

Phenylsilanetriol — synthesis, stability, and reactivity

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Abstract

Crystalline phenylsilanetriol, $\text{PhSi}(\text{OH})_3$ (**1**) was obtained by smooth hydrolysis of phenyltrimethoxysilane and characterised by different analytical methods (wide angle X-ray powder diffraction, NMR, IR, thermogravimetric analysis). The title-compound is surprisingly stable in the solid state but slowly condenses in acetone solution. Reaction of **1** with Me_3SiCl and $\text{Me}_2(\text{CH}_2\text{Cl})\text{SiCl}$ gave the corresponding tris-triorganosilyloxy substituted derivatives in high yields.

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1. Introduction

At present much attention is paid to the synthesis, characterisation and investigation of the chemical and physical properties of polysilanol [1–7]. Due to the formation of a complex H-bond network in the solid state as well as in solution these compounds are very promising precursors for the formation of siloxane based materials. Among them phenylsilanetriol (**1**), containing three hydroxyl-groups at one silicon atom, is one of the most interesting and promising compounds. Tyler first published the synthesis of **1** more than 40 years ago [8], Andrianov and co-workers repeated and optimised the synthesis [9]. Both authors confirmed the structure of phenylsilanetriol by IR-spectroscopy and elemental analysis and approved a high instability of the compound in solution as well as in the solid state.

According to our principle investigations on the reactivity of trifunctional organosilanes and their metal complexes, it was the aim of our work to synthesise phenylsilanetriol and to investigate its stability as well as its reactivity against triorganylchlorosilanes. Finally, we

want to use phenylsilanetriol for the production of new materials with well-controlled structural features.

2. Results and discussion

According to Scheme 1, phenylsilanetriol was obtained as a white crystalline solid as described in [8] but with slight synthetic modifications in yields up to 68%. Its crystallinity was confirmed by wide angle X-ray powder diffraction (WAX) analysis and the structure was proven by ¹H-, ²⁹Si-NMR, IR-spectroscopy, and elemental analysis.

The IR spectrum of solid phenylsilanetriol (Fig. 1) shows a broad intense band with a complicated contour. The centre of gravity being located at about 3197 cm^{-1} points to a strong intermolecular H bond of the $\text{OH} \cdots \text{O}$ type. No absorption band corresponding to Si–O–Si vibration was detected in the region $1130\text{--}1000\text{ cm}^{-1}$.

In the ¹H-NMR spectrum of **1** (Fig. 2a) two signals for the protons of the phenyl-group are detected: $\delta = 7.70\text{ ppm}$ (2H, *o*-Ph) and $\delta = 7.32\text{ ppm}$ (3H, overlapping triplets of *m*- and *p*-Ph); the relative intensity of the signals is 2:3. The singlet for the protons of the hydroxyl-groups is found at $\delta = 5.53\text{ ppm}$. The relative intensity of the signals for the phenyl and the OH-

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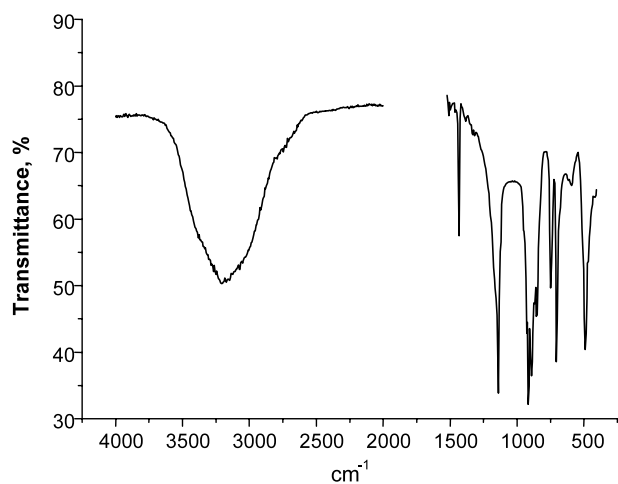
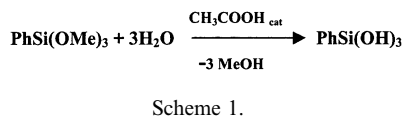


Fig. 1. IR spectra of solid **1** at 1530–400 cm^{-1} (KBr pellets) and 4000–2000 cm^{-1} (hexachlorobutadiene mulls).

protons is 5:3. The ^{29}Si -NMR spectrum shows one signal at $\delta = -53.07$ ppm (Fig. 2b).

Thermogravimetric investigations on **1** performed under air (Fig. 3, curve 1) revealed some stages of weight loss. The first one between 100 and 200 °C corresponds to thermal condensation processes of silanol groups resulting in water elimination, the second stage between 400 and 720 °C is due to thermodestruction of condensation products. The residue obtained at 720 °C is equal to 38–40 mass% of the initial amount, and quantitatively corresponds to SiO_2 formation at the last stage of destruction. The process of weight loss in the low temperature range can be divided into two parts, the first ranging from 100 to 143 °C which makes up ~12%, and which is characterised by a sharp weight loss corresponding to the elimination of one water molecule. The second weight loss occurs between 143 and 200 °C when the sample loses less than 2.5%. From that we conclude that in the resulting condensation product still unreacted hydroxyl-groups remain.

The DTA curve (Fig. 3, curve 2) in the low temperature range exhibits only one endo peak between 85 and 160 °C. The minimum is detected at 134 °C and includes both, the melting of a crystalline phase of phenylsilanetriol, and condensation processes occurring in the phenylsilanetriol sample.

In Figs. 4 and 5 graphs of the WAX investigations of a sample of PhSi(OH)_3 , detected at different temperatures, are presented. On heating up to 106 °C (Fig. 4) no qualitative changes in the patterns can be detected except a slight shift of the Bragg peaks in the field of smaller angles reflecting the usual thermal expansion of

the crystals. Considering the data obtained on further stepwise heating a change in crystallinity of the sample is monitored. Within the temperature range of 109–130 °C the intensity of the Bragg peaks is gradually decreasing while two amorphous halos are developing with 2θ -centres at about 7° and 19° [10]. All Bragg peaks proving crystallinity disappear at 130 °C (Fig. 4, curve 6). The angular position of the first amorphous halo is very close to that of the first Bragg peak observed for the crystalline phase. Hence, the structural changes at 130 °C are not associated with a melting process of the phenylsilanetriol. On carrying out comparison of the X-ray and thermogravimetric analysis (TGA) data it becomes evident that the structural changes of **1** at 130 °C are induced by the beginning of the condensation processes [11]. The partially condensed product (**PCP-1**), obtained at 130 °C, obviously inherits the main structural features of crystalline **1**.

Further stepwise heating of **PCP-1** at 148, 180, 215 and 250 °C does not lead to qualitative changes in the XRD patterns (Fig. 5). In accordance with TGA data it is assumed that condensation processes within the sample are completed at the latter temperature.

The final product of condensation (**FPC-1**) obtained at 250 °C (Fig. 5, curve 4) was subsequently cooled to room temperature (Fig. 4, curve 5) and was then reheated (Fig. 6).

Starting the condensation process first results in the formation of defects in crystallinity. The long-range order, inherent to the crystalline phenylsilanetriol, is not observed for both, the partially condensed product (**PCP-1**) obtained at 130 °C, and the final product of condensation obtained above 250 °C (**FPC-1**). Notably, **PCP-1** and **FPC-1** are characterised by very similar structural features, but differ from each other by the degree of condensation.

Referring to the data obtained, some conclusions about the crystalline structure of PhSi(OH)_3 (**1**) and the non-crystalline **PCP-1** and **FPC-1** can be drawn. As mentioned, by heating **PCP-1** from 130 to 250 and **FPC-1** from 20 to 250 °C the first amorphous halo slightly shifts towards the small angular region, thus indicating a thermal expansion of the specimen. Simultaneously, the intensity of the first halo increases and a value of its half-width reduces without changes of the integral intensity (Fig. 7).

Similar thermotropic changes of the XRD patterns were observed for ladder polymers [12] and for the condensation product of cyclic tris-*cis*-tris-*trans*- $[\text{PhSi(O)OH}]_{12}$ (**PC-D**₁₂) [13]. Consequently, structural characteristics of **FPC-1** might be compared with structural features of the ladder polyphenylsilsesquioxane and of **PC-D**₁₂ at different temperatures (Figs. 8 and 9).

Fig. 9 shows values of the interlayer spacing **d** of **FPC-1** which are on one hand similar to those of **PC-**

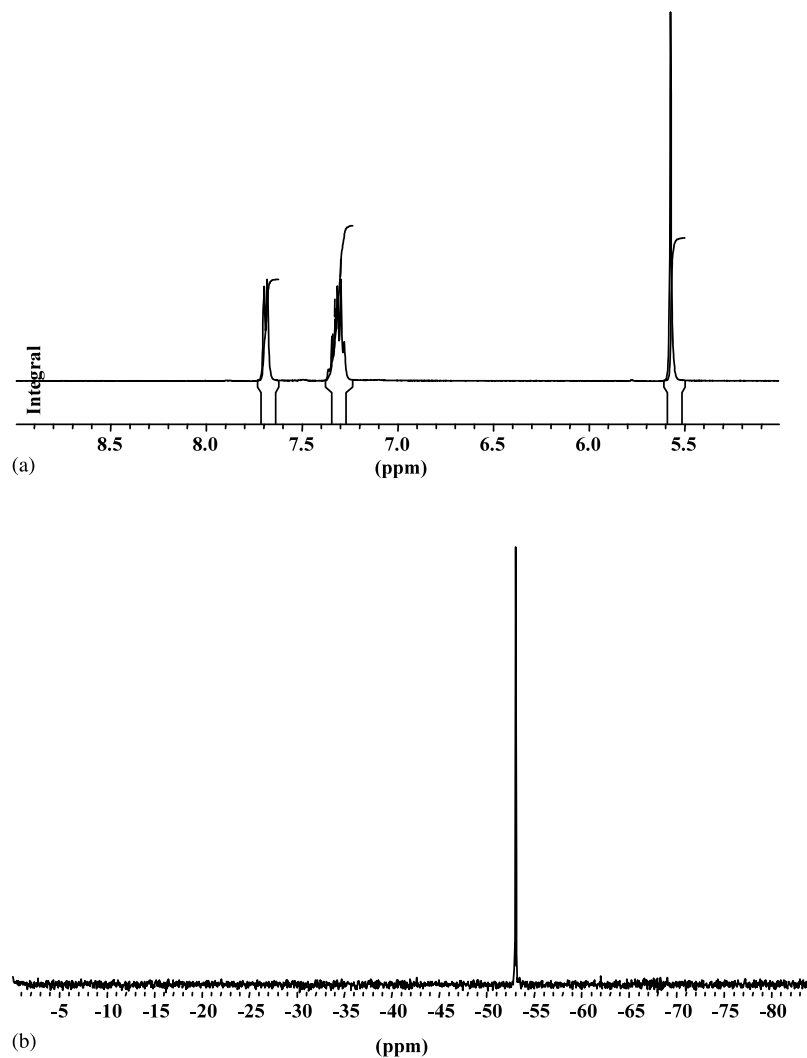


Fig. 2. (a) ^1H - and (b) ^{29}Si -NMR spectra of **1** in acetone- d_6 .

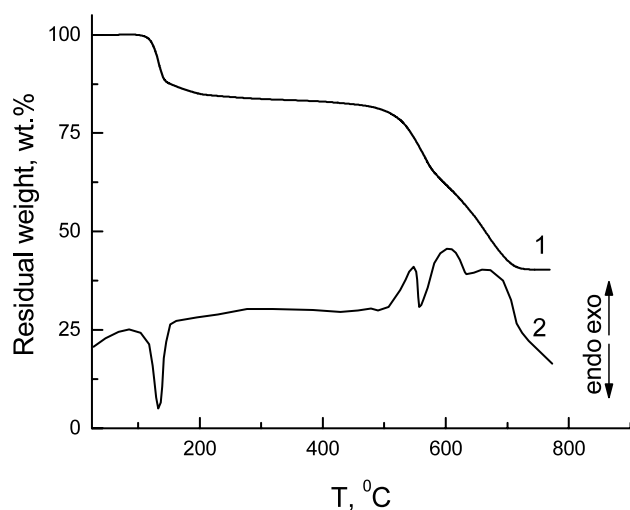


Fig. 3. TG (1) and DTA (2) curves for phenylsilanetriol; sample in air, heating rate $5\text{ }^\circ\text{C min}^{-1}$.

D_{12} , but on the other hand distinctly larger than those observed for the polyphenylsilsesquioxane. However, for all three compounds the coefficients of the thermal expansion are comparable. Therefore, based on the structural features of $\text{PhSi}(\text{OH})_3$ and on the different possibilities of H-bonded associates, two alternative structures for **FPC-1** might be discussed. First, its structure differs slightly from that of the ladder polymer. The differences observed may be associated with disturbances of the crystalline structure of **1** and a wide distribution of crystallite sizes, which effects the final product of condensation. Second, the **FPC-1** structure may be described as a layered non-smectic type structure that is very similar to that of PC-D_{12} (Fig. 10) [13].

The interlayer spacing d of **FPC-1** agrees to values calculated for a bilayer ordering, in which the Si atoms form a double layer, which is linked by oxygen bridges, and in which the Ph-groups are directed outwards the plane of the layer. As pointed out earlier, the product of triol-condensation inherits the main structural features

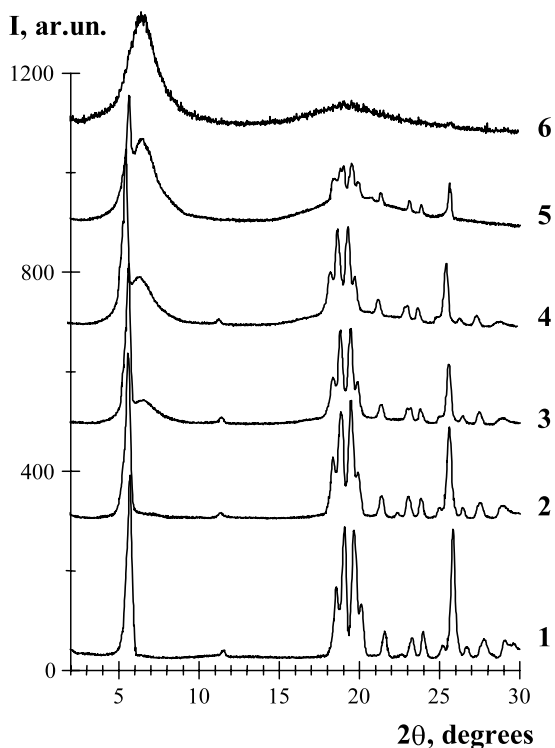


Fig. 4. XRD patterns obtained upon heating of (1) 20 °C; (2) 98 °C; (3) 107 °C; (4) 115 °C; (5) 127 °C and (6) 130 °C (partially condensed product, obtained at 130 °C PCP-1).

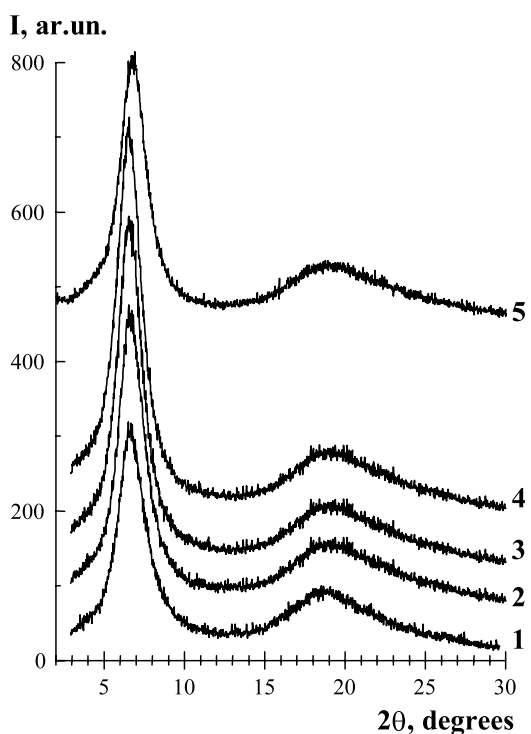


Fig. 5. XRD patterns recorded upon further heating of PCP-1 at (1) 148 °C; (2) 180 °C; (3) 215 °C; (4) 250 °C and 5: 20 °C after cooling from 250 °C (the final product of condensation obtained at 250 °C and cooled up to room temperature — FPC-1).

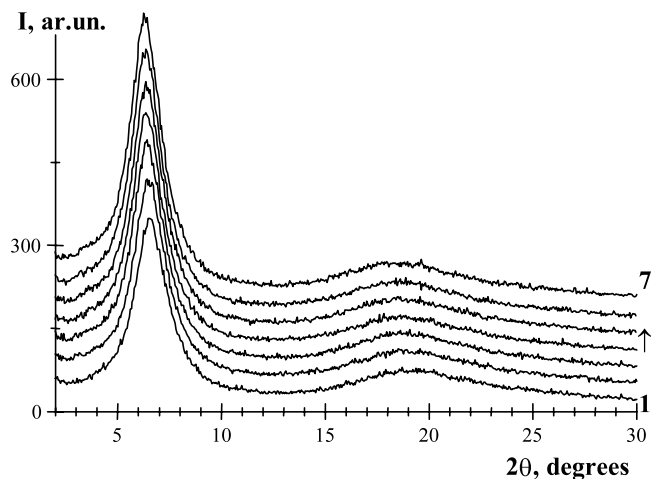


Fig. 6. XRD patterns of FPC-1 recorded at (1) 20 °C; (2) 75 °C; (3) 127 °C; (4) 170 °C; (5) 196 °C; (6) 226 °C and (7) 250 °C.

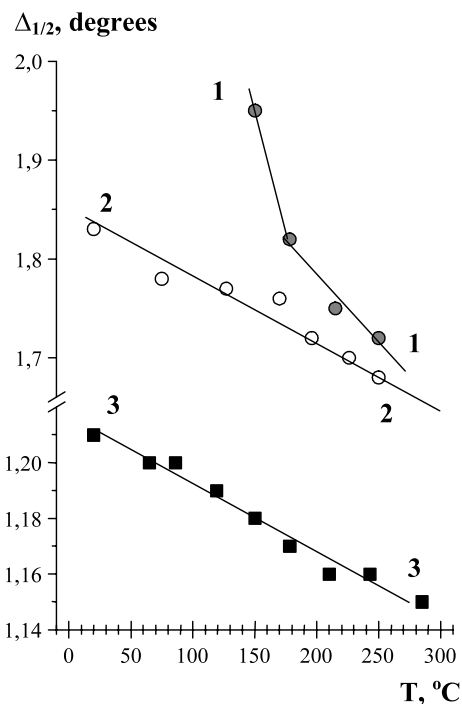


Fig. 7. Temperature dependency of the half-width $\Delta_{1/2}$ of the first amorphous halo for PCP-1 on first heating (curve 1), for FPC-1 (curve 2) and for the ladder polyphenylsilsesquioxane (curve 3).

of the crystalline **1**; furthermore, Corriu and co-workers [6a,b] showed that the crystalline $(\text{OH})_3\text{SiC}_6\text{H}_4\text{Si}(\text{OH})_3$, whose chemical structure should be similar to that of $\text{PhSi}(\text{OH})_3$, shows bilayer ordering in the crystal. Hence, it might be concluded that the crystalline phenylsilanetriol possesses an identical structure. An additional argument in favour of this conclusion is the similarity of the parameters d estimated for FPC-1 and PC-D₁₂.

One of the main objectives of our studies was to investigate the phenylsilanetriol stability in both the

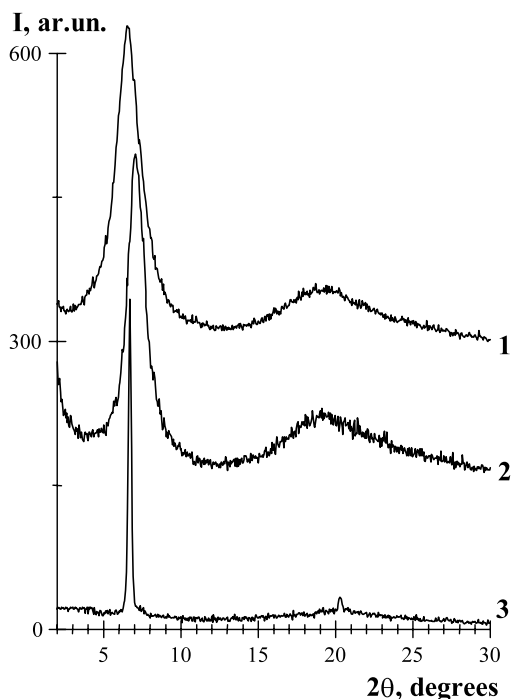


Fig. 8. XRD patterns recorded for FPC-1 at 20 °C (curve 1), the ladder polyphenylsilsesquioxane (curve 2), and PC-D₁₂ — the product of tris-*cis*–tris-*trans*-[PhSi(O)OH]₁₂ condensation [10] (curve 3).

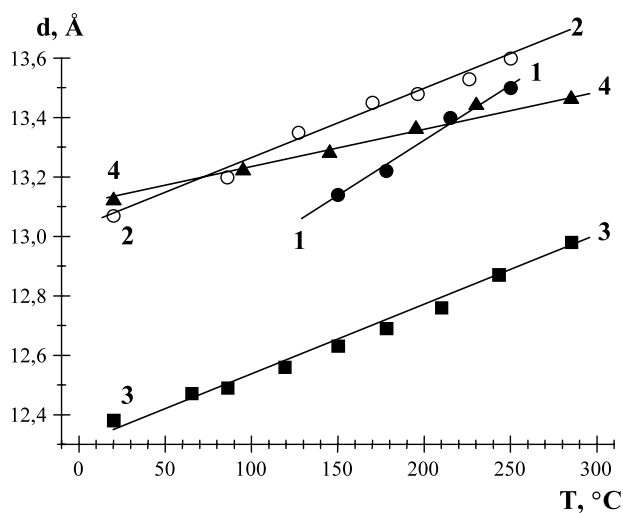


Fig. 9. Temperature dependency of the interplanar distances *d*, calculated from the angular positions of the first non-crystalline peak for PCP-1 (curve 1), for FPC-1 (curve 2), for the ladder polyphenylsilsesquioxane (curve 3) and for the PC-D₁₂ (curve 4).

solid state as well as in solution by NMR spectroscopy. We found that crystalline phenylsilanetriol is fairly stable (especially in the dark) and does not undergo condensation reactions over a period of 4 months, but only under strict exclusion of any ionic impurities; e.g. storage in a plastic container is required.

The stability of the solid triol was proven by weekly preparations of fresh solutions in acetone-*d*₆ over a time period of 9 months. Within a period of the first 4

months all the material dissolved completely. The ¹H-NMR spectra showed the characteristic signals expected for phenylsilanetriol without any change: the phenyl protons resonance at 7.70 and 7.32 and the hydroxyl protons between 5.52 and 5.60 ppm with a relative intensity of 5:3. After 4 months **1** did not dissolve completely, about 4% of the material remained as precipitate, while the filtered solution did not show any changes in the ¹H-NMR spectrum. We found that the amount of insoluble solid increased with time. When the stability of phenylsilanetriol was checked once again after about 18 months nearly 30% of the initial solid remained insoluble, but still without NMR spectroscopic change of the dissolved starting material.

In solution phenylsilanetriol is less stable and both the rate of condensation and the consistency of products formed depends on the concentration of the starting material. ¹H-NMR spectroscopy proved that condensation occurs very slowly in dilute solution (concentrations of **1** up to *C* = 0.07 mol l⁻¹ in acetone-*d*₆). Thus, a small amount of disiloxane (δ = 5.73 ppm: protons of OH-groups of the disiloxane) had been found at the 7th day. This amount increased slightly during storage, but even after 28 days there was still much more starting material than disiloxane. After 17 days one more weak singlet could be detected at δ = 5.98 ppm providing evidence for trisiloxane formation in traces. In conclusion, after nearly 7 weeks we found that the amount of disiloxane had increased only slightly during storage, but phenylsilanetriol still remained in high excess.

¹H-NMR spectra shown in Fig. 11 document that condensation processes of **1** are much faster in higher concentrated acetone-*d*₆ solution (*C* = 0.3 mol l⁻¹). Within 3 days after preparation the solution already contains considerable amounts of disiloxane (δ = 5.71 ppm) and trisiloxane (*d* = 6.04 ppm.) (Fig. 11b). Simultaneously, the signal for the hydroxyl protons of phenylsilanetriol decreased dramatically. Notably, this signal became already very dim within 12 days after preparation of the solution (Fig. 11c) and the signals of the phenyl protons broadened. In addition a group of signals emerged proving the formation of oligomers in the mixture. After 34 days the signal for the hydroxyl protons of phenylsilanetriol disappears completely (Fig. 11d) and simultaneously the intensities of the hydroxyl proton signals of the di- and tri-siloxane were drastically reduced.

From this experimental findings we conclude that condensation processes of **1** proceed more consistently and controlled in dilute solutions than in higher concentrations, e.g. at *C* = 0.3 mol l⁻¹. Thus, phenylsilanetriol might be used for the preparation of well-organised polymeric materials in the presence of a template.

According to Scheme 2 phenylsilanetriol was reacted with Me₃SiCl and Me₂(CH₂Cl)SiCl. The corresponding

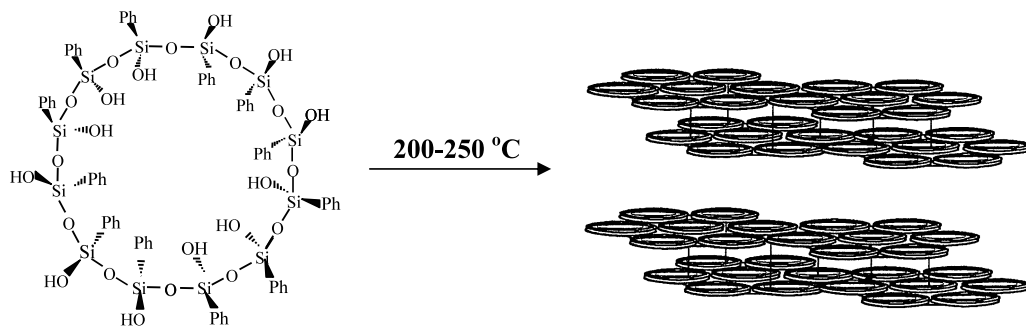


Fig. 10. Schematic depiction of the non-smectic layered structure of PC-D₁₂, obtained after condensation of tris-*cis*-tris-*trans*-[PhSi(O)OH]₁₂ at 200–250 °C.

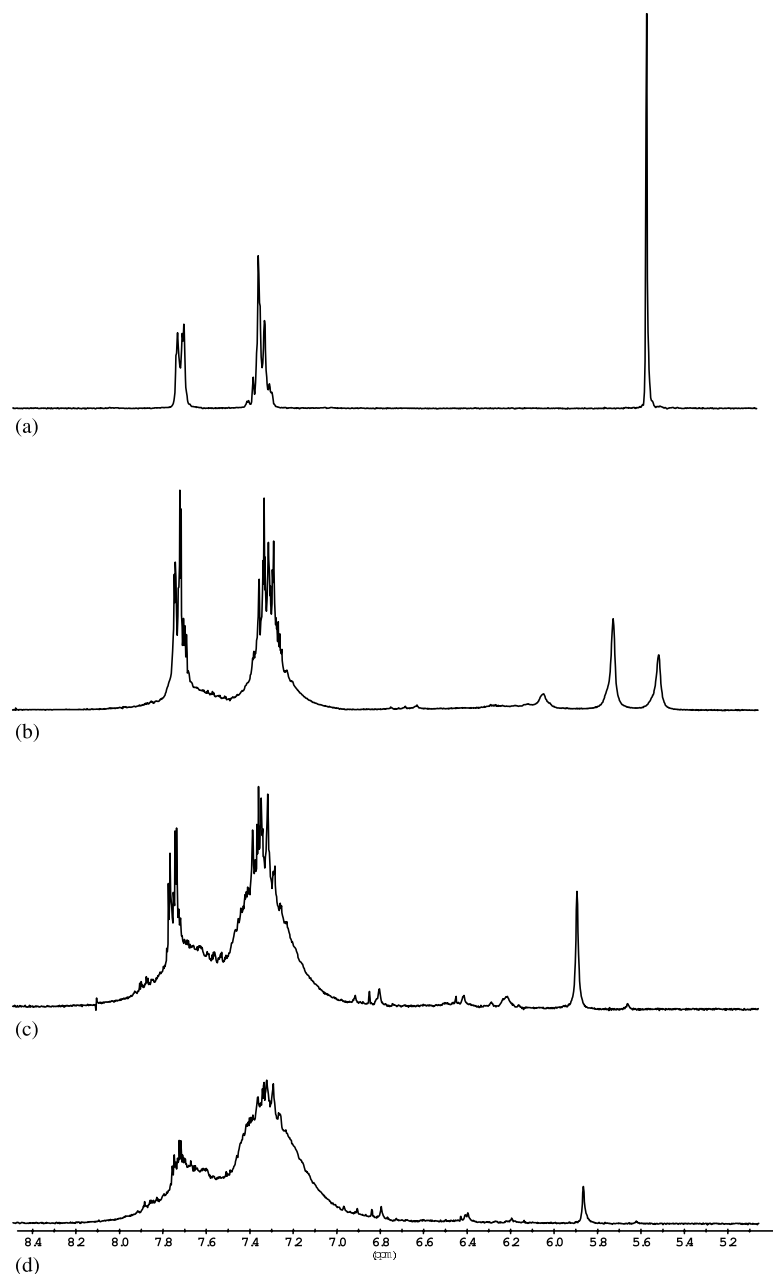
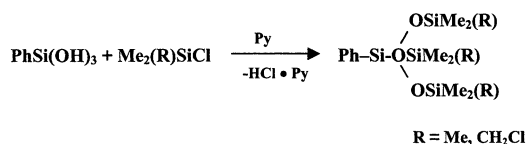


Fig. 11. ¹H-NMR spectra of **1** in acetone-*d*₆ (*C* = 0.3 mol l⁻¹) ((a) fresh solution; (b–d) 3, 12 and 34 days after preparation).



Scheme 2.

tris-triorganylsiloxyphenylsilanes were obtained in yields up to nearly 85% and characterised by the usual analytical methods. This specific example proves the ability of silanetriol **1** to serve as starting material for the introduction of new functionalities at the silicon–oxygen bonds and therefore it might be useful as building block for the formation of new siloxane based materials. This work is just being performed in our laboratories.

3. Experimental

¹H- and ²⁹Si-NMR spectra were recorded on either a Bruker DRX-500 spectrometer operating at 500.12 MHz for ¹H and 99.325 MHz for ²⁹Si or a Bruker-AMX spectrometer (400.13 MHz for ¹H and 79.495 MHz for ²⁹Si) at 20 °C in (CD₃)₂CO as solvent for phenylsilanetriol, and in CDCl₃ or C₆D₆ for the triorganylsiloxy-substituted derivatives. Chemical shifts are given in parts per million relative to Me₄Si. For the investigation of the phenylsilanetriol stability in solution two different solutions were prepared, one with a concentration C₁ = 0.07 mol l⁻¹ and the second with C₂ = 0.2–0.3 mol l⁻¹.

The IR spectra were recorded for KBr pellets (1600–400 cm⁻¹) and hexachlorobutadiene mulls (4000–2000 cm⁻¹), using a M-82 Carl Zeiss spectrometer.

X-ray characterisation of **1** (powder) was performed with filtered Cu–K_α radiation using a DRON-3M X-ray diffractometer with an asymmetric focusing monochromator (a bent quartz crystal), equipped with both the heating and cooling camera wherein the temperature was automatically regulated. X-ray diffraction patterns were obtained in a wide temperature range.

The TGA was performed on a ‘Derivatograph-K’ (MOM production, Hungary). TGA measurements were carried out in an air environment. The TGA sample size was 20–30 mg and the heating rate was 5 K min⁻¹.

3.1. Synthesis of phenylsilanetriol

14.58 ml of 0.5% acetic acid solution (14.49 ml (0.805 mol) of water and 0.0915 ml of acetic acid) were placed in a three-necked flask and 25 ml (0.134 mol) of PhSi(OMe)₃ were added dropwise under vigorous stirring at 5–10 °C. The molar ratio of the reactants was 0.01CH₃COOH/1PhSi(OMe)₃/6H₂O. The reaction mixture was stirred for 4 h at the above temperature. A

white crystalline product precipitated. The reaction mixture was cooled to –15 °C for 30 min and then filtered, washed once with cold water and then five times with toluene and hexane. The product was dried overnight at room temperature (r.t.) under CaCl₂. Yield 14.2 g (68%) of phenylsilanetriol. Anal. Calc. for C₆H₈SiO₃: C, 46.13; H, 5.16; Si, 17.98; Found: C, 46.46; H, 5.64; Si, 17.91%; NMR data as discussed in the text.

3.2. Synthesis of tris-(trimethylsiloxy)phenylsilane

In a three-necked flask 18.24 ml (0.144 mol) of Me₃SiCl and 11.6 ml (0.144 mol) of pyridine and 5 g (0.032 mol) of PhSi(OH)₃ were mixed and 50 ml of toluene were added. The reaction mixture was stirred under reflux for 7 h. After cooling to r.t. the precipitate was filtered. The toluene filtrate was washed free of chloride with water and then dried over sodium sulfate. The toluene was removed in vacuum to afford 8.1 g (89.6%) of a transparent liquid. Distillation in vacuum gave 7.65 g (84.6%) of tris-(trimethylsiloxy)phenylsilane, b.p. = 78–80 °C/1 mmHg. Anal. Calc. for C₁₅H₃₂Si₄O₃: C, 48.33; H, 8.65; Si, 30.1. Found: C, 48.43; H, 8.69; Si, 29.90%. ¹H-NMR (δ, ppm): 7.55 (d, *o*-2H, Ph), 7.33 (m, *p*-1H and *m*-2H, Ph), 0.12 (s, 9H Me) ²⁹Si-NMR (δ, ppm): 3.95 ppm (OSiMe₃) and 82.60 (PhSiO₃).

3.3. Synthesis of tris-[(dimethyl)(chloromethyl)siloxy]phenylsilane

3.15 g (63%) of tris-[(dimethyl)(chloromethyl)siloxy]phenylsilane were obtained similarly from 2 g (0.0128 mol) of **1** and 6.04 g (0.42 mol) of Me₂(CH₂Cl)SiCl in the presence of pyridine (3.34 g, 0.042 mol) in 30 ml toluene. Anal. Calc. for C₁₅H₂₉Cl₃O₃Si₄: C, 37.82; H, 6.14; Si, 23.59; Found: C, 38.02; H, 6.30; Si, 22.97%; ¹H-NMR (δ, ppm): 7.57 (d, *o*-2H, Ph), 7.39 (m, *p*-1H and *m*-2H, Ph), 0.27 [s, 6H (Me)], 2.76 (s, 2H, CH₂Cl). ²⁹Si-NMR (δ, ppm): 4.18 ppm [(OSiMe₂(CH₂Cl)] and –77.50 (PhSiO₃).

References

- [1] (a) P.D. Lickiss, S.A. Litster, A.D. Redhouse, C.J. Winsener, J. Chem. Soc. Chem. Commun. (1991) 173; (b) P.D. Lickiss, Adv. Inorg. Chem. 42 (1995) 147 (and references therein); (c) P.D. Lickiss, in: N. Auner, J. Weis (Eds.), Organosilicon Chemistry III, From Molecules to Materials (and references therein), VCH, Weinheim, 1997, p. 369 (and references therein).
- [2] (a) F.J. Feher, T.A. Budzichowski, R.L. Blanski, K.J. Weller, J.W. Ziller, Organometallics 10 (1991) 2526; (b) F.J. Feher, J.J. Schwab, D. Soulivong, J.W. Ziller, Main Group Chem. 2 (1997) 123.
- [3] (a) R. Murugavel, V. Chandrasekhar, H.W. Roesky, Acc. Chem. Res. 29 (1996) 183; (b) M.G. Walawalker, R. Murugavel, H.W. Roesky, Tailor-Made

- Silicon Oxygen Compounds, in: R. Corriu, P. Jutzi (Eds.), Vieweg Verlag, Braunschweig Weisbaden, 1996, p. 61.;
- (c) R. Murugavel, A. Voigt, M.G. Walawalkar, H.W. Roesky, in: N. Auner, J. Weis (Eds.), Organosilicon Chemistry III, From Molecules to Materials, VCH, Weinheim, 1997, p. 376.
- [4] (a) P. Jutzi, M. Schneider, H.-G. Stammler, B. Neumann, *Organometallics* 16 (1997) 5377;
(b) M. Schneider, B. Neumann, H.-G. Stammler, P. Jutzi, *Monatsh. Chem.* 130 (1999) 33.
- [5] (a) M. Unno, K. Takada, H. Matsumoto, *Chem. Lett.* (2000) 242;
(b) M. Unno, A. Suto, K. Takada, H. Matsumoto, *Bull. Chem. Jpn* 73 (2000) 215.
- [6] (a) G. Cerveau, R.J.P. Corriu, B. Dabiens, J. Le Bideau, *Angew. Chem. Int. Ed.* 39 (2000) 4533;
(b) F. Carre, G. Cerveau, R.J.P. Corriu, B. Dabiens, *J. Organomet. Chem.* 624 (2001) 354;
(c) G. Cerveau, S. Chappellet, R.J.P. Corriu, B. Dabiens, J. Le Bideau, *Organometallics* 21 (2002) 1560.
- [7] O.I. Shchegolikhina, Yu.A. Pozdnyakova, Yu.A. Molodtsova, S.D. Korkin, S.S. Bukalov, L.A. Leites, K.A. Lyssenko, A.S. Peregudov, N. Auner, D.E. Katsoulis, *Inorg. Chem.* 41 (2002) 6892.
- [8] L.J. Tyler, *J. Amer. Chem. Soc.* 77 (1955) 770.
- [9] A.G. Kuzntsova, K.A. Andrianov, D.Ya. Zhinkin, *Plastmassi* (1960) 16.
- [10] The XRD patterns comprising two amorphous halos (Fig. 4, curve 6) are typical for isotropic melts of siloxane monomers and polymers as well as for non-crystalline siloxane polymers including ladder polymers.
- [11] This specifies that condensation processes be slightly shifted to areas of lower temperatures in the course of X-ray measurements, than detected by TGA studies. That is explained by the different experimental conditions used for different analytical methods (see Section 3).
- [12] D.Ya. Tsvankin, V.Yu. Levin, V.S. Papkov, V.P. Zhukov, A.A. Zhdanov, K.A. Andrianov, *Vysokomol. Soedin.* 21A (1979) 2126.
- [13] V. Matukhina, Yu.K. Godovskiy, N.N. Makarova, O.I. Shchegolikhina, Yu.A. Molodtsova, Abstracts of Fourth Russian Symposium Liquid crystal. polym., Moscow, 24–28 January (1999), 108.