

Silicon based materials for biooptoelectronics

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Abstract

This work presents a new class of σ -conjugated silicon-based polymers. Polyhydrosilanes were synthesized by coupling of methylchlorosilane with methyl- and diphenyldichlorosilane in a homogeneous system using soluble metal complexes of crown ethers. Investigations concerning optoelectronic properties of these materials were performed by spectral analysis. In view of applications as biosensors the synthesized polyhydrosilanes were submitted to bio-compatibility tests.

Keywords: silicon; biosensor; biocompatibility; cell culture.

Introduction

Polysilanes are a distinct class of conjugated polymers where the spatially delocalized band-like structure involves σ electrons and is similar to the alternating single and double bonds in polyenes [1-6]. This peculiar structure allows the motion of the charge carriers within the conjugated backbone and gives them conductive properties [7-10].

Polyhydrosilanes are a relatively new class of polyorganosilanes containing unsubstituted hydrogen side groups. This class of polymers possesses different properties compared to poly(diorganosilylene)s. Polyhydrosilanes can undergo oxidative crosslinking through pyrolysis or irradiation in the presence of oxygen [11] as well as they can also react with some functional compounds such as acrylonitrile, alcohols, or mercuric acetate [12].

Polyhydrosilanes can be synthesized using common Wurtz-type reductive coupling reaction in heterogeneous system with dispersed metallic sodium in toluene at 100°C. This method leads usually to polymodal molecular weight distributions, low yields and cyclic products in important amounts ranging up to 40% depending on the substituents in the polymer [13].

It was found that using the homogeneous reductive coupling of methyl(H)dichlorosilane, in THF solution of sodium/potassium alloy complex with 18-crown-6 having well defined composition of alkali metal ion pairs ($Mt^{(+)}/crown\ ether, Mt^{(-)}$) and negligible amount of electrons [7,8] at low temperature, it is possible to obtain in relatively high yield polyhydrosilanes possessing unimodal narrow molecular weight distribution [14].

Important results were obtained in the domain of polysilanes with unconventional structures [15-17] by discovering new reaction procedures and mechanisms, resulting in new chemical structures with unexpected properties and applications. Synthesis of a reactive polysilane

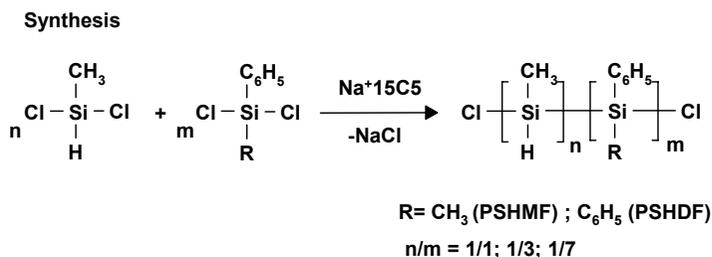
structure [13] made possible the exploitation of the semiconductive property of polysilanes by taking into account a new concept. This is based on the idea of a new conduction mechanism due to the attachment to the main polysilane chain of some electrono-active groups. Such polymer could work like an electronic relay sensitive to the electrochemical potential variation of the biological environment. This work shows the scientific results toward preparing a new polysilane useful for biosensors. Through this, the optoelectronic and biocompatibility properties of a poly[diphenyl-co-methyl(H)]silane copolymer are presented.

Materials and methods

Reagents. Diphenyldichlorosilane, methylphenyl-dichlorosilane and methyl(H) dichlorosilane (98.5% wt., from Aldrich) were distilled before use. 15-Crown-5 (15C5), (1,4,7,10,13-pentaoxacyclopentadecane) (from Fluka) was dried as described in ref. [7].

Measurements. The ^1H and ^{13}C spectra were recorded using a Varian VXR-300 multinuclear spectrometer in CDCl_3 at room temperature. GPC experiments were carried out in THF solution at 30°C , at a flow rate $1\text{ cm}^3/\text{min}$ using a Spectra Physics 8800 gel permeation chromatograph. FTIR spectra were recorded with an FTS 40A Bio-Rad spectrometer at room temperature in THF solution or in KBr. UV/VIS spectra were recorded in THF solution using a Beckman Acta M4 spectrometer. TGA and DSC analyses were performed using a MOM Paulik-Paulik-Erdey derivatograph and a Mettler DSC12E calorimeter respectively at a heating rate of $10^\circ\text{C}/\text{min}$., in air. Excitation and emission spectra were recorded in CH_3Cl solution using a Perkin-Elmer Hitachi MPF 43B spectrofluorometer at room temperature.

Synthesis of polysilanes. polymethylphenylsilane and polyhydrosilanes were synthesized in homogeneous system, through the reductive coupling of organodichlorosilanes in predetermined molar ratios, using Na-crown ether 15C5 complex in anhydrous toluene [14]. The following polysilane structures were obtained as white powders (Scheme 1):



Scheme 1. Reaction pathway

Polymethylphenylsilane- homopolymer (PSMF, yield= 75 %).

IR (KBr, cm^{-1}): 3020-3000 (C-Harom.), 2920 and 2850 (C-H), 1210 and 870 (Si-CH₃), 750 and 700 (Si-C), 470 (Si-Si).

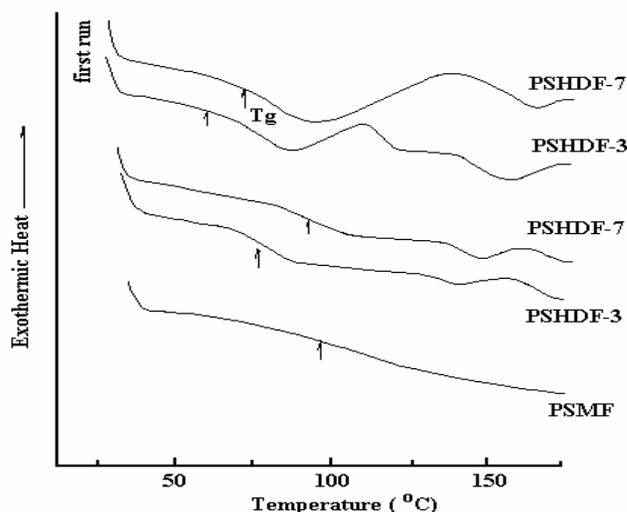
$^1\text{H-NMR}$ (CDCl_3): δ : 0.05-0.15 (broad, Si-CH₃), 7.2-7.5 (m, -SiC₆H₅).

$^{13}\text{C-NMR}$ (CDCl_3): δ : 4.0 (1C: -Si-CH₃), 125.3-133.2 (6C: -SiC₆H₅).

UV-VIS (CHCl_3): $\lambda_{\text{max}}(\epsilon)=280$ ($6000\text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$), 330 ($14600\text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$).

$M_w=62\times 10^3\text{ g}\cdot\text{mol}^{-1}$ and $M_w/M_n=1.32$

TGA analysis displays a single decomposition differential peak at 388°C . The DSC analysis shows a glass transition temperature (T_g) at 88°C (Figure 1).



PSHDF-3: polysilane with Mr= 1/3; PSHDF-7: polysilane with Mr= 1/7

Figure 1. DSC Thermogram

Poly[methyl(H)-co-methylphenyl] silane (PSHMF, yield =30 %).

IR (KBr, cm^{-1}): 3100-3000 (C-Harom.), 2950 and 2880 (C-Haliph.), 2050 (Si-H), 1230 and 880 (Si- CH_3), 750 and 700 (Si-C), 450 (Si-Si).

$^1\text{H-NMR}$ (CDCl_3): δ : 0.08-0.18 (broad, Si- CH_3), 3.5 (s, Si-H), 7.02-7.19 (m, - SiC_6H_5).

$^{13}\text{C-NMR}$ (CDCl_3): δ : 4.13 (1C: - SiCH_3), 8.9 (1C: H-Si- CH_3), 126.7-137.2 (6C: - SiC_6H_5).

UV-VIS (CHCl_3): $\lambda_{\text{max}}(\epsilon)=280$ nm ($6000 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$), 340 nm ($14700 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$).

$M_w=22 \times 10^3 \text{ g} \cdot \text{mol}^{-1}$ and $M_w/M_n=1.45$

TGA analysis shows two decomposition peaks as indicated in Table 1.

DSC analysis shows a Tg temperature (45-66°C), an exothermic peak (100-132°C) and an endothermic peak within 120-145°C (Table 1, Figure 1).

Molar ratio $\text{CH}_3(\text{H})\text{Si-}/(\text{CH}_3)(\text{C}_6\text{H}_5)\text{Si-}$ ($^1\text{H-NMR}$ and Si elemental analysis), Mr= 1/0.9, 1/2.5, 1/6.6.

Sample	PSMF	PSHMF			PSHDF		
Mr	-	1/0.9	1/2.5	1/6.3	1/0.8	1/2.0	1/5.8
T ₁ , °C	388	316	330	356	316	330	358
T ₂ , °C		470	475	470	465	466	466
Tg, °C	88	45	53	66	48	54	64
Tg, °C*	88	63	72	83	64	75	85
Exothermic peak		100	112	132	101	110	135
Endothermic peak		120	133	145	131	140	150

Table 1. Thermogravimetric analysis of polysilanes

Poly[methyl(H)-co-diphenyl]silane (PSHDF, yield= 70%).

IR (KBr, cm^{-1}): 3070-3000 (C-Harom.), 2980 and 2860 (C-Haliph.), 2080 (Si-H), 1455 and 1100 (Si- C_6H_5), 1250 and 880 (Si- CH_3), 750 and 705 (Si-C), 460 (Si-Si).

$^1\text{H-NMR}$ (CDCl_3): δ : 0.15-0.65 (broad, Si- CH_3), 3.80 (s, Si-H), 7.3-7.6 (- SiC_6H_5).

$^{13}\text{C-NMR}$ (CDCl_3): δ : 4.01 (1C: - SiCH_3), 8.2 (1C: H-Si- CH_3), 126.5-135.7 (6C: - $\text{Si-C}_6\text{H}_5$).

UV-VIS (CHCl_3): $\lambda_{\text{max}}(\epsilon)=285$ nm ($6500 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$), 350 nm ($14800 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$).

$M_w = 32 \times 10^3 \text{ g.mol}^{-1}$ and $M_w/M_n = 1.50$

TGA analysis gave two decomposition peaks as shown in Table 1. The DSC analysis shows a T_g temperature (48-64°C), an exothermic peak (101-135°C) followed by an endothermic peak within 131-150°C (Table 1, Figure 1).

$\text{CH}_3(\text{H})\text{Si-}/(\text{C}_6\text{H}_5)_2\text{Si-}$ ($^1\text{H-NMR}$ and Si elemental analysis), $M_r = 1/0.8, 1/2.7, 1/6.5$.

Photoluminescence (FL) experiments were performed on PSHDF samples in CHCl_3 solution and compared to results obtained for PSMF homopolymer. Excitation wavelength was fixed at 367.5 nm for PSHDF and 355.0 nm for PSMF (Figure 2).

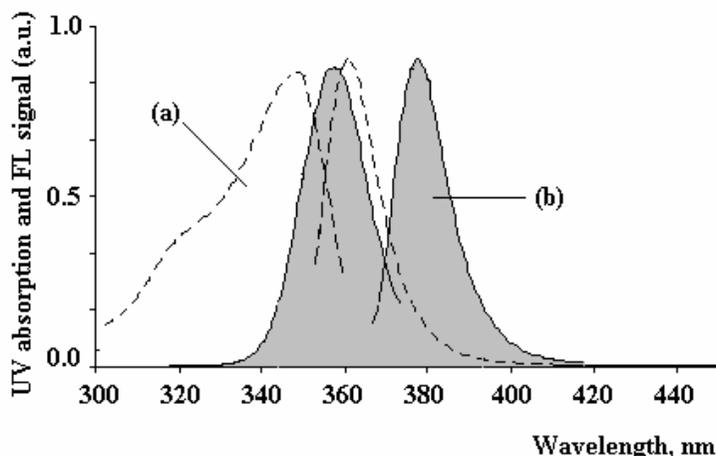


Figure 2. UV Absorption, FL of PSMF (a) and PSHDF (b) in CHCl_3 at room temperature

Results and discussions

Investigation of the optical properties of polysilanes

Polymethylphenylsilane, poly[methyl(H)-co-methylphenyl]silane, and poly[methyl(H)-co-diphenyl]silane were synthesized through homogeneous coupling reaction using 15C5 crown ether complex with Na. By this technique, high molecular weight polymers were obtained in opposition to earlier assumptions which present the sodium metallic particle as a necessary solid support [18].

TGA analysis of PSMF homopolymer shows a single decomposition peak at 388°C and two thermal decomposition stages for PSHMF and PSHDF with maxima depending more on the Si-H content than on the nature of the substituents (Table 1). This observation leads to the idea that during decomposition, oxidation processes start within the methylhydrosilyl-segments leading to a specific restructuring of the polymeric chain.

Further investigation by DSC shows a strong variation of the T_g values proportional to the amount of the methylhydrosilyl- segments (Table 1, Figure 1). Since higher molecular ratios gave lower T_g values, it was assumed that the methylhydrosilyl- fragments represent the flexible part of the polysilane backbone. Unexpectedly, the thermograms of PSHMF and PSHDF show an exothermic peak within 100-135°C depending also on the methylhydrosilyl content (Table 1, Figure 1). The specific position in the proximity of the T_g , the modification of the T_g value in the subsequent DSC runs and the shape of the peak indicate that this transition corresponds to the thermo-induced restructuring of the methylhydrosilyl- segments.

These processes occur without fragmentation of the main polymeric chain leading to formation of intermolecular bonds.

The UV spectrum of PSMF homopolymer shows an absorption band at 280 nm indicating the presence of σ - π transitions due to the phenyl substituent and another at 340 nm corresponding to the σ - σ^* transitions of the conjugated silicon chain which also could be observed in the UV spectrum of PSHMF. Because the position of the absorption maximum in polysilanes depends on the number of conjugated silicon atoms, it was assumed that the dimensions of the methylphenylsilyl segments in both structures were similar [1-4]. When two aryl groups are attached to the polysilane chain, like in PSHDF, the interaction between the π orbitals of the phenyls and the σ conjugated silicon chain lead to a decreased optical band gap, causing the absorption maximum to shift to around 350 nm.

PSMF and PSHDF structures were investigated further by FL measurements. The mirror-image relationship and the bandwidth between absorption and emission give information concerning the regularity of the main chain spatial conformation [19]. The FL spectral profile of PSMF with $fwhm = 25$ nm is very different from the mirror image of the absorption band at 340 nm indicating that the stiff helical chain conformation of PSMF has frequent irregularities generated by the chiral inversions or twisting from P to M motifs (Figure 2) [19]. In contrast, PSHDF show relatively narrow UV absorptions with $fwhm = 15$ nm and the FL spectral profile closer to the mirror image of the 350 nm absorption band. This is somehow surprising because the small methyl(H)silyl fragments which create bending and fractures of the main silicon chain, should produce a UV absorption maximum shift to lower wavelengths, widening of the bands and strong irregularities in the FL spectra. The absence of such effects indicates that the long diphenylsilyl segments with a stiff and regular helical global conformation [20] are coupled through trans-planar small fragments which eliminate the internal conformational tensions allowing a free rotation of the chain around the -Si-Si-Si-Si- dihedral angle of the methyl(H)silyl's. Therefore, the σ -electron delocalization within the polydiphenylsilane blocks is unaffected by the low temperature restructuring of the small methylhydrosilyl fragments.

Results of the biocompatibility tests

We chose a human adherent cell line to test the cytotoxicity and biocompatibility of the polysilane samples. Cells were grown in a cell culture medium supplemented with the polymers added as powder. Two days after cultivation of cells together with the samples, their morphology was investigated by optical microscopy and compared to that of control cells.

The cells adhere, proliferate and migrate on the cell culture dish surface. These events confirm that the materials tested are not cytotoxic, are biocompatible and do not interfere with basic cell processes. There is a difference though between cells grown with and without polysilane powders, and that is the growing rate of the cells. Hek293 cells cultivated in the presence of polysilanes grow slower. While in the control well the cells form a uniform monolayer, which covers almost entirely its surface, cells grown in the presence of polysilanes are semiconfluent.

We have determined the cell multiplication factor as the ratio between the number of cells grown after three days and the number of seeded cells. Results are shown below (Figure 3).

The viability of cells grown in polysilane media is in normal range, between 95% and 100%. From these preliminary experiments we can conclude that the materials tested are biocompatible. Cells adhere, grow and proliferate in the presence of PSMF and PSHDF-MF powders.

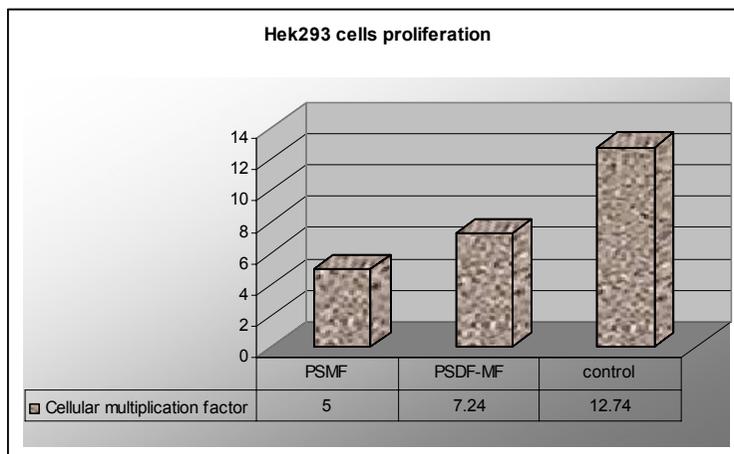


Figure 3. Hek293 cells cultured in standard conditions

Conclusions

Through this study we have presented the optoelectronic properties of some basic polysilane structures and proved the influence of the enclosed reactive units over the dimension of the hyperconjugated macromolecular fragments due to the apparition of new intermolecular bonding. On the other side, this work shows that the synthesized polysilanes are biocompatible materials. These properties could be exploited to create optoelectronic bio-transducers.

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References

1. H. GILMAN, W. H. ATWELL, G. L. SCHWEBKE, Ultraviolet properties of compounds containing the silico-silicon bond *J. Organomet. Chem.* 2: 369-371 (1964).
2. H. GILMAN, D. R. CHAPMAN, Molar absorptivities of some polysilanes *J. Organomet. Chem.* 5: 392-394 (1966).
3. W. G. BOBERSKI, A. L. ALLRED, Preparation of permethyloctadecasilane and permethyltetracosasilane *J. Organomet. Chem.* 71: C27-C28 (1974).
4. W. G. BOBERSKI, A. L. ALLRED, Properties of long-chain permethylpolysilanes *J. Organomet. Chem.* 88: 65-72 (1975).
5. C. SANDORFY, Calculations on saturated hydrocarbons and their substituted derivatives *Can. J. Chem.* 33: 1337-1351 (1955).
6. A. HERMAN, B. DREZEWski, W. WOJNOWSKI, The degree of s-bond delocalization in polysilanes and its influence on reactivity by through-bond interactions the PES scaled Sandorfy C approach *Chem. Phys.* 98: 475-481 (1985).
7. T. SKOTHEIM, *Handbook of Conducting Polymers*, Marcel Dekker, New York (1986).

8. Z. HEPING, L. CHENGYOU, K. MITSUO, S. YUSABURO, Excimer-like emission of an novel s-p alternating polymer 2,2'-bipyridyl in the backbones *J. Phys. B: At. Mol. Opt. Phys.* 32: 225-230 (1999).
9. F. C. GROZENA, L. D. A. SIEBBELES, J. M. WARMAN, S. SEKI, S. TAGAWA, U. SCHERF, Hole conduction along molecular wires: s-bonded silicon versus p-bond-conjugated carbon *Adv. Mater.* 14: 228-231 (2000).
10. N. TAKADA, T. KAMATA, D.C. BRADLEY, Polariton emission from polysilanes-based organic microcavities *Appl. Phys. Lett.* 82: 1812-1814 (2003).
11. D. J. CARLSSON, J. ROOVERS, D. J. WORSFOLD, L. L. ZHOU, Synthesis polycarbosilanes as precursor for silicon-carbide ceramics *ACS Polym.Prep.* 31: 268-269 (1990).
12. H. QIU, Z. DU, Organosilane polymers: formable polymers containing methylsilylene units *J. Polym. Sci., Part A: Polym.Chem.* 27: 2849-2860 (1989).
13. G. SACARESCU, N. VOICULESCU, M. MARCU, L. SACARESCU, R. ARDELEANU, M. SIMIONESCU, Polyhydrosilanes 1. Synthesis *J. Macromol. Sci., Pure Appl. Chem.* A34: 509-516 (1997).
14. G. SACARESCU, L. SACARESCU, R. ARDELEANU, P. KURCOK, Z. JEDLIŃSKI, Si-H functional polysilanes via homogeneous reductive coupling reaction *Macromol. Rapid Comm.* 22: 405-408 (2001).
15. L. SACARESCU, G. SACARESCU, R. ARDELEANU, Crosslinkable silyldihydroarilenes *J. Macromol. Sci.-Pure Appl. Chem.* A39, 103-107 (2002).
16. L. SACARESCU, R. ARDELEANU, G. SACARESCU, M. SIMIONESCU, Synthesis of new polysilane-crown ether *Eur. Polym. J.* 40(1): 57-62 (2003).
17. G. SACARESCU, R. ARDELEANU, L. SACARESCU, M. SIMIONESCU, Synthesis of polysilane-bis(salicylidene)ethylenediamine Ni(II) complex *J. Organomet. Chem.* 202: 685-689 (2003).
18. G. ZIEGLER, J. HEINRICH, G. WOTTING, Review relationships between processing, microstructure and properties of dense and reaction-bonded silicon nitride *J. Mater. Sci.* 22: 3041-3086 (1987).
19. M. FUJIKI, Ideal exciton spectra in single-and double-screw-sense helical polysilanes *J. Am. Chem. Soc.* 116: 6017-6018 (1994).
20. M. FUJIKI, J. R. KOE, K. TERAOKA, T. SATO, A. TERAMOTO, J. WATANABE, Optically Active Polysilanes. Ten Years of Progress and New Polymer Twist for Nanoscience and Nanotechnology *Polym. J.* 35(4): 297-303 (2003).