Macromol. Symp. **2007**, 259, 421–426 DOI: 10.1002/masy.200751348

What Kind of Image is Drawn by a MALDI-Experiment of Grafted Nanoparticles? - How to Distinguish between Chemically and Physically Adsorbed Parts

*Wibke Dempwolf, Lars Nothdurft, Gudrun Schmidt-Naake**

Summary: The modern MALDI-TOF mass spectrometry is a powerful technique for the fast and accurate determination of a number of polymer characteristics like end group analysis. It can also be used to analyze the grafted shell around silane modified nanoparticles. This shell contains physically and chemically adsorbed parts. It is a question of great interest what kind of adsorbent can be visualized by using MALDI-TOF mass spectrometry, while it is not possible to ionize the whole AEROSIL® particle. Therefore we chose the system MPTMS/AEROSIL®200 to address this issue. We grafted AEROSIL®200 with methacryloxy(propyl)-trimethoxysilane (MPTMS) under acid conditions. The grafted nanoparticles were treated via Soxhlet extraction. The resulting fractions (the washed nanoparticles and the Soxhlet extract) were systematically analyzed by using MALDI-TOF MS as well as the grafted nanoparticles themselves. As a crosscheck MPTMS was homopolymerized and analyzed. Our results show that for the system under investigation there is strong evidence that only the physically adsorbed part can be analyzed via MALDI-TOF MS.

Keywords: inorganic materials; matrix-assisted laser desorption/ionization mass spectrometry (MALDI MS); modification; nanoparticles; polysiloxanes

Introduction

The combination of synthetic polymers with inorganic materials is a research field of steadily growing interest and importance because of their potential applications in optics, electronics, engineering and biosciences.[1] Especially, the synergism of polymeric properties like elasticity with organic properties as e.g. hardness, stability or electrical conductivity offer a high potential concerning new materials and applications.

Preparation of polymer composite materials does not always result in the desired synergetic effects. Due to the complementary properties of the components phase separation can occur, which can lead to unsatisfactory material properties. This problem can be solved by linking organic and inorganic parts covalently. An interesting application is the encapsulation of inorganic particles by polymers, the so called core-shell particles synthesis. Therefore, inorganic cores were produced, varying from silica cores to $Al_2O_3^-$, ZrO_2^- and TiO_2^- cores with polymerizable functionalities. In this contribution MALDI-TOF mass spectrometry was used to investigate the polysilsesquioxane shell of modified particles. These shells consist of covalent bound and physically adsorbed fractions.

During the last years MALDI-TOF mass spectrometry has become an essential tool for endgroup characterization of synthetic polymers. It was also used for the investigation of polyalkoxysiloxanes,[2,3] silsesquioxanes,[4–6] silsesquioxane-based nanoparticles[7,8] and silane modified surfaces.[9]

The functionalization of inorganic oxide particles (AEROSIL®200) was performed

---

Technische Universität Clausthal, Institut für Technische Chemie, 38678 Clausthal-Zellerfeld, Germany
Fax: +49 5323 723655;
E-mail: gudrun.schmidt@tu-clausthal.de

using methacryloxy(propyl)trimethoxysilane (MPTMS). The trialkoxysilane MPTMS was hydrolyzed under acid conditions to form trihydroxysilanes which consequently condensate to form siloxane bounds (Si-O-Si). This condensation step takes place between two hydroxyl groups. The surface of silicon dioxide particles like AEROSIL®200 also contains hydroxyl groups. Thus in addition to the condensation of the different trihydroxysilanes, which results in the formation of polysilsesquioxanes with the general formula $(RSiO_{3/2})_n$ (n = even) (Figure 1a), the condensation of those polysilsesquioxanes and the AEROSIL® particles (Figure 1b) can take part. The physical adsorption of unbound polysilsesquioxanes is caused by interactions with the modified AEROSIL® particle (Figure 1b).

The aim of this study is to differentiate between the chemically bound and the unbound structures (physically adsorbed fraction) because it is not possible to ionize the whole AEROSIL® particles. Within this contribution we would like to show which parts are ionized during the MALDI process.

Silicon dioxide particles (AEROSIL® 200) modified with MPTMS are used for this investigation and the separation ofthe chemically bound and physically adsorbed fractions is performed with the help of a Soxhlet extraction. The resulting fractions are analyzed by different techniques.

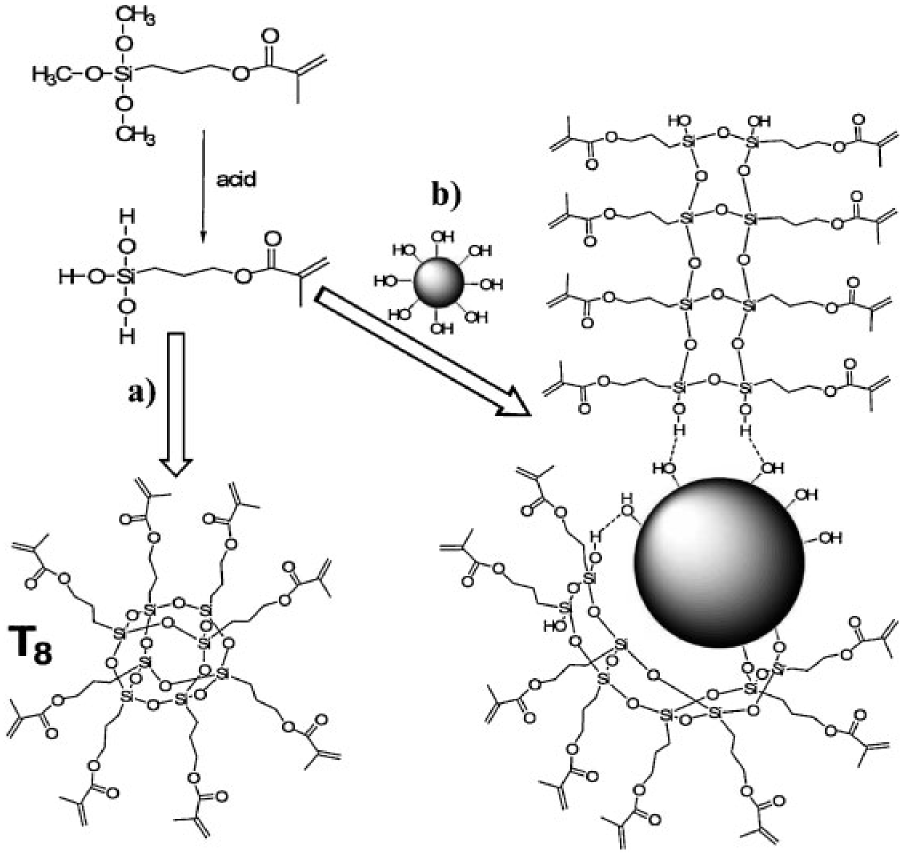

Figure 1.

Hydrolysis of trialkoxysilane (MPTMS) followed by a) homocondensation to form silsesquioxane structures e.g. T_8 species $(RSiO_{3/2})_8$, b) silane modification of a nanoparticle and indication of physical adsorbed silsesquioxane structures.

Experimental Part

Synthesis of MPTMS Modified Nanoparticles

The modified nanoparticles were prepared according to a procedure reported in ref. [10]. 2.5 g of AEROSIL®200 (DEGUSSA), 150 mL acetone, 0.037 g maleic anhydride (MA; MERCK) and the corresponding amount of MPTMS (2 mmol/g; SIGMA-ALDRICH) were put into a flask and heated to reflux for two hours. Afterwards the reaction mixture was cooled down to room temperature. Then the solvent was removed and the modified nanoparticles were dried in an oven at 50 °C overnight followed by drying under vacuum (5 mbar) for two days at 40 °C.

To separate the physically adsorbed fraction 2.0 g modified nanoparticles were extracted with 150 mL of acetone via Soxhlet extraction. The extraction time was 22 hours. The solvent was removed and both the acetone extract and the extracted particle were dried as mentioned above.

Analytical Techniques

MALDI-TOF-MS measurements were performed on a BRUKER Biflex III equipped with a 337 nm nitrogen laser. Positive ion spectra were acquired in linear mode with 20 kV acceleration voltage. The mass spectrometer was calibrated with a peptide calibration standard from BRUKER within the mass range from 1000 to 3000 Da. The sample preparations were carried out by mixing a solution of matrix (20 mg/mL in THF), sample (10 mg/mL, dispersion in THF) and sodium trifluoracetate (NaTFA) (10 mg/mL in THF) in a ratio of 20:10:1. Dispersions were prepared by sonication (30 min). In the case of homocondensates and Soxhlet extracts the samples were soluble (10 mg/mL in THF) and the used ratio was 10:1:1. All results presented here were measured with the matrix 2-[(2E)-3-(4-tert-butyl)-2-methylprop-2-enylidene]-malononitrile (DCTB).[6] Matrix and salt were used as provided. The monoisotopic peak was used for the structure calculations. Molecules were obtained as sodium adducts. All calculations concerning the possible structures were made by using a program written in our department.[11]

Infrared studies were performed on a FTS 7000 (BIORAD) equipped with a photoacoustic measuring cell (model 300 MTEC).

The ^{1}H and ^{13}CNMR spectra were recorded on a BRUKER AVANCE NMR spectrometer at 400 Mhz. All spectra were taken in $CDCl_3$ with tetramethylsilane (TMS) as internal standard.

The physically and chemically adsorbed amounts were determined by thermogravimetric analysis (TGA) (TGA 850, METTLER TOLEDO).

The carbon content was obtained by elemental analysis (EA) (VARIO EL ELEMENTAR ANALYSE SYSTEME GmbH).

Results and Discussion

In Figure 2 the TGA curves of the different fractions under investigation are shown. As expected no weight loss in case of the unmodified particles (AEROSIL®200) is observed. In contrast to that the modified particles show a weight loss of 17.7 wt.-% which is an indication for a successful modification. The organic content of modified particles consists of the chemically bounds and the physically adsorbed parts. The difference between the maximum weight loss of the modified particles before extraction (17.7 wt.-%) and the modified particles after extraction (11.3 wt.-%) represents the physically adsorbed fraction of the whole organic content of the particles. In our case the physically adsorbed fraction is 6.4 wt.-%. The maximum weight loss of 11.3 wt.-% obtained for the modified particles after extraction specifies the chemically bound fraction. Figure 2 obviously shows that the Soxhlet extraction of the modified particles is almost complete after 22 hours. A second extraction did not lead to a further separation of physically adsorbed parts. A comparison of the Soxhlet extract and the MPTMS homocondensate shows similarities, too.

The theoretical carbon content of a polysilsesquioxane with the general formula

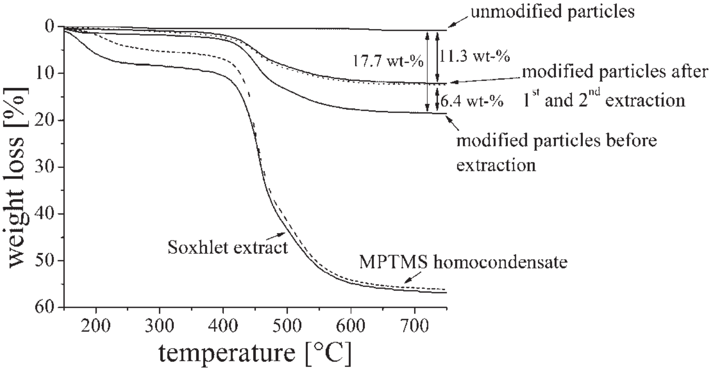

Figure 2.

TGA curves of MPTMS modified AEROSIL®200 (2 mmol/g), of all resulting fractions of the Soxhlet extraction, of the MPTMS homocondensate and of the unmodified particles (AEROSIL®200).

$(RSiO_{3/2})_n$ formed by MPTMS homocondensation is 46.9 wt.-%. Therefore the carbon contents of the Soxhlet extract (43.9 wt.-%) and the MPTMS homocondensate (45.8 wt.-%), obtained via elemental analysis, are in good agreement with the theoretical value.

The results of the TGA and the EA clearly demonstrate a complete separation of the physically adsorbed fraction by means of Soxhlet extraction.

The characterization of MPTMS homocondensates by means of MALDI MS is well known in the literature.[4,5] The hydrolysis-condensation reaction of MPTMS was carried out using comparable conditions like for the modification of the particles under investigation. Thus a reference material with known structures has been prepared. A complete hydrolysis can be assumed because no methoxy groups can be found in the corresponding FT-IR spectrum. These should appear in the spectrum at a wavelength of 2842 cm^{-1}. Furthermore the NMR spectroscopy shows no indication for methoxy groups which should otherwise appear in the ^{1}HNMR spectrum at 3.57 ppm and at 50.5 ppm in the ^{13}CNMR spectrum, respectively.

A representative spectrum of the MPTMS homocondensate is shown in Figure 3a. The spectrum shows clusters of more than 20 repeat units. The mass difference between the clusters corresponds to the MPTMS repeat unit with 188 Da (Figure 4).

Every cluster splits up into two or three series (Figure 3b). The distance between

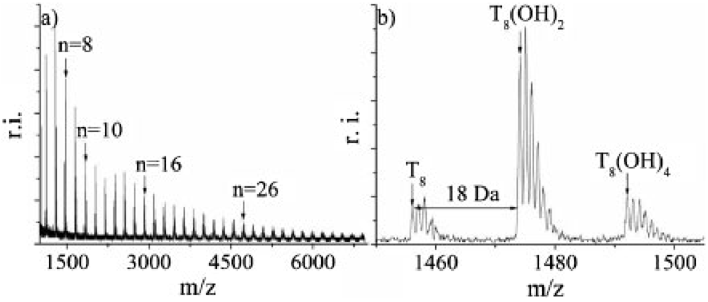

Figure 3.

MALDI spectra a) whole spectrum of a MPTMS homocondensate, b) zoom of the n = 8 series (all molecules were observed as sodium adducts).

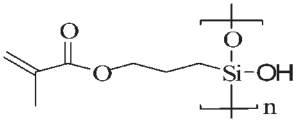

Figure 4.
MPTMS repeat unit (188 Da).

the series is 18 Da which corresponds to the loss of one molecule of water. The calculation shows that the MPTMS homocondensate consists of ladder-like- $[T_8(OH)_4]$, polycyclic- $[T_8(OH)_2]$ and high condensed cage-like-structures $[T_8]$.

BAUER et al. analyzed different organosilane modified nanoparticles with ^{29}Si MAS NMR and MALDI-TOF MS.[12] To prove the silane grafting on silica an ultrasonic assisted extraction was carried out. No silane species could be found in the extract, but it was stated that it could not be excluded that after the extraction unbound oligomeric silane were still present around the particle which could be detected by MALDI-TOF MS.[13] The following investigation clearly shows which fractions can be detected under typical MALDI preparation conditions.

In Figure 5 the MALDI spectra of the modified particle before extraction (a), the Soxhlet extract (b) and the analogously produced MPTMS homocondensate (c) in a mass range of 1400–1900 Da are depicted. The assignment of the MALDI peaks is summarized in Table 1. In contrast to Figure 5a the spectrum of extracted modified particles shows no analyte signals. Only matrix signals can be detected.

Table 1.
Assignment of MALDI-TOF MS peaks in the mass range of 1400–1900 Da; a) MPTMS modified particles before extraction, b) Soxhlet extract, c) MPTMS homocondensate as a cross check (all molecules were observed as sodium adducts)

	Structure	theoretical [Da]	experimental [Da]		
			a)	b)	c)
	$[T_8]$	1455.35	1456.06	1455.94	1456.10
8	$[T_8(OH)_2]$	1473.36	1474.13	1473.81	1474.18
	$[T_8(OH)_4]$	1491.37	–	–	1492.28
	$[T_9(OH)]$	1643.40	1644.22	1644.18	1644.27
9	$[T_9(OH)_3]$	1661.41	1662.16	1663.17	1662.26
	$[T_9(OH)_5]$	1679.42	–	–	1680.24
	$[T_{10}]$	1813.44	–	1814.18	–
10	$[T_{10}(OH)_2]$	1831.45	1832.40	1832.32	1832.45
	$[T_{10}(OH)_4]$	1849.46	1850.50	–	1850.34
	$[T_{10}(OH)_6]$	1867.47	–	–	1868.48

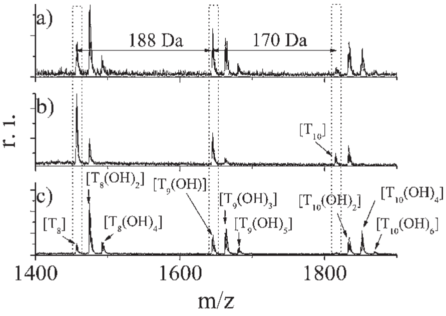

Figure 5.
MALDI spectra of the resulting fractions in the mass range of 1400–1900 Da; a) MPTMS modified particles before extraction, b) Soxhlet extract, c) MPTMS homocondensate as a cross check (all molecules were observed as sodium adducts).

As already discussed above, the spectrum of the modified particles before extraction (Figure 5a) shows the same polysilsesquioxane series as the MPTMS homocondensate (Figure 3 and 5c). An alternating distance of 170 and 188 Da can be observed.[12]

Looking at the spectrum of the Soxhlet extract (Figure 5b) nearly the same series can be found as for the MPTMS homocondensate (Figure 3 and 5c), but a distinct tendency to high condensed structures is observed. For example the signal of the high condensed T_8 structure with an experimental mass of 1455.94 Da (Table 1) shows a considerable higher intensity than in case of the modified particles before extraction (Figure 5a). Additionally the third signal of this cluster which corresponds to a less condensed structure $[T_8(OH)_4]$ is missing. The same tendency can be observed for the other clusters. These results can be explained by the additional thermal treatment during the Soxhlet extraction and the second drying process after extraction.

The comparison of the spectra shown in Figure 5a and 5c leads to the conclusion that similar oligomeric silsesquioxane structures can be identified for both the modified particle before extraction and the MPTMS homocondensate. Therefore we assume that the physically adsorbed fraction most likely is a MPTMS homocondensate. This statement is also based on the fact that no detectable analyte signals could be observed in the spectra of the extracted modified particles. As already mentioned above we were able to prove that these particles only consist of chemically bound structures using TGA. Our investigations clearly demonstrate that the MALDI-TOF technique can only be used to detect the physically adsorbed fractions of organosilane modified surfaces.

Conclusion

The separation of the chemically bound and physically adsorbed fractions of modified AEROSIL® particles was achieved by a Soxhlet extraction. By using TGA the amounts of the various fractions contained in the modified particles have been determined.

The MALDI spectra of the particles before extraction and of the Soxhlet extract show the same series like the MPTMS homocondensate. Highly condensed oligomeric silsesquioxane structures which contain more than 20 repeat units can be observed. The investigation clearly shows that the MALDI-TOF analysis can only be used to detect the physically adsorbed fraction of silane modified surfaces. Based on these results the analysis of organic/inorganic hybrid materials is improved fundamentally.

The generality of these results will be shown in a forthcoming publication by analysis of different other particles.

Acknowledgements: The authors acknowledge the Deutsche Forschungsgemeinschaft for financial support within the European Graduate School ''Microstructural Control in Free-Radical Polymerization''.

[1] A. Rahimi, P. Shokrolahi, *Int. J. Inorg. Mater.* **2001**, *3*, 843.
[2] X. Zhu, M. Jaumann, K. Peter, M. Möller, *Macromolecules* **2006**, *39*, 1701.
[3] M. Jaumann, E. A. Rebrov, V. V. Kazakova, A. M. Muzafarov, W. A. Goedel, M. Möller, *Macromol. Chem. Phys.* **2003**, *204*, 1014.
[4] W. E. Wallace, C. M. Guttman, J. A. Antonucci, *J. Am. Soc. Mass. Spectrom.* **1999**, *10*, 224.
[5] R. J. J. Williams, R. E-Balsells, Y. Ishikawa, H. Nonami, A. N. Mauri, C. C. Riccardi, *Macromol. Chem. Phys.* **2001**, *202*, 2425.
[6] M. Valencia, W. Dempwolf, F. Günzler, O. Knöpfelmacher, G. Schmidt-Naake, *Macromolecules* **2007**, *1*, 40.
[7] H. Mori, M. G. Lanzendörfer, A. H. E. Müller, *Macromolecules* **2004**, *37*, 5228.
[8] H. Mori, M. G. Lanzendörfer, A. H. E. Müller, *Langmuir* **2004**, *20*, **1934**.
[9] F. Bauer, H. J. Gläsel, H. Langguth, R. Hinterwaldner, *Int. J. Adhes. Adhes.* **2004**, *24*, 519.
[10] F. Bauer, H. Ernst, U. Decker, M. Findeisen, H. J. Gläsel, H. Langguth, E. Hartmann, R. Mehnert, C. Peuker, *Macromol. Chem. Phys.* **2000**, *201*, 2654.
[11] O. Knöpfelmacher, TCL Script (personal communication), Technische Universität Clausthal **2006**.
[12] F. Bauer, V. Sauerland, H. J. Gläsel, H. Ernst, M. Findeisen, E. Hartmann, H. Langguth, B. Marquardt, R. Mehnert, *Macromol. Mater. Eng.* **2002**, *287*, 546.
[13] F. Bauer, V. Sauerland, H. Ernst, H. J. Gläsel, S. Naumov, R. Mehnert, *Macromol. Chem. Phys.* **2003**, *204*, 375.