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New Results in Cyclosilane Chemistry: Siloxene-like Polymers

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Summary: Several linear and cyclic silanes (four-, five- and six-membered rings) with silicon-halogen or silicon-triflate functions were prepared and hydrolyzed to polymeric structures similar to Wöhler siloxene and Kautsky siloxene. Optical investigations on the fluorescence of these polymers were carried out. The color and the fluorescence of the polymers are influenced by the ring size and the kind of substituents. Depending on the starting material the fluorescence maxima range from 400 to 550 nm.

Introduction

Calcium disilicide reacts with acids to form the Wöhler siloxene [1] or Kautsky siloxene [2], depending on the reaction conditions. These compounds show interesting optical behavior [3]. In the Kautsky formula, silicon six-membered rings are connected by oxygen atoms forming a polymeric layer (Fig. 1).

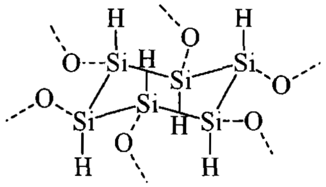

Fig. 1. Structure of siloxene.

To elucidate the question whether or not cyclosilane structures are essential for the color and fluorescence of the polymers, linear and cyclic silanes with silicon halogen or -triflate functions were prepared and hydrolyzed to siloxene-like structures.

Syntheses of Halogen Containing Linear and Cyclic Silanes

Several methods, all starting from appropriate phenylated or methylated silanes were used to prepare the following chlorinated linear silanes (Scheme 1).

$$\mathrm{Me_3Si\text{-}SiMe_3} + 2\,\mathrm{MeCOCl} \xrightarrow{\mathrm{AlCl_3}} \underset{\mathbf{1}}{\mathrm{ClMe_2Si\text{-}SiMe_2Cl}}$$

$$\mathrm{PhMeSiCl_2} + 2\,\mathrm{PhMe_2SiLi} \longrightarrow \mathrm{PhMe_2Si\text{-}SiPhMe\text{-}SiMe_2Ph}$$

$$\mathrm{PhMe_2Si\text{-}SiPhMe\text{-}SiMe_2Ph} \xrightarrow{\mathrm{CF_3SO_3H}} \xrightarrow{\mathrm{LiCl}} \underset{\mathbf{2}}{\mathrm{ClMe_2Si\text{-}SiMeCl\text{-}SiMe_2Cl}}$$

$$\mathrm{(Ph_2MeSi)_2} \xrightarrow{\mathrm{2CF_3SO_3H}} \xrightarrow{\mathrm{2PhMe_2SiLi}} \mathrm{PhMe_2Si\text{-}(SiMePh)_2\text{-}SiMe_2Ph}$$

$$\mathrm{PhMe_2Si\text{-}(SiMePh)_2\text{-}SiMe_2Ph} + \mathrm{HCl} \xrightarrow{\mathrm{AlCl_3}} \underset{\mathbf{3}}{\mathrm{ClMe_2Si\text{-}(SiMeCl)_2\text{-}SiMe_2Cl}}$$

$$\mathrm{(Ph_2MeSi)_2} \xrightarrow{\mathrm{2CF_3SO_3H}} \xrightarrow{\mathrm{2Ph_2MeSiLi}} \mathrm{Ph_2MeSi\text{-}(SiMePh)_2\text{-}SiMePh_2}$$

$$\mathrm{Ph_2MeSi\text{-}(SiMePh)_2\text{-}SiMePh_2} + \mathrm{HCl} \xrightarrow{\mathrm{AlCl_3}} \underset{\mathbf{4}}{\mathrm{Cl_2MeSi\text{-}(SiMeCl)_2\text{-}SiMeCl_2}}$$

Scheme 1. Syntheses of chlorinated linear silanes.

The starting materials for the four-, five and six-membered ring systems, $\mathrm{Si_4Ph_8}$, $\mathrm{Si_5Ph_{10}}$, $\mathrm{Si_6Ph_{12}}$, and $\mathrm{Si_6Me_6Ph_6}$, were synthesised by well-known Wurtz-type reactions (Eqs. 1-2).

$$\mathrm{Ph_2SiCl_2} + \mathrm{Na/K} \longrightarrow \mathrm{(SiPh_2)}_n \qquad (n = 4;\ 5;\ 6)$$

Eq. 1.

$$\mathrm{MePhSiCl_2} + \mathrm{Li} \longrightarrow \mathrm{(SiMePh)_6}$$

Eq. 2.

The triflic acid derivatives were prepared from the perphenylated cyclosilanes by dearylation with triflic acid (Eq. 3). The subsequent reaction of $\mathrm{Si_5Ph_8(CF_3SO_3)_2}$ with lithium aluminium hydride and with hydrogen chloride in a second step led to 1,3-dihydrooctachlorocyclo-pentasilane (Eq. 4).

$$(SiPh_2)_n + n\,CF_3SO_3H \longrightarrow (SiPh(CF_3SO_3))_n \quad (n = 4; 5) \quad \mathbf{5; 6}$$

Eq. 3.

$$(SiPh_2)_5 + 2\,CF_3SO_3H \longrightarrow 1,3\text{-}(CF_3SO_3)_2Si_5Ph_8 \xrightarrow{LiAlH_4} 1,3\text{-}H_2Si_5Ph_8$$

$$1,3\text{-}H_2Si_5Ph_8 + HCl \longrightarrow 1,3\text{-}H_2Si_5Cl_8 \quad \mathbf{7}$$

Eq. 4.

The reaction of perphenylated cyclosilanes with hydrogen halides under pressure or with aluminum halides as catalysts allows the preparation of $(SiCl_2)_5$ and $(SiCl_2)_6$ (Eq. 5) as well as the preparation of $Si_5Ph_5I_5$ (Eq. 6).

$$(SiPh_2)_n + HCl \xrightarrow{AlCl_3} (SiCl_2)_n \quad (n = 5; 6) \quad \mathbf{8; 9}$$

Eq. 5.

$$(SiPh_2)_5 + HI \longrightarrow (SiPhI)_5 \quad \mathbf{10}$$

Eq. 6.

The methyl(chloro)cyclosilanes were achieved by the reaction of the corresponding phenyl-(methyl)cyclosilanes with hydrogen chloride (Eqs 7-8).

$$(SiPh(CF_3SO_3))_5 + 5\,MeLi \longrightarrow (SiPhMe)_5 \xrightarrow{HCl/AlCl_3} (SiMeCl)_5 \quad \mathbf{11}$$

Eq. 7.

$$(SiMePh)_6 \xrightarrow{HCl/AlCl_3} (SiMeCl)_6 \quad \mathbf{12}$$

Eq. 8.

Hydrolysis and Condensation

The hydrolysis of the halides was carried out by dropwise addition of an excess of aqueous tetrahydrofuran (1:5) to a solution of the halides in THF. The solid (if any) was filtered off and washed with dry THF to remove the water and the remaining lower molecular fractions. The triflic acid derivatives were hydrolyzed in another way, because the triflic acid that was released in the hydrolysis step caused the tetrahydrofuran to form polymers. Thus toluene or dichloromethane solutions of the triflic acid derivatives were first stirred overnight with water. The aqueous layer was removed, tetrahydrofuran added and the remaining solids filtered off. Finally, the products were dried in vacuum at 50 °C for 5 hours. In order to investigate the condensation step, a sample of one of these polymers, namely the hydrolysis product of $(SiMeCl)_5$, was not subjected to the drying procedure. It remained partially soluble in THF and so we were able to record a GPC (size exclusion chromatogram) and a ^{29}Si NMR (INEPT pulse sequence). The polymer showed two distinct peaks at 672 g/mol (17%) and 1191 g/mol (13%). The main part (70%) was a very broad peak with a maximum at 1751 g/mol. Evaluation of the chromatogram resulted in 1912 g/mol as number average molecular weight (M_n) and 5554 g/mol as weight average molecular weight (M_w). The calculations refer to a poly(styrene) standard. A very broad signal, reaching from +7 to -20 ppm, with its maximum at -4.1 ppm was found in the ^{29}Si NMR spectrum, referred to TMS as standard. Interpreting these facts it seems to be, that the condensation already starts in the hydrolysis step and that oligomers with a chain length of n = 7 - 18 are formed. To obtain maximum condensation and insolubility in consequence a rigoros drying step is necessary. The polymers obtained by this way exhibit the following specifications (Table 1).

Table 1. Summary of the hydrolysis and condensation products

No	Starting Material	Product Description	Fluorescence Maximum [nm]
1	$Si_2Me_4Cl_2$	slightly yellowish, thin oil	none
2	$Si_3Me_5Cl_3$	opaque, thick oil	none
3	$Si_4Me_6Cl_4$	white solid	very weak (399)
4	$Si_4Me_4Cl_6$	white solid	weak (413)
5	$Si_4Ph_4(OTf)_4$	dark yellow solid	553
6	$Si_5Ph_5(OTf)_5$	dark yellow solid	522
7	$1,3\text{-}H_2Si_5Cl_8$	pale orange solid	486
8	Si_5Cl_{10}	white solid	400
9	Si_6Cl_{12}	white solid	432
10	$Si_5Ph_5I_5$	dark yellow-green solid	540
11	$Si_5Me_5Cl_5$	slightly yellow-green solid	505
12	$Si_6Me_6Cl_6$	slightly yellow-green solid	436

Fluorescence Spectra

The fluorescence emission spectra were recorded with photoluminescence excitation-emission equipment, consisting of a Xe-arc source monochromatized by a grating double monochromator for the excitation. The fluorescence intensity from the samples was collected by lens optics into the entrance slit of a high resolution grating monochromator connected to a cooled photon-counting system. The fluorescence spectra presented here are uncorrected, since the spectral response of the emission setup is nearly constant in the wavelength region 450-800 nm. The liquid samples were measured in a 0.5 cm Infrasil cuvette, whereas the solid samples were prepared as a powder coat on paper. The preparation of the samples and the measurements were done using argon as protective gas.

The polymers obtained from linear starting materials (di-, tri and tetrasilane halides) exhibit neither a significant fluorescence emission nor noticeable optical absorption in the visible. However, a weak blue-ultraviolet fluorescence is observed, which we attribute to impurity emission centers. As expected, the products from cyclic silanes show quite strong fluorescence emission accompanied by an optical absorption in the visible range. The fluorescence spectra of the cyclic materials are depicted in Fig. 2 and Fig. 3.

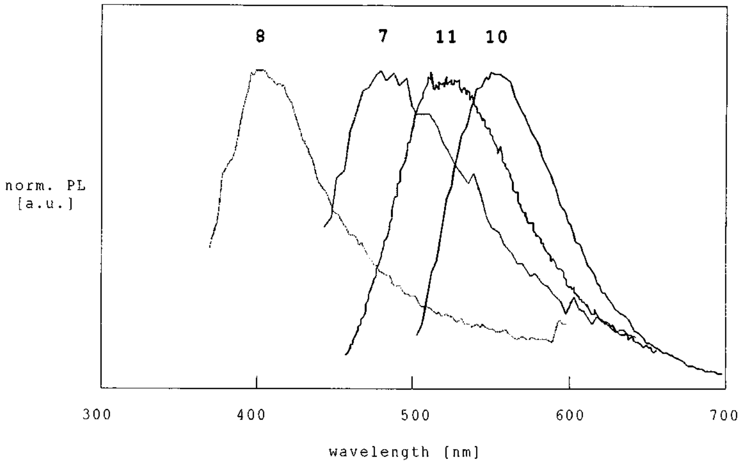

Fig. 2. Photoluminescence spectra of the polymers of various cyclopentasilane derivatives.

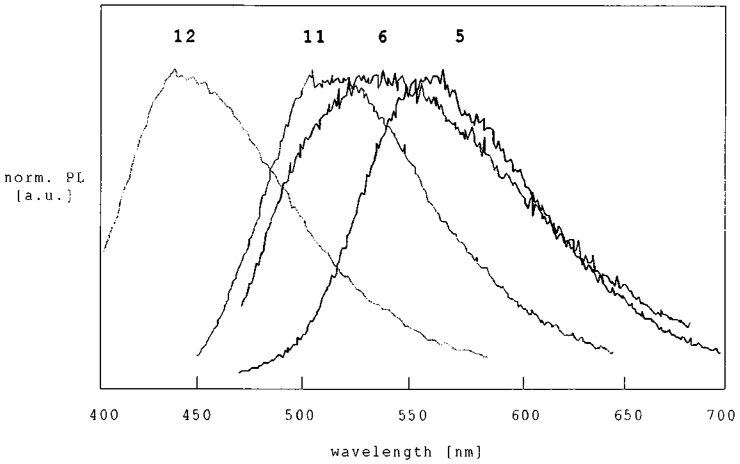

Fig. 3. Photoluminescence spectra of the polymers of cyclosilanes with various ring size.

A bathochromic shift of the fluorescence maxima depending on the substituents takes place in the order of the starting materials (Fig. 2): $Si_5Cl_{10} < Si_5H_2Cl_8 < Si_5Me_5Cl_5 < Si_5Ph_5I_5$

A comparison of similar substitution products such as the methyl and phenyl compounds shows that the four-membered ring seems to be a stronger chromophore than the five- and six-membered rings. In our present knowledge only cyclic systems (and probably also cage structures) seem to be able to form fluorescent polymers in a matrix of oxygen.

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