]dimethylsiloxy}-1,3,5,7,9,11,14-heptaisobutyltricyclo[7.3.3.^{15,11}]heptasiloxane—PEG-POSS (2): The reaction was based on a hydrosilylation process. In a round-bottom flask equipped with a magnetic stirrer and a reflux condenser, were placed toluene (20 mL), 3,7,14tris[dimethylsiloxy]-1,3,5,7,9,11,14-heptaisobutyltricyclo[7.3.3.^{15,11}]heptasiloxane (5 g, 5.18×10^{-3} mol), and allyl polyether with terminal hydroxyl groups (6 g, 0.0171 mol) of an average molecular weight of 350 g mol⁻¹. This was followed by adding Karstedt's catalyst to the mixture at room temperature. The amount of the catalyst corresponded to 5×10^{-5} mol Pt per one mol of Si-H present 3,7,14-tris[dimethylsiloxy]-1,3,5,7,9,11,14-heptaisobutyltricyin clo[7.3.3.^{15,11}]heptasiloxane and then the whole mixture was heated to 90 °C and maintained at this temperature for 7 h. The process was monitored by infrared spectroscopy, observing the disappearance of the band at $\tilde{\nu} = 904 \text{ cm}^{-1}$ originating from the Si–H bond present in the parent compound (i.e., 3,7,14-tris[dimethylsiloxy]-

Chem. Eur. J. 2016, 22, 1–13 www.chemeurj.org

9

These are not the final page numbers! **77**



1,3,5,7,9,11,14-heptaisobutyltricyclo[7.3.3.^{15,11}]heptasiloxane). After completion of the process, the post-reaction mixture was cooled down followed by evaporation of the solvent and olefin excess under reduced pressure. It resulted in 10.2 g (97.7%) of the product **2**. The obtained product was subjected to spectroscopic analysis. ¹H NMR (400 MHz, C₆D₆, 25 °C, TMS): δ=0.21 (s, 18H; Si(CH₃)₂), 0.64–0.58 (m, 6H; (CH₃)₂SiCH₂), 0.71–0.65 (m, 6H; SiCH₂), 0.98 (d, *J*=5.5 Hz, 42H; CH₃), 1.69–1.60 (m, 6H; CH₂), 2.02–1.84 (m, 7H; CH), 3.34–3.28 (m, 6H; CH₂O), 3.50–3.35 (m, 84H; OCH₂CH₂O), 3.54 (s, 3H; OH), 3.63–3.58 ppm (m, 6H; CH₂OH); ¹³C NMR (75.5 MHz, C₆D₆, 25 °C, TMS): δ=0.17 (Si(CH₃)₂), 14.09 ((CH₃)₂SiCH₂), 22.40 (SiCH₂), 23.53 (CH₂), 24.09 (CH), 25.67 (CH₃), 61.29 (CH₂OH), 70.39 (OCH₂CH₂O), 72.78 (OCH₂), 73.76 ppm (CH₂O); ²⁹Si NMR (59.6 MHz, C₆D₆, 25 °C, TMS): δ=-68.06, -67.68, -67.03, 9.75 ppm.

Synthesis of 3,7,14-tris{[3-(2,2,3,3,4,4,5,5-octafluoropentyloxy)-propyl]dimethylsiloxy}-1,3,5,7,9,11,14-heptaisobutyltricy-

clo[7.3.3.^{15,11}]**heptasiloxane**—**OFP-POSS (3)**: The reaction was based on a hydrosilylation process. In a round-bottom flask equipped with a magnetic stirrer and a reflux condenser, were placed toluene (20 mL), 3,7,14-tris[dimethylsiloxy]-1,3,5,7,9,11,14-heptaisobutyltricyclo[7.3.3.^{15,11}]heptasiloxane (5 g, 5.18×10^{-3} mol), and 5-(allyloxy)-1,1,2,2,3,3,4,4-octafluoropentane (4.7 g, 0.0173 mol). This was followed by adding Karstedt's catalyst to the mixture at room temperature. The amount of the catalyst corresponded to 5×10^{-5} mol Pt per one mole of Si–H present in 3,7,14-tris[dimethylsiloxy]-1,3,5,7,9,11,14-heptaisobutylotricy-

clo[7.3.3.15,11] heptasiloxane and then the whole mixture was heated to 90°C and maintained at this temperature for 3 h. The process was monitored by infrared spectroscopy, observing the disappearance of the band at $\tilde{\nu} = 904 \text{ cm}^{-1}$ originating from the Si–H bond present in the parent compound (i.e., 3,7,14-tris[dimethylsiloxy]-1,3,5,7,9,11,14-heptaisobutyltricyclo[7.3.3.^{15,11}]heptasiloxane). After completion of the process, the post-reaction mixture was cooled down followed by evaporation of the solvent and olefin excess under reduced pressure. It resulted in 8.8 g (95.4%) of the product 3. The obtained product was subjected to spectroscopic analysis. ¹H NMR (400 MHz, C_6D_6 , 25 °C, TMS): $\delta = 0.37$ (s, 18 H; Si(CH₃)₂), 0.76-0.67 (m, 6H; (CH₃)₂SiCH₂), 0.89-0.81 (m, 14H; SiCH₂), 1.16 (d, J = 4.7 Hz, 42 H; CH₃), 1.79–1.66 (m, 6H; CH₃), 2.19–2.01 (m, 7H; CH), 3.44–3.29 (m, 6H; CH₂O), 3.66 (t, J=13.9 Hz, 6H; OCH₂), 5.74– 5.37 ppm (m, 3H; CF₂H); ¹³C NMR (75.5 MHz, C₆D₆, 25 °C, TMS): $\delta =$ 0.41 (Si(CH₃)₂), 14.13 ((CH₃)₂Si<u>C</u>H₂), 22.89 (SiCH₂), 23.65 (CH₂), 24.58 CH), 26.02 (CH₃), 67.63 (OCH₂), 75.70 (CH₂O), 108.14, 110.67, 116.02, (CF₂), 111.52 ppm (CF₂H); ²⁹Si NMR (59.6 MHz, C₆D₆, 25 $^{\circ}$ C, TMS): $\delta =$ -67.57, -67.20, -66.85, 9.45 ppm.

NMR spectroscopy: ¹H NMR (400 MHz), ¹³C NMR (75 MHz), and ²⁹Si MNR (59 MHz) spectra were recorded on a Bruker Ascend 400 MHz NanoBay spectrometer at room temperature by using C_6D_6 as a solvent.

FTIR spectroscopy: FT-R spectra were recorded on a Bruker Tensor 27 Fourier transform infrared spectrometer equipped with a Specac Golden Gate diamond ATR unit. In all cases, sixteen scans with a resolution of 2 cm^{-1} were collected for a spectrum.

Real-time FTIR spectroscopy: Real-time infrared spectroscopy has been applied to monitor the hydrosilylation of the olefins with 3,7,14-tris[dimethylosiloxy]-1,3,5,7,9,11,14-heptaisobutyltricy-

clo[7.3.3.^{15,11}]heptasiloxane. The measurements were performed on a Mettler-Toledo ReactIR 15 spectrometer equipped with a 9.5 mm AgX DiComp (diamond) probe and a liquid nitrogen-cooled MCT detector. The spectra were taken with a resolution of 4 cm⁻¹ collecting fifty scans for each spectrum at intervals of 15 s. The reaction progress in the studied systems of parent compounds and catalysts was quantified by observing the rate of changes occurring with time in the area of the band at $\tilde{\nu} = 904 \text{ cm}^{-1}$ originating from stretching vibrations of the Si–H bond.

Isotherm measurements: Langmuir trough (KN 0033, KSV Nima) with a surface area of 273 cm² (L×W×D, $364 \times 75 \times 4 \text{ mm}^3$) and a subphase volume of 190 mL was used for the preparation of the monolayers. Before the experiments the Teflon trough was cleaned with chloroform and ethanol and rinsed with ultrapure water. At the beginning of the experiment, a double-barrier trough was filled with ultrapure water (18.2 M Ω cm, 71.98 \pm 0.01 mN m⁻¹) and then the surface of the water was cleaned by using a suction pump until the change in the surface pressure after maximum compression was below 0.2 mN m⁻¹. In the next step of the experiment, the POSS derivatives studied (dissolved in chloroform) were spread evenly onto the surface of the subphase with a Hamilton microliter syringe. After evaporation of chloroform (\approx 20 min) the monolayers were compressed with a rate of 5 mm min⁻¹. A platinum Wilhelmy plate (KSV Nima) connected with the balance was used to record the surface pressure π to a resolution of \pm 0.01 mNm⁻¹. The mean molecular area (A) was recorded in [Å²]. The π -A isotherms were obtained upon symmetrical compression caused by the movement of two barriers. During all measurements the temperature of the subphase was kept constant on the level of $(25.0\pm0.1)^{\circ}$ C by using a Julabo water circulating bath. A floating optical table (Standa) under the Langmuir trough and all other devices, minimized the vibrations. A Laminar flow hood surrounding the equipment ensured a dust-free environment with a relative humidity kept around 60-70%. Each isotherm was repeated at least three times to ensure the reproducibility of the curves to $\pm 2 \text{ Å}^2$. The cross-sectional areas and space-filling models for both molecules were obtained by using the VEGA ZZ software.^[36]

Brewster angle microscopy (BAM): The morphology of the monolayers was visualized with a Brewster angle microscope (Micro BAM; KSV Nima) coupled with the Langmuir trough and installed on an anti-vibration table. Different domain shapes and sizes observed as different reflection density or gray levels indicate the monolayer phases. These morphologies are also related to changes in the thickness of the monolayer due to the formation of three-dimensional aggregates. BAM images were taken with a CCD camera during the monolayer compression. The light source was a laser diode ($\lambda = 659$ nm). The field of view was 3.6×4 mm² and the resolution was approximately six microns per pixel (i.e., better than twelve microns resolution according to Rayleigh's criterion; the system is not diffraction limited). During the experiment, a flat black glass plate was placed under the subphase to absorb the refracted beam.

Surface potential: The surface potential (ΔV) was measured by using the non-contact and non-destructive vibrating capacitor method. The surface potential meter (SPOT, KSV Nima) recorded the ΔV simultaneously with the π -A isotherm by using two electrodes; the first one was placed just above the water surface, whereas the counter electrode was immersed into the subphase. The dynamic range of the measurement was -5 to +5 V with the sensitivity ± 1 mV.

Substrate preparation: Quartz slides (purchased from PHASIS, L× W×D 25×25×1 mm³) were used as substrates for the LB film deposition. Prior to starting the Langmuir–Blodgett experiments, the quartz slides were prepared by heating to (75 ± 5) °C in a 5:1:1 by volume mixture of H₂O/NH₄OH (27% concentrated)/H₂O₂ (30% by volume) for 0.5 hour. After rinsing with an abundant amount of ultrapure water and drying in the atmosphere, the hydrophilic substrates were ready (with a contact angle equal to 15°) for the LB film deposition.

Chem. Eur. J. **2016**, 22, 1–13

www.chemeurj.org

10



Langmuir–Blodgett (LB) deposition experiments: The monolayer was deposited on the solid substrate (quartz slides) by using a commercial LB trough (KSV Nima) and a vertical dipping method at a dipping speed of 1 mm min^{-1} , maintaining the temperature at 25 °C and the surface pressure at 30 mN m⁻¹ for PEG-POSS film and at 10 mN m⁻¹ for OFP-POSS film deposition.

The deposition of the monolayer on a hydrophilic quartz substrate was performed as follows. The substrate was immersed in the water subphase and then the POSS/chloroform solution was spread on the water surface. The POSS monolayer compressed up to an appropriate pressure was transferred onto the substrate by withdrawing the quartz slides from the water subphase (upstroke deposition). LB films of PEG-POSS and OFP-POSS of one layer were prepared.

Oscillatory barrier experiment: The oscillatory barrier method^[37] was used to determine the dilatational viscoelasticity of the POSS monolayers at the air-water interface. In this experiment the monolayers were subjected to small periodic compressions and expansions. During these oscillations the changes of the surface pressure were continuously recorded. Oscillations were performed for different frequencies ranging from approximately 0.02 to about 0.15 Hz. Ten oscillation cycles were recorded for each frequency and between the subsequent oscillations cycles was an interval of 60 s. After compression of the monolayers to a desired surface pressure (5, 10, or 25 mNm⁻¹), the molecular area started to change as a result of small amplitude oscillations of barriers. The induced changes in the surface area were equal to approximately 1%.

Contact angle measurements: The quartz surfaces modified with the POSS films were characterized by their water contact angle (WCA). The contact angle measurements were made with a Theta Lite Optical Tensiometer TL101 (Attension, KSV) by using the sessile drop method. A drop (3 mL) of ultrapure water was pushed out of the capillary and deposited on a stationary surface of the sample under an air atmosphere. The measurements were repeated five times for each sample and the average values of the water contact angle were reported.

Atomic force microscopy: The surface of the monolayers was imaged with Innova SPM (Bruker) in the intermittent (tapping) mode under air. The measurements were performed at room temperature (19–21 °C) by using silicon probes with a spring constant in the range of 1-5 Nm⁻¹ and a tip radius of 8-12 nm. The obtained images were only background corrected (without further processing) by using the WSxM software.^[40]

Acknowledgements

This work was financially supported by the National Science Center (Poland), Project UMO-2012/05/B/ST 02200. The authors wish to thank Dr. Jarosław Makowiecki for fruitful discussion and his assistance in the realization of the AFM measurements.

Keywords: hydrosilylation · Langmuir–Blodgett films · POSS · silsesquioxanes · surface chemistry

- [1] Applications of Polyhedral Oligomeric Silsesquioxanes, Advances in Silicon Science 3 (Ed.: C. Hartmann-Thompson), Springer, Heidelberg, **2011**.
- [2] P. D. Lickiss, F. Rataboul, Adv. Organomet. Chem. 2008, 57, 1-116.
 [3] D. B. Cordes, P. D. Lickiss, F. Rataboul, Chem. Rev. 2010, 110, 2081-2173.
- [4] B. Marciniec, H. Maciejewski, C. Pietraszuk, P. Pawluć in *Hydrosilylation:* A Comprehensive Review on Recent Advances, (Ed.: B. Marciniec), Springer, Heidelberg, 2009.

These are not the final page numbers! 77

- CHEMISTRY A European Journal Full Paper
- [5] F. J. Feher, T. A. Budzichowski, Polyhedron 1995, 14, 3239-3253.
- [6] J. D. Lichtenhan, Comments Inorg. Chem. 1995, 17, 115-130.
- [7] D. A. Loy, K. J. Shea, Chem. Rev. 1995, 95, 1431-1442.
- [8] A. Kuehnle, C. Jost, H. Haeger; R. Richter; F. G. Schmidt, DE10321556, 2004.
- [9] A. Kuehnle, C. Jost, B. Schleich, E. Nun, F. G. Schmidt, H. C. L. Abbenhuis, DE10249453, 2003.
- [10] H. Weickmann, R. Delto, R. Thomann, R. Brenn, W. Doell, R. Muelhaupt, J. Mater. Sci. 2007, 42, 87–92.
- [11] M. Yamahiro, H. Oikawa, K. Yoshida, K. Ito, Y. Yamamoto, M. Tanaka, N. Ootake, K. Watanabe, K. Ohno, Y. Tsujii, T. Fukuda, WO2004026883, 2004.
- [12] S. Ding, Z. Ding, W. Zhang, CN103159955, 2013.
- [13] M. Miyasaka, Y. Fujiwara, H. Kudo, T. Nishikubo, Polym. J. 2010, 42, 799– 803.
- [14] Y. Hirai, S. Murata, JP2005062235, 2005.
- [15] A. Kuehnle, C. Jost, H. C. L. Abbenhuis, WO2003095547, 2003.
- [16] H. Satake, N. Ootsuka, Y. Yamamoto, K. Ito, N. Otake, K. Yoshida, US20060204192, 2006.
- [17] T. Nishikubo, H. Kudo, M. Miyasaka, JP2009269989, **2009**.
- [18] I. Y. Rushkin, O. N. Dimov, S. Malik; B. De Binod, WO2008098189, 2008.
- [19] T. Miyashita, A. Watanabe, T. Hattori, K. Yoshida, JP2008112942, 2008.
- [20] T. Miyashita, A. Watanabe, N. Otsuka, T. Kikugawa, JP2007298841, 2007.
- [21] W. P. Freeman, P. T. Furuta, R. Dubrow, J. W. Parce, US20140275598, 2014.
- [22] J. Deng, J. T. Polidan, J. R. Hottle, C. E. Farmer-Creely, B. D. Viers, A. R. Esker, J. Am. Chem. Soc. 2002, 124, 15194–15195.
- [23] J. Deng, B. D. Viers, A. R. Esker, J. W. Anseth, G. G. Fuller, *Langmuir* 2005, 21, 2375–2385.
- [24] J. Deng, J. R. Hottle, J. T. Polidan, H.-J. Kim, C. E. Farmer-Creely, B. D. Viers, A. R. Esker, *Langmuir* **2004**, *20*, 109–115.
- [25] J. Paczesny, I. Binkiewicz, M. Janczuk, K. Wybranska, Ł. Richter, R. Hołyst, J. Phys. Chem. C 2015, 119, 27007–27017.
- [26] G. R. Yandek, B. M. Moore, S. M. Ramirez, J. M. Mabry, J. Phys. Chem. C 2012, 116, 16755–16765.
- [27] H. Maciejewski, J. Karasiewicz, B. Marciniec, Polimery 2012, 57, 449-455.
- [28] M. Przybylak, H. Maciejewski, B. Marciniec, Polimery 2013, 58, 741-747.
- [29] Interfacial Rheology (Eds.: R. Miller, L. Liggieri), CRC Press, Boca Raton, 2009.
- [30] Interfacial Phenomena (Eds.: J. T. Davies, E. K. Rideal), Academic Press, New York, 1963.
- [31] H. Mahfuz, F. Powell, R. Granata, M. Hosur, M. Khan, *Materials* 2011, 4, 1619–1631.
- [32] W. Yin, J. Deng, A. R. Esker, Langmuir 2009, 25, 7181-7184.
- [33] G. L. Gaines, Jr., Langmuir 1991, 7, 834-839.
- [34] N. Kim, S. Shin, J. Chem. Phys. 1999, 110, 10239-10242.
- [35] M. Broniatowski, I. Sandez Macho, P. Dynarowicz-Łątka, Thin Solid Films 2005, 493, 249–257.
- [36] A. Pedretti, L. Villa, G. Vistoli, J Comput Aided Mol Des. 2004, 18, 167– 173.
- [37] H. Hilles, F. Monroy, L. J. Bonales, F. Ortega, R. G. Rubio, Adv. Colloid Interface Sci. 2006, 122, 67–77.
- [38] E. Guzmán, E. Santini, M. Ferrari, L. Liggieri, F. Ravera, J. Phys. Chem. C 2015, 119, 21024–21034.
- [39] K. Dopierala, A. Wamke, M. Dutkiewicz, H. Maciejewski, K. Prochaska, J. Phys. Chem. C 2014, 118, 24548-24555.
- [40] I. Horcas, R. Fernandez, J. M. Gomez-Rodriguez, J. Colchero, J. Gomez-Herrero, A. M. Baro, *Rev. Sci. Instrum.* 2007, 78, 013705-013708.
- [41] H. Arribart, D. Abriou, Ceram.-Silik. 2000, 44, 121-128.
- [42] E. Ayandele, B. Sarkar, P. Alexandridis, J. Nanomater. 2012, 2, 445-475.
- [43] P. Nitoń, A. Żywociński, J. Paczesny, M. Fiałkowski, R. Hołyst, B. Glettner, R. Kieffer, C. Tschierske, D. Pociecha, E Górecka, *Chem. Eur. J.* 2011, *17*, 5861–5873.
- [44] J. N. Israelachvili, Intermolecular and Surface Forces: Revised Third Edition, Academic Press, 2011.
- [45] H.-J. Butt, K. Graf, M. Kappl, *Physics and Chemistry of Interfaces*, Wiley-VCH, Weinheim 2003.
- [46] A. Kozbial, Z. Li, C. Conaway, R. McGinley, S. Dhingra, V. Vahdat, Langmuir 2014, 30, 8598–8606.

Chem. Eur. J. **2016**, *22*, 1–13 www.chemeurj.org

11





- [47] J. I. Rosales-Leal, M. A. Rodríguez-Valverde, G. Mazzaglia, P. J. Ramón-Torregrosa, L. Díaz-Rodríguez, O. García-Martínez, *Colloids Surf. A* 2010, 365, 222–229.
- [48] A. J. Meuler, S. S. Chhatre, A. R. Nieves, J. M. Mabry, R. E. Cohen, G. H. McKinley, Soft Matter 2011, 7, 10122-10134.
- [49] S. M. Ramirez, Y. J. Diaz, R. Campos, R. L. Stone, T. S. Haddad, J. M. Mabry, J. Am. Chem. Soc. 2011, 133, 20084–20087.
- [50] C. P. Pascholati, E. P. Lopera, F. J. Pavinatto, L. Caseli, T. M. Nobre, M. E. D. Zaniquelli, T. Viitala, C. D'Silva, O. N. Oliveira, *Colloids Surf. B* 2009, 74, 504–510.
- [51] T. E. Goto, L. Caseli, Langmuir 2013, 29, 9063-9071.
- [52] K. Y. C. Lee, Rev. Phys. Chem. Jpn. 2008, 59, 771-791.

Received: May 23, 2016 Published online on



FULL PAPER



Two POSS derivatives with open-cage structures, containing fluoroalkyl- or hydroxy-terminated polyether groups have been synthesized and were subjected to the analysis of their surface properties and interfacial behavior (see figure). The properties of monolayers formed on the water surface depend strongly on the chemical structure of the POSS compound. The results suggest that they can be good candidates for obtaining nanostructured thin film coatings.

Silsesquioxanes

M. Dutkiewicz, J. Karasiewicz, M. Rojewska, M. Skrzypiec, K. Dopierała, K. Prochaska, H. Maciejewski*

Synthesis of an Open-Cage Structure POSS Containing Various Functional Groups and Their Effect on the Formation and Properties of Langmuir Monolayers