

Bridged polysilsesquioxane xerogels containing amine-
and thiol- groups: structural properties as a function
of synthesis conditions

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Amino- and thiol- functionalized polysilsesquioxanes were obtained by hydrolytic polycondensation of 1,2-bis(triethoxysilyl)ethane or 1,4-bis(triethoxysilyl)benzene and trifunctional silane bearing amine- or thiol-groups in the presence of a fluoride-ion catalyst in an ethanol solution. All the xerogels obtained have a porous structure (500-1000 m²/g) and a high content of functional groups (1.2-2.8 mmol/g). AFM data show that xerogels are formed by aggregation of spherical primary particles. The main factors influencing structural characteristics of these materials are: the nature of the functional group, the spacer flexibility, and in some cases – the ratio of reacting alkoxy silanes.

1. INTRODUCTION

Bridged polysilsesquioxane xerogels are a class of hybrid organic-inorganic materials, formed by molecular building blocks. Such building units include a bridge of organic origin that links two or more Si atoms by forming hydrolytically stable Si–C bonds. BPS xerogels are prepared by sol-gel processing of monomers which be presented as bis(trialkoxysilane) structures (RO)₃Si–R'–Si(OR)₃, where R is the alkoxy group, and R' is the organic bridge (spacer) [1-3]. This bridging group can be varied in length, rigidity, geometry of substitution and functionality so by choosing of the appropriate precursors in the reaction of hydrolytic polycondensation it is possible to design on a molecular level the considered materials keeping control over their chemical and physical properties, including

structure-adsorption characteristics. From this point of view, it was interesting to examine how the presence of additional functional groups (introduced to the system by co-condensation of bis(trialkoxysilane) with trialkoxysilane bearing a functional group) influences above mentioned characteristics.

2. EXPERIMENTAL

The following compounds were used: 1,2-bis(triethoxysilyl)ethane (BTESE, 96%, Aldrich); 1,4-bis(triethoxysilyl)benzene (BTESB, obtained according to the method described in [1]; 3-aminopropyltriethoxysilane (APTES, 98%, Aldrich); 3-mercaptopropyltri-methoxysilane, (MPTMS, 95%, Aldrich); NH_4F (98%, Aldrich).

Synthesis of samples 1 and 2 by BTESE and APTES cocondensation (ratio 4:1 and 2:1, respectively). To the solution of 0.04 mol (or 0.025 mol in the case of sample 2) BTESE in 15 cm³ ethanol (or 7 cm³ in the case of sample 2) a solution of NH_4F was added (0.9×10^{-3} mol NH_4F in 0.135 mol water (or 0.63×10^{-3} mol in 0.094 mol)). After 5 min to this mixture APTES in 15 cm³ ethanol (or 0.0125 mol in 7 cm³) was added. Stirring stopped after a minute. Transparent gel formed in a few minutes. After 30 days, the gel was pounded and dried in vacuum at 20/50/105°C for 2 hours at each temperature.

Synthesis of samples 3 and 4 by BTESE and MPTMS cocondensation (ratio 4:1 and 2:1, respectively). To the solution 0.04 mol (or 0.025 mol) BTESE in 15 cm³ ethanol (or in 7 cm³ in the case of a sample 6) a solution of NH_4F (0.9×10^{-3} mol NH_4F in 0.135 mol water (or 0.63×10^{-3} mol in 0.094 mol)) was added. After 5 min to this mixture 0.01 mol MPTMS in 15 cm³ ethanol (or 0.0125 mol in 7 cm³) was added. Transparent gel formed in a few minutes. After 30 days the gel was pounded and dried in vacuum at 20/50/105°C for 2 hours at each temperature.

Synthesis of samples 5 and 6 by BTESB and APTES cocondensation (ratio 4:1 and 2:1, respectively). The techniques of synthesis of these samples were similar to the techniques of synthesis of samples 1 and 2 with the exception of the ageing time, which decreased to 14 days.

Synthesis of samples 7 and 8 by BTESB and MPTMS cocondensation (ratio 4:1 and 2:1, respectively). The techniques of synthesis of these samples were similar to the techniques of synthesis of samples 3 and 4 with the exception of the ageing time, which decreased to 14 days.

3. RESULTS AND DISCUSSION

The reaction of hydrolytic polycondensation was used to obtain bridged polysilsesquioxane xerogels functionalized by amino- and thiol- groups, what is schematically depicted on Figure 1.

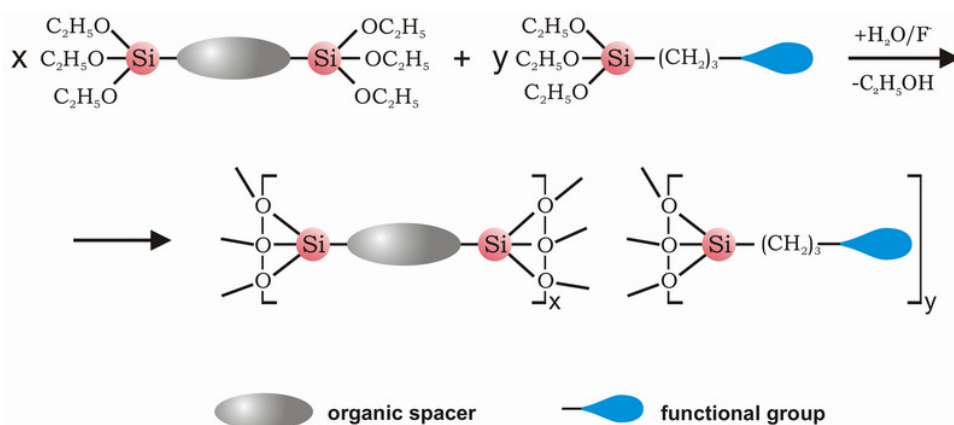






Fig. 1. Schema of the polycondensation of structure forming agent and functionalizing agent (in case of MPTMS methoxy groups are attached to silicon atom instead of ethoxy groups).

Drying in vacuum of the milled glassy gels resulted in the required xerogels – white powdery compounds, insoluble in water and non-swelling in nonaqueous solvents. After synthesis all xerogels were investigated by IR, NMR, AFM, SEM, TEM (only a part of these data is given here). The content of functional groups in the synthesized xerogels was estimated by titration and is presented in the Table 1.

Isotherms of nitrogen adsorption-desorption of the synthesized samples are presented on Figure 2. They can be divided into two groups: the first one includes isotherms of xerogels containing amine groups and the second one - isotherms of xerogels containing thiol groups. Isotherms of xerogels **1** and **2** with an ethylene bridge stand out among the isotherms of the first group samples: they belong to IV type according to IUPAC classification [2]. The presence of a well-defined hysteresis loop indicates the presence of mesopores in the structure of these xerogels. Isotherms of samples **5** and **6** containing amino groups and a phenylene bridge have less defined hysteresis loops and their attribution to this group is conditional to a certain extent. Isotherms of samples from another group (xerogels **3**, **4**, **7**, **8**) belong to I type, which have small hysteresis loops. This is in accord with

the value of an average diameter of their pores, d , calculated using the isotherms mentioned. Obviously, in the case of the second group samples the size of their pores is close to the border of meso- and microporosity. As the conditions of the synthesis of every xerogel were the same so the difference in the types of xerogels is determined first of all by the acid-base nature of the functional groups (more exactly by the nature of the medium created by these groups).

Tab. 1. Synthesis conditions and structural-adsorption characteristics of obtained xerogels.

No	Spacer	Functional group	Initial Ratio M/F	Ageing time [days]	Content of functional groups [mmol/g]	Structural-adsorption characteristics		
						S_{BET} [m^2/g]	V_p [cm^3/g]	d [nm]
1	–CH ₂ –CH ₂ –	–(CH ₂) ₃ NH ₂	4:1	30	1.4 ^a (1.6) ^b	611	1.489	15.0
2	–CH ₂ –CH ₂ –	–(CH ₂) ₃ NH ₂	2:1	30	2.5 (2.8)	637	0.945	7.8
3	–CH ₂ –CH ₂ –	–(CH ₂) ₃ SH	4:1	30	1.9 (1.6)	834	0.333	2.9
4	–CH ₂ –CH ₂ –	–(CH ₂) ₃ SH	2:1	30	2.5 (2.8)	630	0.261	3.0
5		–(CH ₂) ₃ NH ₂	4:1	14	1.4 (1.2)	910	0.561	3.0
6		–(CH ₂) ₃ NH ₂	2:1	14	2.6 (2.2)	926	0.649	3.2
7		–(CH ₂) ₃ SH	4:1	14	1.0 (1.3)	968	0.601	2.5
8		–(CH ₂) ₃ SH	2:1	14	2.7 (2.2)	931	0.473	3.0

^a from the data of titration, ^b theoretical content, S_{BET} - functional surface area by BET method, V_p - total pore volume, d - average pore diameter

As it can be seen from the Table 1, all materials have high values of specific surface area (S_{BET}) from 610 to 830 m^2/g (in the case of xerogels with an ethylene bridge) and from 910 to 970 m^2/g (in the case of xerogels with a phenylene bridge). This is a typical situation for xerogels containing spacers of organic origin [1,3]. The ratio of the reacting alkoxy-silanes in the case of the 3-aminopropyl groups (for example, samples **1** and **2**) slightly influences the value of the specific surface area. However, it affects distinctly the volume and size of the pores. Thus, both, the pore volume and its average diameter increase with the increasing BTESE/APTES ratio. It may be supposed that in the case of xerogels **1** and **2** with similar sizes of globules (values of S_{BET} is nearly the same) an increase of the relative content of APTES in the case of sample **2** leads to more compact packing. In contrast to these dependences an opposite situation is observed in the case of xerogels with a 3-mercaptopropyl groups and $\equiv\text{Si}-\text{C}_2\text{H}_4-\text{Si}\equiv$ bridges. Thus

an influence of the ratio of the reacting alkoxysilanes is clearly noticeable: a significant increase of S_{BET} (samples **3** and **4**) is observed at an increasing relative amount of bis(trialkoxysilane) in the system while the pore volume and sizes do not change.

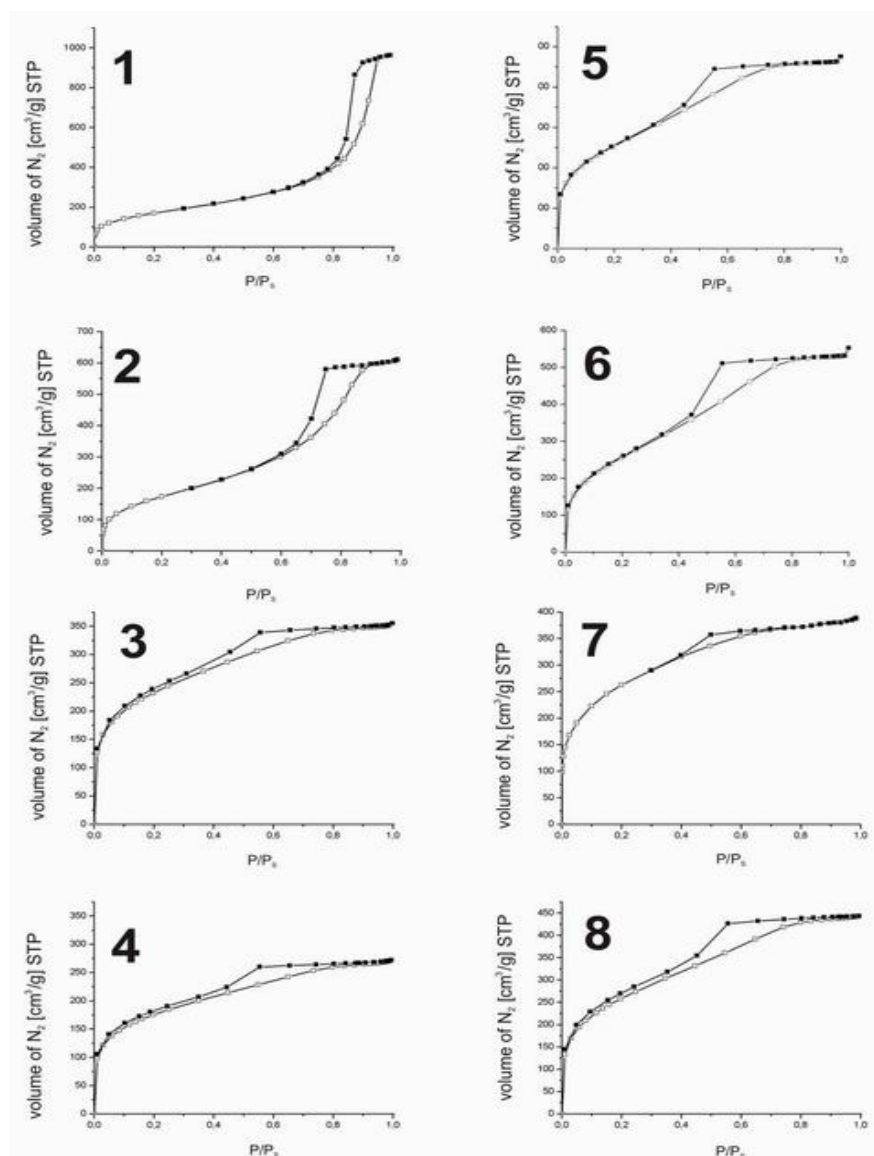


Fig. 2. Nitrogen adsorption-desorption isotherms of xerogels **1-8**.

Comparing the isotherms of samples **2** and **4** (the same ethylene spacer) and the data of ^{29}Si CP/MAS NMR spectroscopy, it may be noted that in the case of a practically microporous sample **4** the dominating signal is a signal attributed to T^2 structure unit and in the case of a mesoporous sample **2** the signal is that from T^3 structure unit. In other words, the greater extent of polycondensation in these xerogels is associated with mesoporous structure. A similar situation was observed earlier in the case of xerogels synthesized using only BTESE [3]. However, it should be stressed that there is not a direct connection between the extent of polycondensation and texture characteristics of xerogels [4].

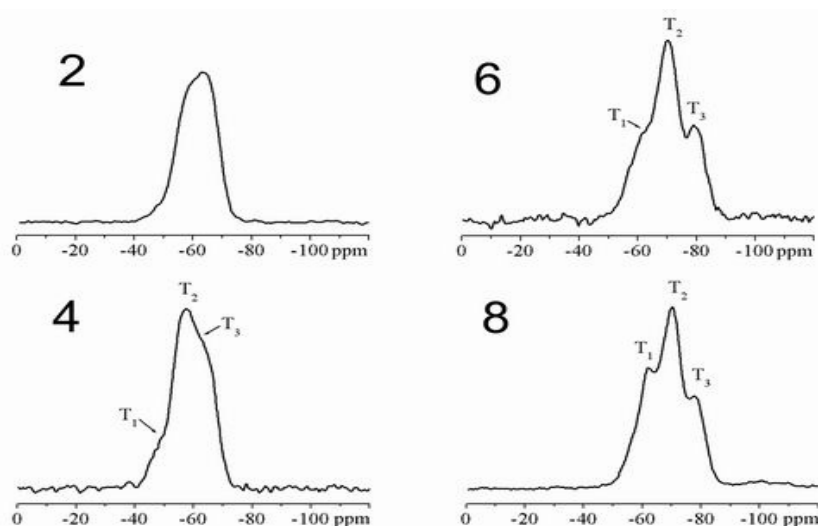


Fig. 3. ^{29}Si CP/MAS NMR spectra of xerogels **2**, **4**, **6**, **8**

All these dependences for aminocontaining xerogels stay unchanged to a certain extent in the case of aminocontaining samples whose framework is formed by $\equiv\text{Si}-\text{C}_6\text{H}_4-\text{Si}\equiv$ bridges (Table 1, samples **5** and **6**). Furthermore, an absence of the influence of the ratio of reacting alkoxy silanes on texture characteristics is observed in the case of samples with a 3-mercaptopropyl group (samples **7** and **8**) while a opposite situation is observed for xerogels with a $\equiv\text{Si}-\text{C}_2\text{H}_4-\text{Si}\equiv$ bridge. In the case of xerogels with a phenylene spacer and NH_2 and SH groups neither the ratio of reacting alkoxy silanes nor the nature of functional groups affects significantly their structural-adsorption characteristics and xerogels with a high values of specific surface area ($>900\text{ m}^2/\text{g}$) are formed in all cases. Moreover, the sizes of their pores are on the border of meso-microporosity regardless of the functional group nature (samples **5-8**). This is also true for xerogels synthesized

using only BTESB [1]. Apparently, the rigidity of the spacer plays a main role here.

It can be seen from the Figure 4 that the obtained functionalized bridged polysilsesquioxane xerogels are composed of aggregated spherical particles. Their sizes are between 30 and 65 nm. In the case of amino-containing xerogels with a phenylene spacer the sizes of these particles are slightly smaller (~35-50 nm, samples **5** and **6**) than in the case of analogous xerogels with an ethylene bridge (~35-65 nm, samples **1** and **2**). The size of particles in xerogels with an ethylene spacer decreases almost doubly at the replacement of the amine functional group with a thiol one (samples **1**, **2**). However, this is not observed in the case of xerogels with a phenylene bridge. The change of the ratio of reacting alkoxysilanes practically does not affect the sizes of such particles.

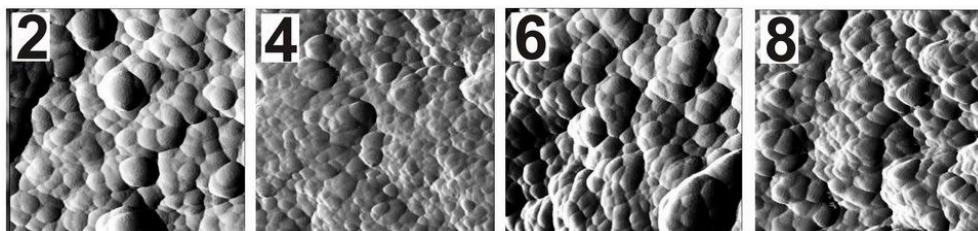


Fig. 4. AFM images of xerogels **2**, **4**, **6**, **8** (the size of each image is 500×500 nm)

4. CONCLUSIONS

The principal features of amino- and thiol- containing polysilsesquioxanes obtained by hydrolytic polycondensation of BTESE (or BTESB) with trifunctional silanes (APTES or MPTMS) have been investigated. T¹, T² and T³ structural units form the molecular frame of these materials. 3-aminopropyl or 3-mercaptopropyl groups are fixed on the surface by siloxane bonds. The data of IR, ¹³C CP/MAS NMR (not given here) and ²⁹Si CP/MAS NMR show that unhydrolyzed silanol and uncondensed ethoxy groups are also present on the surface.

By use of BTESE and BTESB as structure-forming agents it is possible to obtain functionalized polysilsesquioxane xerogels with a high porous structure (500-1000 m²/g) and with high contents of surface functional groups (1.4-2.6 mmol/g). AFM data confirm that xerogels are formed by particle aggregates; the size of aggregates is in range 30-65 nm. The principal factors influencing structural-adsorption properties of these materials are the nature of the functional group, the spacer flexibility, and in some cases, the ratio of reacting alkoxysilanes. Then, by control of the aforementioned factors it is possible to

control the texture of bridged polysilsesquioxane xerogels with amino- and thiol-groups.

5. REFERENCES

- [1] K.J. Shea, D.A. Loy, O. Webster, *J. Am. Chem. Soc.*, 114, 6700 (1992)
- [2] F. Rouquerol, J. Rouquerol, K. Sing. *Adsorption by Powders and Porous Solids. Principles, Methodology and Application*, Academic Press, London, 1999, p. 18
- [3] H.W. Oviatt, K.J. Shea, J.H. Small. *Chem. Mater.*, 5, 943 (1993)
- [4] G.Cerveau, R.J.P. Corriu, E. Framery, *Chem. Mater.*, 13, 3373 (2001)

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