

Polymer route for silicon quantum dots

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This work presents an intriguing phenomenon which takes place in polyhydrosilanes. Study of the chemical properties of these structures reveals that even at room temperature elemental silicon particles appear within the polymer thin films. To investigate this process polyhydrosilanes with various contents of methylhydrosilyl- groups were synthesized by homogeneous coupling of methylchlorosilane with diphenyldichlorosilane in specific molecular ratios. Through advanced physico-chemical analyses techniques it was shown that the formation of these particles takes place within the methylhydrosilyl- fragments by self-induced chemical processes.

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1. Introduction

In recent years an intense research was developed for the ability to alter a wide variety of material properties simply by reducing the material domain size in order to obtain quantum non-negligible effects. Semiconductor materials have been the subject of much of this work, particular attention being paid to silicon. Silicon quantum size effects have been exploited to investigate properties like: photoluminescence [1], melting and sintering [2], band gap energy [3], physical strength of derivative ceramics [4] and phosphorescence [5]. Due to the importance of silicon in modern technology, modifications of its properties have a major impact on leading industrial sectors including: electronics, aerospace, computers, energy and sensors [6-10].

Until now polysilanes were known as precursors for silicon carbide, a highly mechanical strength material which is obtained by the thermo-chemical transformation of an insoluble polymer into ceramics through a polycarbosilane fiber forming intermediate state. Research in this field proved that under specific conditions, polysilanes could produce elemental silicon. Therefore, it was shown that irradiation in UV light or thermal processing lead to a slight enrichment in elemental silicon especially when the material is deposited as a thin layer.

This work presents that a specific polysilane structure is capable of producing small particles of elemental silicon and that the dimension of these particle could be controlled through the polymer structure. Formation of the elemental silicon particles starts at room temperature by self-induced chemical processes.

A particular case is when a small altering of the main chain chemical structure causes major transformations of the polymer basic properties or the appearance of unexpected ones.

Through this procedure a special class of polysilanes was investigated. These polymers were obtained by the reductive coupling of diphenyldichlorosilane in the presence of various amounts of methylchlorosilane. The resulted soluble high molecular weight poly[diphenyl-methyl(H)]silanes copolymers showed unexpected low

temperature processes which lead to the appearance of a separate phase formed by highly pure crystalline silicon. The dimension of these particles could be controlled through the amount of methylhydrosilyl units enclosed within the main polysilane chain.

2. Experimental

Materials

Diphenyldichlorosilane, $\text{Cl}_2\text{Si}(\text{C}_6\text{H}_5)_2$ (purum, >98%) and methylchlorosilane, $\text{CH}_3(\text{H})\text{SiCl}_2$ (purum, >98%) were purchased from Fluka and distilled prior to use.

Toluene and tetrahydrofuran (THF) were purchased from a commercial source and used after distillation over sodium wire.

Polymethylphenylsilane homopolymer (PSMF) was synthesized: $M_w = 62 \times 10^3 \text{ g} \cdot \text{mol}^{-1}$ and $M_w/M_n = 1.32$. IR (KBr): 3020-3000 (C-Har), 2920 and 2850 (C-H), 1210 and 870 (Si-CH₃), 750 and 700 (Si-C), 470 (Si-Si) cm^{-1} . ¹H-NMR (CDCl_3): $\delta = 0.05-0.15$ (broad, Si-CH₃), 7.2-7.5 (m, -SiC₆H₅). ¹³C-NMR (CDCl_3): $\delta = -4.0$ (-SiCH₃), 125.3-133.2 (Si-C₆H₅). UV-VIS (CHCl_3): $\lambda_{\text{max}}(\epsilon) = 280$ (8000); 330 ($15800 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$).

Apparatus

FTIR spectra were recorded with an FTS 40A Bio-Rad spectrometer at room temperature on KBr pellets. ¹H-NMR and ¹³C-NMR spectra were recorded with a Bruker NMR instrument (Model DRX 400 MHz). Chemical shifts are given in parts per million (ppm) without TMS as internal standard.

GPC experiments were carried out in THF solution at 30°C, at a flow rate 1 cm^3/min using a Spectra Physics 8800 gel permeation chromatograph.

Thermogravimetric analysis was performed in air on a MOM Paulik-Paulik-Erdey derivatograph at a 10 °C/min heating rate, then in nitrogen using a thermogravimetric cell Mettler 851e, at a heating rate 15 K/min.

Differential scanning calorimetry (DSC) measurements were carried out in a Mettler DSC12E calorimeter at a heating rate of 10 °/min., in air.

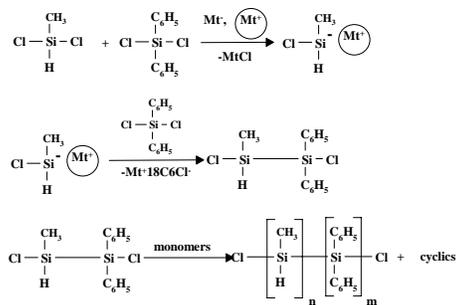
The polarized light microscopy (PLM) study was made using an Euromex 90 95 trinocular microscope equipped with an infrared controlled heating bench. Samples of polysilanes were prepared by depositing the polymer powder between two thin glass slides which were then mounted on the heating bench of the microscope. These samples were then heated with a constant rate of 10 °C/min until complete melting of the polymer. The heating process was stopped when the temperature reached 200 °C and allowed to cool down to the room temperature.

The XPS measurements were carried out in an Ultra High Vacuum (UHV). The unmonochromatized AlK α line at 1486.6 eV and constant analyzer pass energy of 97 eV, giving a full width at half maximum (*fwhm*) of 1.7 eV for the Au4f_{7/2} peak, were used in all XPS measurements. The XPS core level spectra were analyzed with a fitting routine that decomposes each spectrum into individual mixed Gaussian-Lorentzian (G-L) peaks after a Shirley background subtraction. The error in the XPS core level peak positions for a good signal to noise ratio is ± 0.05 eV. The binding energy (*BE*) scale was calibrated by assigning the main C1s peak at 284.6 eV.

The polymers in the form of powder were pressed in pellets under ambient atmosphere, before their introduction to the UHV system.

Synthesis of poly[diphenyl-co-methyl(H)silane]

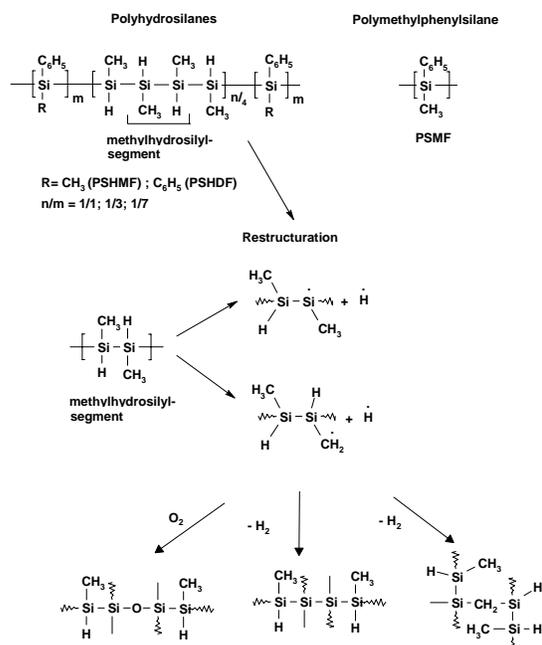
The synthesis of the polydiphenylsilane copolymer with a variable content of Si-H groups and narrow molecular weights distribution was performed through the homogeneous coupling of diphenyldichlorosilane with calculated amounts of methyl(H)dichlorosilane (Scheme 1 and 2).



Scheme 1

30 cm³ of a 0.2 mol/dm³ THF solution of sodium/potassium alloy complex with 18-crown-6 was titrated with the THF solution (0.2 mol/dm³) of a CH₃HSiCl₂/ (C₆H₅)₂SiCl₂ mixture at -75 °C in argon atmosphere until discoloration of the blue metal solution occurred. Next, the reaction was quenched with 2 cm³ of methanol and the solvent was evaporated. The remaining product was extracted two times with 5-10 cm³ of chloroform and combined chloroform extracts were washed with water. Finally a white solid polymer was obtained by precipitation from the chloroform solution with 100 cm³ of methanol. Yield: 75%. After separation

the polymer was fractionated in 100 cm³ of boiling diethyl ether. The solid fraction representing the product was filtrated and vacuum dried at 50 °C for 24 h.



Scheme 2

A varying composition of the poly[diphenyl-co-methyl(H)]silane (PSHDF) was obtained through selection of the CH₃HSiCl₂/ (C₆H₅)₂SiCl₂ monomers ratios as: 1/1 (a-PSHDF), 1/7 (b-PSHDF) and 1/20 (c-PSHDF).

IR (KBr): 3070-3000 (C-Har), 2980 and 2860 (C-H), 2080 (Si-H), 1455 and 1100 (Si-C₆H₅), 1250 and 880 (Si-CH₃), 750 and 705 (Si-C), 460 (Si-Si) cm⁻¹.

¹H-NMR (CDCl₃): δ = 0.15, 0.65 (Si-CH₃), 3.80 (Si-H), 7.3-7.6 (-SiC₆H₅). ¹³C-NMR (CDCl₃): δ = -8.2, -0.8 (Si-CH₃), 126.5-135.7 (Si-C₆H₅).

UV-VIS (CHCl₃):

a-PSHDF, λ_{\max} (ϵ) = 285 (6500); 350 (14800 L · mol⁻¹ · cm⁻¹).

b-PSHDF, λ_{\max} (ϵ) = 280 (6600); 340 (14300 L · mol⁻¹ · cm⁻¹).

c-PSHDF, λ_{\max} (ϵ) = 283 (6800); 330 (14500 L · mol⁻¹ · cm⁻¹).

PSMF, λ_{\max} (ϵ) = 280 nm (6000); 340 nm (14700 L · mol⁻¹ · cm⁻¹).

Photoluminescence (FL) experiments were performed on PSHDF samples in CHCl₃ solution and compared with results obtained for PSMF homopolymer. Excitation wavelength was fixed at 367.5 nm for PSHDF and 355.0 nm for PSMF.

GPC analysis was performed in solution (1% in chloroform). The Si-H functionalized polysilanes show the following unimodal molecular weights distributions:

- Mw = 50.2 × 10³ g · mol⁻¹ and Mw/Mn = 1.20, a-PSHDF;

- Mw = 45.1 × 10³ g · mol⁻¹ and Mw/Mn = 1.12, b-PSHDF;

- Mw = 48.0 × 10³ g · mol⁻¹ and Mw/Mn = 1.18, c-PSHDF;

Thermogravimetric analysis of polyhydrosilanes in air reveals two decomposition stages with the onset

temperatures bigger than 300 °C for the first stage and around 450 °C for the second as presented in Table 1.

In nitrogen, a-PSHDF shows two decomposition peaks with onset temperatures at 330 °C and 540 °C; b-PSHDF presents two decomposition stages starting at 250 °C and 470 °C respectively; c-PSHDF present a single decomposition peak with the onset temperature at 250 °C. TGA analysis of PSMF in nitrogen shows a single decomposition peak starting at 230 °C with maximum at 430 °C.

Table 1. Thermal analysis of polysilanes.

Sample	PSMF	PSHDF		
		1/1	1/7	1/20
<i>Mr</i>	-	1/1	1/7	1/20
T ₁ , °C	388	316, 330*	358, 250*	360, 250*
T ₂ , °C		465, 540*	466, 470*	466
T _g , °C	88	64	85	85
Exo peak, °C	-	101	135	135
Endo peak, °C	-	131	150	150

Mr = molecular ratio as prescribed;

T₁ = temperature corresponding to the first decomposition peak;

T₂ = temperature corresponding to the second decomposition peak;

* = measured in nitrogen;

T_g = glass transition temperature;

DSC shows similar analysis profiles for the investigated structures. Therefore all polymers have low T_g temperatures within 48-64 °C, an exothermic peak at 101-135 °C followed by an endothermic peak within 131-150 °C (Table 1).

Polarized light microscopy (PLM) was used to investigate the optical properties of polysilane samples scanned within 50-200 °C. During the melting process of a-PSHDF and b-PSHDF, the formation of small birefringent particles within the liquefied polymer drops was observed. This process stopped after 5-10 min and further heating or cooling did not produce any significant modifications (Fig. 1).

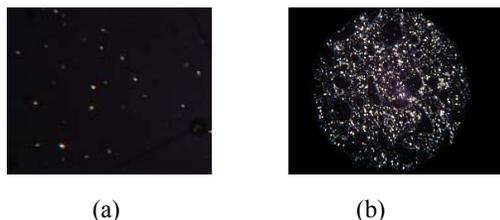


Fig. 1. PLM images of a-PSHDF: (a) at room temperature; (b) after melting.

Samples of c-PSHDF analyzed by PLM within the same temperature range produced different results (Fig. 2). Until beginning of the melting process no birefringent

particles formation could be observed. In polarized light, at temperatures higher than 180 °C, blue colored areas appeared within the liquefied polymer. After cooling to room temperature the sample maintained unaltered its aspect.

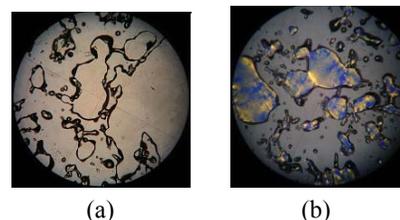


Fig. 2. Microscopy images of c-PSHDF: (a) non-polarized light; (b) polarized light.

PSMF homopolymer study by PLM showed an isotropic amorphous material within

the scanned temperature range. Slow cooling of the melted polymer did not produce any particles visible in polarized light (PL).

PLM analysis was performed also on polymer thin films. Therefore, at room temperature, a-PSHDF and b-PSHDF showed the presence of a very small amount of scattered particles visible in PL. Increasing the film temperature from 20 to 200 °C leads to formation of new particles. The process stops after maintaining the sample at the melting temperature for 5-10 min. Under the same conditions samples of PSMF films did not reveal the presence of particles visible in PL.

The XPS analysis was performed on a-PSHDF and b-PSHDF copolymers (Fig. 3). The results were compared with those obtained for the Si-H free homopolymer (PSMF#2). XPS spectra showing the core level Si2p photoelectron lines of the samples are presented in Fig. 3.

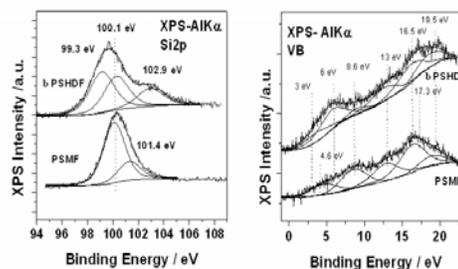


Fig. 3. XPS spectra.

3. Results and discussion

A polydiphenylsilane homopolymer structure is an insoluble crystalline material with a long range highly ordered conformation. Small amounts of methylhydrosilyl groups enclosed within the main chain of polydiphenylsilane could affect in an unpredictable manner its physico-chemical properties.

This work reveals the presence of some new and intriguing chemical processes in polyhydrosilanes. It is

shown that the methylhydrosilyl- fragments enclosed within the polysilane chain are thermally unstable and have the tendency to generate elemental silicon particles through local structural modifications.

The polyhydrosilanes structures with various reactive methylhydrosilyl contents studied within this work were prepared by low temperature homogeneous Wurtz coupling of diphenyldichlorosilane with controlled amounts of methylchlorosilane. The homogeneous reaction system was obtained using crown ethers sodium metal complexes solutions in THF. A specific mechanism ensures a high molecular weight monomodal distribution and avoids destruction of the Si-H reactivities through side reactions.

The spectral characterization shows the specific details related to the synthesized polyhydrosilanes. Therefore, it was observed that the main difference is concerned with the intensity of the signal assigned to the Si-H functionality. Using a high molecular ratio of $\text{CH}_3\text{HSiCl}_2/(\text{C}_6\text{H}_5)_2\text{SiCl}_2$ monomers it was possible to obtain a polyhydrosilanes structure containing an almost undetectable amount of Si-H groups. Experimentally was determined that a quantity of about 0.03 % reactive hydrogen was present within the polymeric structure. Therefore the IR spectrum of c-PSHDF did not show the characteristic Si-H absorption band at 2150 cm^{-1} . Only the 400 MHz $^1\text{H-NMR}$ analysis could reveal the chemical shift of the Si-H proton which is barely visible at $\delta=3.5$ ppm. Beside this, both the IR spectra and $^1\text{H-NMR}$ analysis displayed the signals corresponding to the assigned polymeric structures.

DSC thermal scanning of polyhydrosilanes samples shows, T_g values at temperatures below $60\text{ }^\circ\text{C}$ for all polyhydrosilanes excepting PSMF. As expected, a strong variation of the T_g values proportional to the amount of the methylhydrosilyl- segments (Table 1) could be observed. Since higher molecular ratios gave lower T_g values, the assumption that the methylhydrosilyl-fragments represent the flexible part of the polysilane backbone was confirmed. Increasing of the Si-H groups' content within polydiphenylsilane has a major effect only on the glass transition temperature (T_g) of polymer and less on the thermal decomposition onset temperature.

In addition, beside the T_g 's, the thermograms of polyhydrosilanes show an intriguing exothermic peak at $100\text{-}135\text{ }^\circ\text{C}$ with the position depending on the methylhydrosilyl content. The specific location in the proximity of the T_g and the shape of the peak indicate that this transition could be the result of some unexpected self-induced chemical transformation of the methylhydrosilyl-segments. Further investigations focused on these processes to reveal their nature and effects.

The TGA analysis performed both in air and under nitrogen atmosphere shows that in all cases the thermal decomposition of the polyhydrosilanes starts above $350\text{ }^\circ\text{C}$. Because the DSC exotherm is located within the thermally stable domain resulted that these self-induced processes proceed without any measurable weight loss solely by re-arrangements of the methylhydrosilyl fragments into thermally stable products which should remain in the polymer sample.

To observe the effects of these self-induced chemical processes, PLM studies were performed on the synthesized

polysilanes. By this technique it was observed that polyhydrosilanes thin films contain scattered small particle visible in polarized light which did not appear in the case of PSMF homopolymer. Moreover, polysilanes with various contents of Si-H groups contain various amounts of particle. The same situation was observed even in thin polyhydrosilane films obtained by deep coating. When the studied samples were heated to the melting temperature, the number of particles visible in PL increased significantly. Melting of polymer with extremely low content of Si-H, as in the c-PSHDF case, lead to the appearance of blue colored large area also visible in polarized light. Repeated cooling or heating did not modify significantly the sample presentation. The presence of the small particles was not observed in PSMF homopolymers films. If this observation is connected with the DSC and TGA data it could be assumed that the formation of the particles is the result of the self-induced restructuration processes at the methylhydrosilyl fragments level. By comparing the number and dimension of particle resulted from polysilanes a-PSHDF and b-PSHDF with those of c-PSHDF it could be observed that there is a relation between the dimension of the methylhydrosilyl fragments and the number/ dimension of the produced particles. In the c-PSHDF case, the particles could not be observed at room temperature. But, the appearance of the blue colored regions at high temperature clearly indicates the existence of small particles which are able to scatter the light generating the well-known Tyndal (Reyleigh) effect. The dimension of these particles is far smaller than that observed for polyhydrosilanes a-PSHDF and b-PSHDF. It is evident that through the methylhydrosilyl fragments dimension or comonomer ratio it is possible to control the dimension of the particles.

To get information concerning the nature of the particles further analyses were carried out by XPS.

The survey spectra of a-PSHDF compared with PSMF reveal the Si2p, Si2s, C1s and O1s photoelectron lines. An estimate of the Si2p *BE* (Fig. 3) in the bonding environment of $(-\text{Si}(\text{C}_6\text{H}_5)(\text{CH}_3)-)_n$ can be obtained from the group shift scheme proposed by Gray et al. [11] The experimentally observed $BE=100.1\text{ eV}$ (76% of the total Si2p signal for PSMF) is very close to the scheme estimate of 100 eV for a Si atom coordinated by two other silicon atoms a phenyl and a methyl group.

Concerning the second Si2p peak, according to the same scheme, if one of the two silicon atoms is replaced by oxygen then the Si2p peak would shift for another 0.95 eV resulting $BE\sim 101\text{ eV}$, a value that is close to the one experimentally observed.

The C/Si and O/Si surface atomic ratios were calculated from the total intensities of the C1s, Si2p and O1s peaks, corrected by their atomic sensitivity factors 0.25, 0.27 and 0.66 respectively, and by the inelastic mean free paths of the photoelectrons on question assuming a model semi-infinite solid with homogeneous composition. It was found that for PSMF $C/Si=7.1$ that is close to the nominal value for this structure. The O/Si atomic ratio was 0.43. If for the calculation of the oxygen content only the Si2p peak at $BE=101.4\text{ eV}$ is considered, then $O/Si(\text{ox})=2$ suggests that about 24% of the silicon atoms are coordinated with two oxygen atoms. In this

case, the C/Si ratio close to the nominal indicates that the surface of the sample is slightly contaminated with graphitic like species.

The C1s spectrum of sample b-PSHDF consists of two main components at $BE=284.6$ eV (C-C, C=C and C-H species) and 286.1 eV (C-O). The weak signal at the high BE side of the main peak (~ 292 eV), is the shake up satellite due to the phenyl groups.

The Si2p spectrum of the sample has been analyzed into three components at BEs 99 eV, 100 eV and 102.9 eV. The component at 102.9 eV represents partially oxidized Si atoms (27%). The O/Si surface atomic ratio is calculated to be 0.82. If only the Si2p peak with $BE=102.9$ is considered then the calculated $O/Si(ox)=3.5$ shows that part of the oxygen detected here is bonded directly to C atoms. The C1s spectrum of b-PSHDF consists of only one component at 284.6 eV (C-C). The C/Si =10.9 atomic ratio calculated taking into account the total C1s and Si2p signals is close to 10.6, a value which is expected for a $Ph_2Si/MeHSi=7/1$ molar ratio. The difference is probably due to surface contamination of the sample by residual graphitic like carbon species.

Most interesting is the appearance of the peak at 99 eV representing elemental Si. The intensity of this peak is about 32.5% of the total Si2p signal.

Fig. 3 shows the valence band region of samples b-PSHDF and PSMF analyzed with mixed G-L components each one having $fwhm=4$ eV. Comparison of the two spectra reveals that at sample b-PSHDF an additional peak appears at $BE=6$ eV and can be attributed to Si-Si bonds.^[14] This peak is very prominent in agreement with the Si2p spectrum that indicates the existence of elemental Si. The peak at 19.5 eV assigned to -C-C- bonds from phenyl groups is more prominent at sample b-PSHDF. The peak at 4.6 eV (sample PSMF) has been shifted towards lower BEs (closer to the Fermi level) in the case of b-PSHDF ($BE=3$ eV).

The presence of oxygen is inevitable since the sample has not been prepared in situ and has been exposed to the atmosphere. Therefore, the oxidized Si atoms resulted from the oxidation reactions with the molecular oxygen trapped inside the solid polymer matrix. These processes take place differently. The increased O/Si(ox) atomic ratios obtained in the PSHDF case resulted from the additional contribution of the methylhydrosilyl- segments which participate to oxidative processes.

On the other side, the XPS analysis shows an unexpected phenomenon which takes place only in polyhydrosilanes. As could be seen from Fig. 3, even at low temperatures this kind of structure is able to generate small amounts of elemental silicon (sample b-PSHDF) which are proportional with the Si-H content. This enrichment in silicon was observed previously only when polysilanes had been exposed to intensive irradiation with high energy UV light due to photodecomposition of the -Si-CH₃ bond and the formation of various species of reactive silyl.

Therefore, through the XPS analysis it was shown that within the polyhydrosilane films small particles of elemental silicon appear.

4. Conclusions

Formation of the silicon particles is the result of a self-induced chemical process with restructuration at the methylhydrosilyl- fragments level. It seem that a linear methylhydrosilyl structure manifest a high structural instability due to the high tendency of hydrogen to react both with oxygen or another hydrogen atom with formation of more thermodynamically stable structures. Until now the sole stable hydridosilyl- known compounds are cyclic. Recent studies showed that these compounds could easily generate in high yields crystalline silicon material which could be processed further to various optoelectronic devices. The use of polyhydrosilanes offers another approach in obtaining crystalline silicon but also opens new possibility toward the quantum dimension of optoelectronics.

Acknowledgements

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