

Alkali-Metal-Directed Hydrolytic Condensation of 3-Mercaptopropyltrimethoxysilane

Maria Nowacka · Anna Kowalewska ·
Krystyna Gadzinowska

Received: 8 May 2014 / Accepted: 15 September 2014 / Published online: 11 December 2014
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Abstract A series of solid sodium and potassium cyclotetrasiloxanates was synthesized with high yields by hydrolytic condensation of 3-mercaptopropyltrimethoxysilane in the presence of potassium or sodium hydroxide. The obtained materials were characterized using solid state ^{29}Si and ^{13}C NMR, wide angle X-ray scattering (WAXS), elemental analysis, Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The influence of reaction conditions on the structure and physiochemical properties of the obtained products was studied.

Keywords Cyclosiloxanolate · Hydrolytic condensation · 3-mercaptopropyltrialkoxysilane

1 Introduction

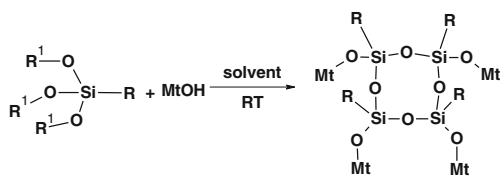
Linear ladder-like polysilsesquioxanes (LPSQs) are polymeric inorganic-organic hybrid materials consisting of a double stranded siloxane backbone with organic functional groups pendant on both sides. Due to their interesting physiochemical properties [1] LPSQs have been attracting a growing interest since their synthesis was announced for the first time by Brown et al. in 1960 [2]. Exhibiting many excellent properties, such as outstanding thermo-oxidative and photochemical stability, low flammability, excellent dielectric properties and mechanical stability, ladder-like polysilsesquioxanes can be applied as protective

coatings, insulating layers, aerospace materials and precursors of ceramics, photoresists etc. [1, 3]. In addition, LPSQs (even those of high molecular weight) are well soluble in organic solvents. Chemical modification of organic side chain groups allows for the introduction of a variety of new functionalities. Physiochemical properties of LPSQs depend on the regularity of the structure of the polysiloxane framework.

Several synthetic methods were proposed for the preparation of ladder-like polysilsesquioxanes, including step wise coupling polymerization [3–7] or hydrolytic condensation of trifunctional organosilanes [2, 8–10]. However, the most promising method for the preparation of defect-free LPSQs is hydrolytic condensation of monomers containing cyclic siloxane units [11–19]. The most popular method for preparation of cyclic siloxane monomers is hydrolytic condensation of trialkoxyorganosilanes (Scheme 1) in the presence of water and an alkali metal hydroxide. It was found that properties of metal cations can influence the structure of the formed moieties since they work as template centers and structural elements helping to bind siloxane bonds into cyclic organosiloxanolate fragments [20–32]. While transition or rare-earth metal cations lead to the formation of varied-size ($n=4$ [20], 5 [21], 6, 8, 12 [22–24]) cyclic species, sodium and potassium cations enable the synthesis of small cyclosiloxanes containing three [25–28] or four [29–31] silicon atoms. Reaction parameters (the amount of water, type of organosilane and solvent) also can affect the ring size of cyclic products [32].

The syntheses of cyclotetrasiloxanates functionalized at the Si atom with simple alkyl [34–37] and aryl [30, 33, 34] groups have been reported. We wanted to prepare cyclotetrasiloxanolate precursors suitable for the synthesis of regular LPSQs, bearing side substituents capable of nucleophilic substitution or other chemical modifica-

M. Nowacka (✉) · A. Kowalewska · K. Gadzinowska
Centre of Molecular and Macromolecular Studies, Polish
Academy of Sciences, Sienkiewicza 112, 90-363 Lodz, Poland
e-mail: mnowacka@cbmm.lodz.pl



Scheme 1 Synthesis of cyclotetrasiloxanolates. R¹ - Me, Et; Mt - metal, L - H₂O, EtOH; R - Ph [28, 33], C₆H₅-OMe [33], Np [33], Np-OMe [33], C₆H₅Br [33, 34], iBu [33, 34, 36], Me [37], Vi [37], Et [37], iPr [37]

tions. The presence of thiol groups in side chains would enable their functionalization by thiol-ene and thiol-yne addition, and thereby preparation of LPSQs with a large variety of functional groups. We have therefore studied the influence of reaction conditions (solvent; metal hydroxide (MtOH): Mt=Na, K; [MtOH]/[silane]; [silane]/[H₂O]) on the structure and properties of cyclotetrasiloxanolates bearing 3-mercaptopropyl groups at silicon atoms.

2 Results and Discussion

Transformation of 3-mercaptopropyltrimethoxysilane into cyclic products was performed in the presence of water and potassium or sodium hydroxide. Two synthetic procedures were applied to study the effect of solvent and the amount of water on the structure of siloxanolate (Table 1, experimental details in the Supporting Information).

The first synthetic method was based on the procedure described by Ito et al. [33], originally for the preparation of cyclosiloxanolates with phenyl groups at the silicon

atom. The reaction was carried out in ethanol using 3-mercaptopropyltrimethoxysilane as the siloxane precursor and sodium or potassium hydroxide as an alkali metal source. The second procedure was described by Pozdnyakova et al. [34] for the synthesis of potassium cyclosiloxanolates with vinyl groups. The reaction was performed in a mixture of hexane and ethanol as a reaction medium, using potassium hydroxide as MtOH.

We have chosen the above methods to compare the influence of the reaction conditions that originally were designed for two significantly different functional groups: small vinyl moieties, and phenyl groups that facilitate formation of regular cyclic products due to their rigid structure and size. Both methods led to the formation of solid, white products with high yields.

The influence of the amount of potassium hydroxide on the structure of cyclotetrasiloxanolate-(CH₂)₃SH was analyzed. Contrary to the synthesis with the ratio [silane]/[KOH]=1, the product obtained with [silane]/[KOH]=2 did not precipitate from the reaction mixture. After 24h at room temperature the solution separated into two phases of different color and viscosity. The product was isolated as an orange powder only after the volatiles were removed from the more viscous phase under reduced pressure. It does not have a crystalline structure. Furthermore, products obtained in the reaction with potassium hydroxide, [KOH]/[silane]=2, contained significantly more crystallization water than other products.

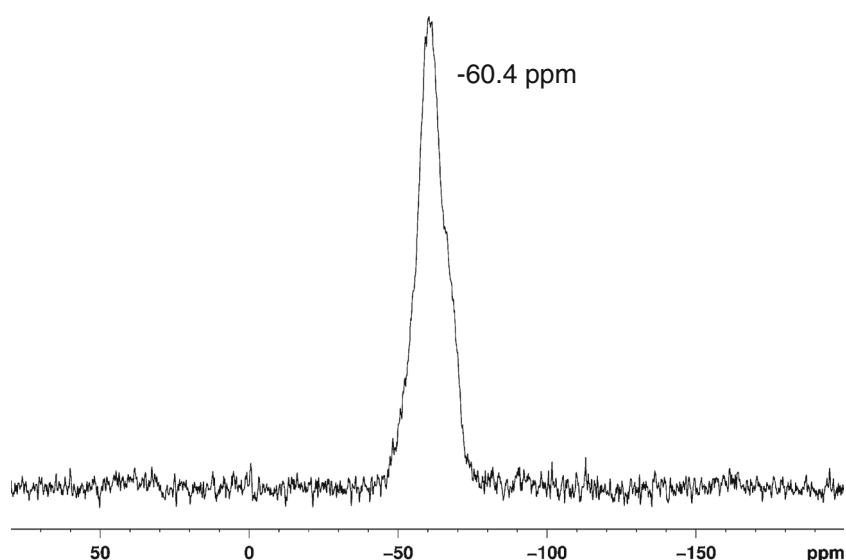
²⁹Si CP MAS NMR analysis (Fig. 1) displayed only one peak, at -60.4 ppm, for the potassium cyclosiloxanolate obtained with method 1 (Table 1/ entry 2). The presence of one peak represents formation of only the all-cis isomer. In other cases the presence of two peaks: a minor one near

Table 1 Summary of reaction conditions and elemental composition of the obtained products

No	Mt	Method	[MtOH] /[silane]	[silane] /[H ₂ O]	Elemental Analysis								
					Found			nEtOH	nH ₂ O	Calculated			Y[%]
					%C	%H	%S			%C	%H	%S	
1	KOH	1	1	1	21.2	3.9	16.1	1	5	20.2	5.3	15.4	71
2	KOH	1	1	1	20.0	4.6	–	–	2	19.7	4.4	17.5	39
3	KOH	1	1	1	19.2	4.8	16.1	–	5	18.3	4.9	16.3	90
4	KOH	1	1	1	20.3	5.3	14.8	1	5	20.2	5.3	15.4	72
5	NaOH	1	1	1	22.3	4.6	14.4	–	1	22.1	4.7	19.7	102
6	KOH	1	2	1	12.7	3.3	11.3	–	15	12.9	4.9	11.5	102
7	KOH	2	1	10	21.5	5.6	12.0	1	4	20.6	5.2	15.7	89
8	KOH	2	1	10	22.1	5.1	15.8	2	1	23.8	5.2	15.9	113
9	KOH	2	1	10	22.4	6.2	12.1	2	3	22.8	5.5	15.2	66

Calculated values correspond to the composition of products according to the results of elemental analysis
nEtOH, nH₂O – number of ethanol and water molecules in the product

Fig. 1 ^{29}Si CP MAS NMR spectrum of the product obtained by method 1, $[\text{KOH}]/[\text{silane}]=1$ (Table 1/ entry 2)



-60 ppm and a much bigger one near -70 ppm was noted. The first one is characteristic for cyclic siloxane structures containing T^2 units [38]. The peak near -70 ppm can be assigned to the formation of oligomeric species containing T^3 units. It is known that cyclic siloxanes can be distinguished from their linear analogues by the differences in shifts in ^{29}Si NMR analysis [38, 39]. Signals of silicon atoms in cyclic compounds are always present in the lower magnetic field than those characteristic for oligomeric structures. According to differences in the intensity of signals of products obtained by method 1: $[\text{NaOH}]/[\text{silane}]=1$ (Table 1/ entry 5) (Figure SI 1), $[\text{KOH}]/[\text{silane}]=2$ (Table 1/ entry 6) (Figure SI 3), and by method 2 (Table 1/ entry 7) (Figure SI 5) one can conclude that only the first method and the reaction with an equimolar amount of potassium hydroxide ($[\text{KOH}]/[\text{silane}]=1$) leads to the formation of the desired cyclotetrasiloxanolate as the main product.

All of the obtained materials were also analyzed by solid state ^{13}C CP MAS NMR. While the analysis of 3-mercaptopropyltrimethoxysilane displayed characteristic resonances at: 9.4 ppm (SiCH_2), 28.5 ppm (CH_2) and 49.8 ppm (CH_2SH), the spectrum (Fig. 2) of the product obtained with method 1 (Table 1/ entry 2) showed peaks characteristic for the 3-mercaptopropyl group: 12.6 ppm (SiCH_2), 27.6 ppm (CH_2), 48.2 ppm (CH_2SH), and an additional peak at 64.7 ppm. The latter one can be assigned as a resonance of the CH_2 group bonded to a SK moiety. A similar down-field shift of appropriate ^{13}C resonances with respect to free ligands was observed for Hg (II) thiolates [40]. The spectra of sodium cyclosiloxanolate (Table 1/ entry 5) (Figure SI 2) as well as products obtained by the second method of synthesis (Table 1/ entry 7) (Figure SI 6) displayed peaks of similar shifts, those corresponding to the 3-mercaptopropyl group and a peak near 64 ppm. The analogous situation was observed for the product obtained in the reaction with

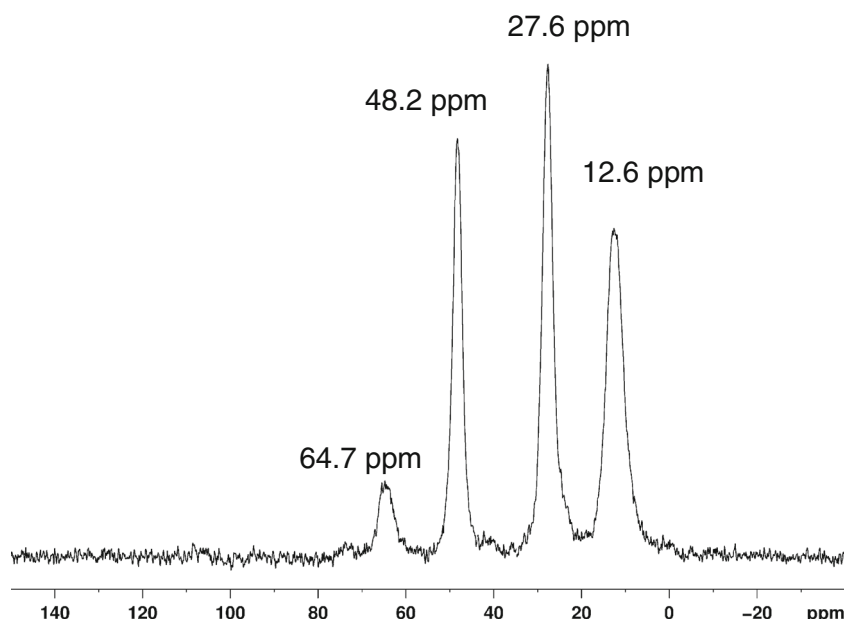
$[\text{KOH}]/[\text{silane}]=2$ (Table 1/ entry 6) (Figure SI 4). The presence of the additional peak as well as that characteristic for CH_2SH can be explained by interactions between potassium silanulates and acidic thiol groups (Scheme 2). Formation of four-centered structures that can lead to equilibrium between potassium silanulates and thiolates was postulated.

Most of the obtained products did not contain ethanol molecules in their structures or the number of alcohol moieties was low. We have not thus observed intense resonances typical for EtOH (19 ppm and 58 ppm) in their ^{13}C CP MAS NMR spectra.

Wide angle X-Ray scattering analysis (Fig. 3) that was carried out for potassium cyclotetrasiloxanolate obtained by method 1 (Table 1/ entry 2) seems to confirm the proposed possible interactions between molecules of siloxanulates (Scheme 2). No literature data on WAXS analysis are available for cyclosiloxanulates that could be directly compared to our results. All data that could be found refer to cyclosilanol [34] or trimethylsilyl derivatives of cyclotetrasiloxanulates [30, 34]. X-Ray diffraction patterns of these compounds exhibit typically a set of two diffraction peaks, near 2Θ 8–12° ($d=7\text{--}12\text{\AA}$) and near 2Θ 15–18° ($d=5\text{--}6\text{\AA}$). We have assigned the recorded diffraction peaks to distances in the postulated structure of 3-mercaptopropylsilanulates (Scheme 2). The structure was constructed on the HyperChem platform [41]. The atomic point charges were calculated using the semi-empirical AM1 method and geometry was optimized by the molecular mechanics method (using MM+ force field parameter set with Polak-Ribiere energy minimization algorithms).

All of the obtained cyclotetrasiloxanulates contained solvate molecules of water and/or alcohol (Table 1). The products obtained by the second synthetic method contained more molecules of ethanol in their structure than

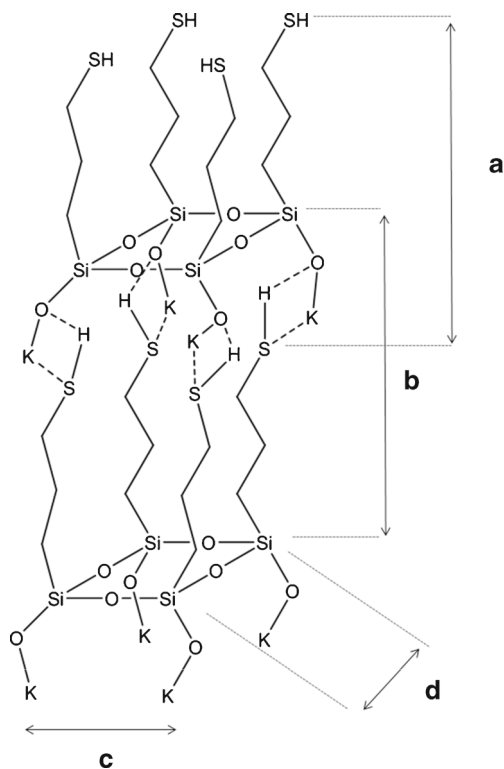
Fig. 2 ^{13}C CP MAS NMR analysis of the product obtained by method 1, $[\text{silane}]/[\text{KOH}]=1$ (Table 1/ entry 2)



products obtained by the first method. The applied alkali metal hydroxide also influenced the kind of ligand molecules present in the final product. According to elemental analysis, potassium cyclotetrasiloxanates ($[\text{KOH}]/[\text{silane}]=1$) contain both water and ethanol moieties, but the corresponding sodium cyclotetrasiloxanates

have on average only one water molecule in their structure.

FTIR spectra (Fig. 4) recorded for the product synthesized by method 1, in the reaction with an equimolar amount of potassium hydroxide, displayed all bands characteristic for mercaptopropyl groups: $660\text{--}700\text{ cm}^{-1}$ (νCH_2), $1380\text{--}1400\text{ cm}^{-1}$ (νCH_2), 2550 cm^{-1} (νSH), 2940 cm^{-1} ($\nu\text{CH}_2\text{SH}$) [42–45] and bands near: 1000 cm^{-1} , 1100 cm^{-1} , 1250 cm^{-1} characteristic for Si-CH₂-R stretching [42–45]. Peaks near $1000\text{--}1130\text{ cm}^{-1}$ and near $600\text{--}700\text{ cm}^{-1}$ are also characteristic for Si-O-Si asymmetric stretching vibrations [42–45]. The band near $800\text{--}900\text{ cm}^{-1}$ can be assigned as stretching vibrations in cyclic siloxane compounds as well as O-Si-O⁻ anionic groups [42, 46, 47]. IR spectra of all products displayed the above mentioned vibration bands but only products obtained in the reactions with potassium hydroxide showed a band near $1600\text{--}1700\text{ cm}^{-1}$. It corresponds to $\delta(\text{H-O-H})$ and $\delta(\text{O-H})$ vibrations and indicates the presence of interstitial water in the samples [48, 49]. The absence of this band in the spectra of the product obtained in the reaction with sodium hydroxide can be explained by a very low amount of water in its structure. On the other hand, the product of reaction with two-fold excess of KOH has a large amount of physically bound H₂O. It is reflected by the presence of a broad band near 3000 cm^{-1} in its FTIR spectrum.



Scheme 2 Postulated interactions between molecules of potassium cyclotetrasiloxanates

Thermogravimetric analysis of products obtained by method 1 in the reaction with potassium (Table 1/ entry 2) (Figure 5) and sodium hydroxide (Table 1/ entry 5) showed two temperature ranges (Figure SI 7) in which the products underwent thermal changes: at 90°C and between $200\text{--}400^\circ\text{C}$. The first peak can be assigned to the removal of water from the crystal structure. The other one corresponds to thermal decomposition of mercaptopropyl groups

Fig. 3 X-Ray diffractogram of the product obtained by method 1 with potassium hydroxide (Table 1/entry 2)

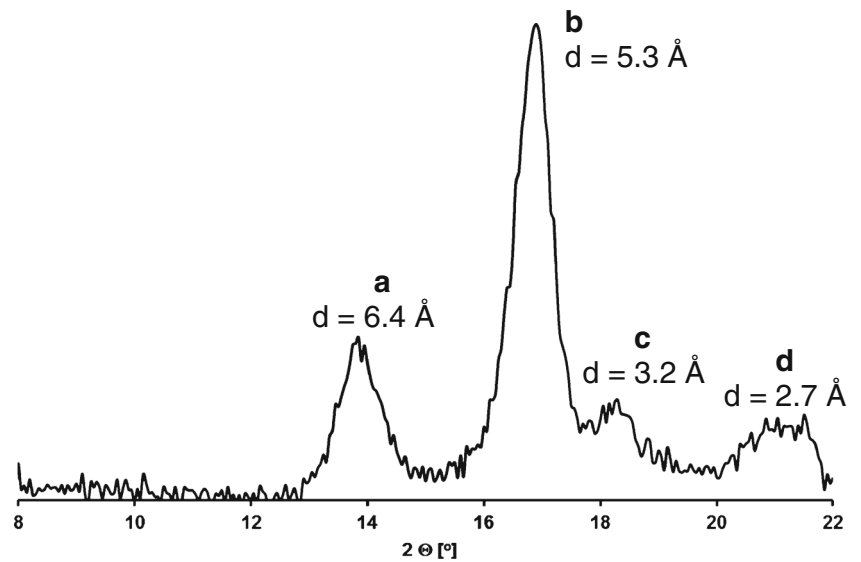


Fig. 4 Comparison of solid state IR analysis for all obtained products: **a** Method 1, [KOH]/[silane]=2 (Table 1/entry 6); **b** Method 1, [KOH]/[silane]=1 (Table 1/entry 2); **c** Method 1, reaction with NaOH; **d** Method 2

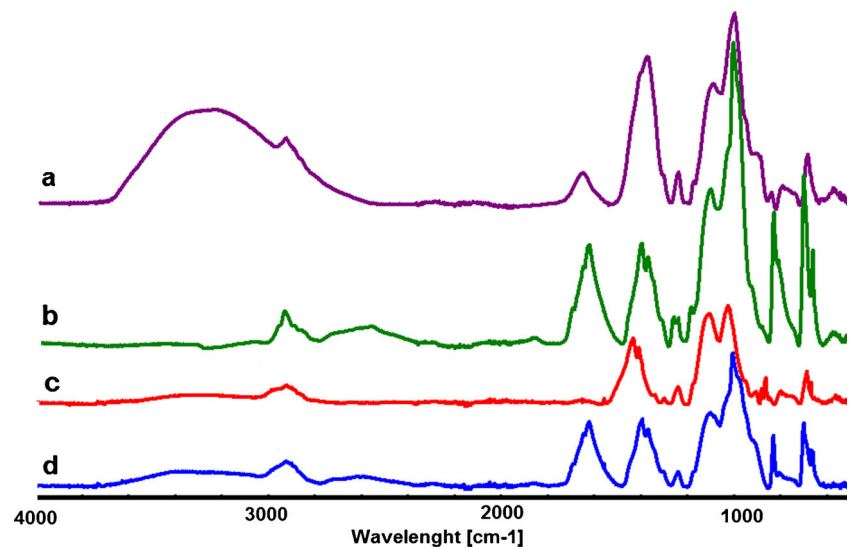


Fig. 5 TGA analysis for product obtained by method 1 [KOH]/[silane]=1 (Table 1/entry 2)

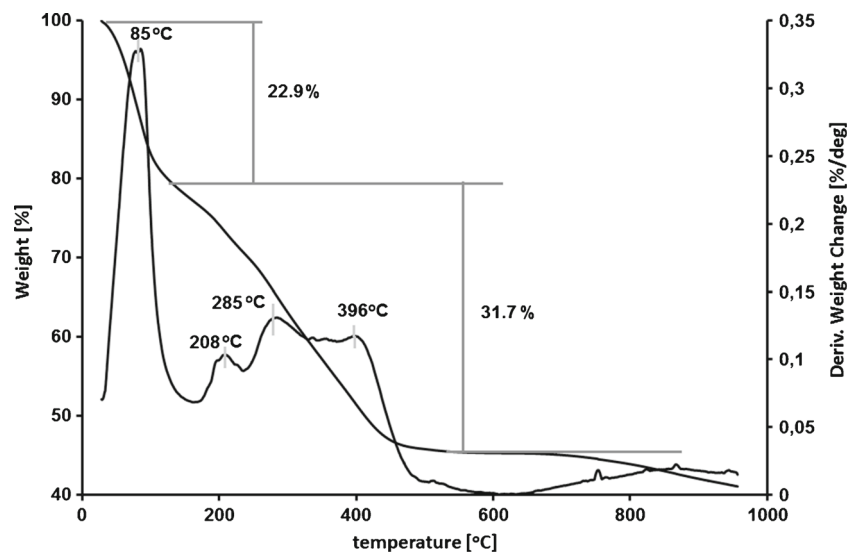
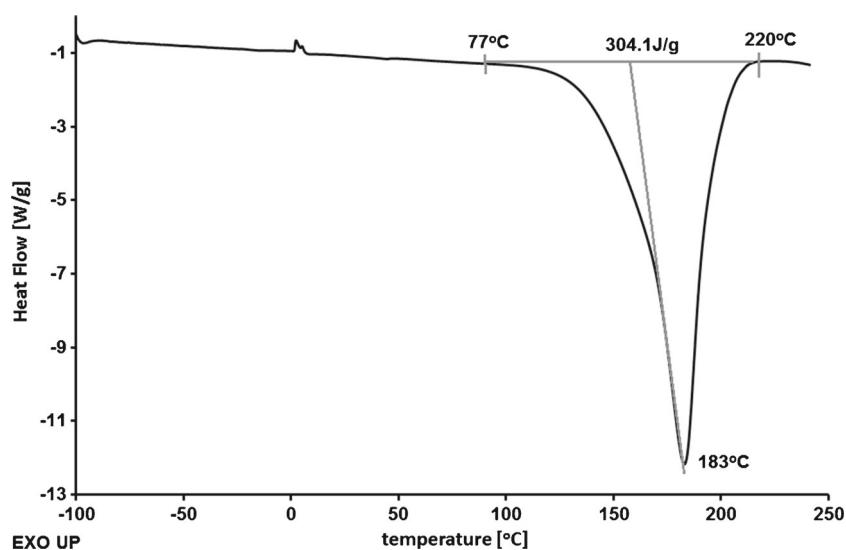


Fig. 6 DSC analysis of the product obtained by method 1 [KOH]/[silane]=1 (Table 1/entry 4), second heating



and takes place in three steps. According to bond dissociation enthalpies these three steps correspond to dissociation of S-C ($\Delta H=713\text{kJ/mol}$), C-C ($\Delta H=618\text{kJ/mol}$) and C-Si ($\Delta H=447\text{kJ/mol}$) bonds [50]. Decomposition of the product obtained in the reaction with [KOH]/[silane]=2 (Table 1/entry6) proceeds in three steps (Figure SI 8). Apart from the peak near 360°C , there are two other peaks: at 60°C and 95°C . These peaks can be associated with removal of different types of water: physically bound through hydrogen bonds and that present in the crystal structure.

DSC analysis of all products obtained by method 1 displayed small peaks near $0\text{--}10^\circ\text{C}$ that can be assigned to melting of free water molecules and a large, endothermic transition at 183°C ([KOH]/[silane]=1 - Table 1/entry4) (Fig. 6) that can be assigned as melting of cyclosiloxanolate. In comparison to other products (Figures SI 9 and SI 10), the endothermic peak of the cyclosiloxanolate obtained by method 1 is sharp and relatively narrow.

3 Conclusions

Cyclotetrasiloxanolate bearing 3-mercaptopropyl groups at silicon atoms have been synthesized for the first time with good yield. Their structure has been studied by ^{29}Si and ^{13}C CP MAS NMR spectroscopy, Wide-Angle X-ray Scattering and vibrational spectroscopy. We have found that under appropriate reaction conditions only the all-*cis* isomer of potassium 2,4,6,8-tetra(3-mercaptopropyl) cyclotetrasiloxanolate or branched oligomeric species can be obtained. Interestingly, it was found that potassium silanolate moieties and thiol groups can interact with each other in the solid (crystalline) state. Formation of four-centered thio-silanolate structures has been postulated.

Acknowledgments This work was supported by the Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences grant 551-30.

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