ACTA CHEMICA IASI, **17**, 121-135 (2009)

Polyhydrosilanes – New Materials with NLO Properties

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Abstract: This work presents new polysilane structures with potential in optoelectronic applications. For this purpose a new polydiphenylsilane structure enclosing small methylhydrosilyl units was created. The electronic spectra of this material reveal the presence of chromophore units as in polymethylphenylsilane, a material which is already in exploitation. Using this structure, new polysilane structures were created by enclosing of electrono-donating metal complex fragments without afecting of the σ-chromophores. The optical properties of these materials could be useful in obtaining of new optoelectronic devices.

Keywords: Polyhydrosilane; optoelectronic properties; polysilane-metal complex.

Introduction

Polysilanes are a specific class of conjugated polymers with intriguing

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optoelectronic properties originating from an unexpected σ-conjugation.[1,2]

The electronic properties of polysilanes could be understood considering two main conjugative effects.

First, a σ conjugation which suggests an interaction and delocalization of σ-electrons, although formally the backbone is saturated.[3] The σ-delocalization can be adequately described by molecular modelling theoretical approach.

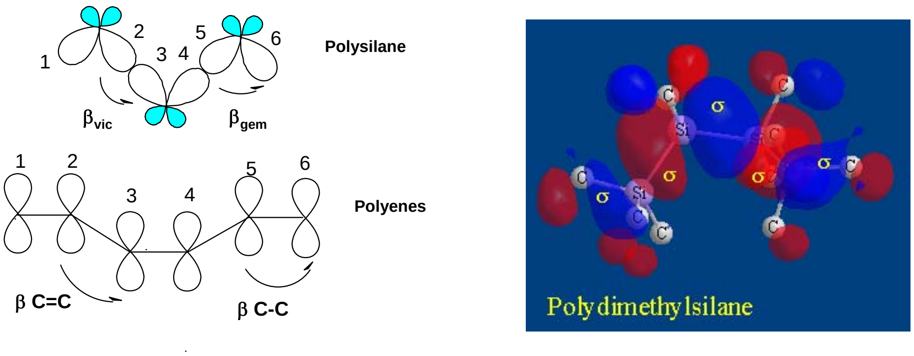


Figure 1. σ- Electrons delocalization in polysilanes.

This model presents the electronic structure of the polysilanes qualitatively as being similar to the alternating single and double bonds in polyenes. The alternation of resonance integrals in the polysilanes is provided by the difference in the values of the vicinal and geminal resonance integrals of sp^3 hybrids. In the simple model the conformation of the backbone is not taken into account. The transition in polysilanes is of σ–σ* type. The excitations correspond to a transition from the Si-Si bonding backbone orbital of s symmetry (HOMO) to the most stable Si-Si antibonding backbone orbital of σ symmetry (LUMO).[4,5] Another interesting fundamental problem in spectroscopic studies of polysilanes, but also of copolymers having silanylene units in the main chain, is the so called σ–π conjugation resulting from the interaction between Si-Si σ-orbitals and C=C π-orbitals. Interest in the electronic properties of aromatic substituted polysilanes was stimulated in the early 1960's by the observation of the strong red shift of the absorption maxima in phenyldisilanes compared to phenyltrimethylsilane.[6] This effect has been explained by an interaction between the Si-Si σ bond and the π system, resulting in so called σ–π conjugation. The effect operates in a direction opposite to the inductive effect and results in a net electron-accepting character of silicon substituents when they are linked directly to a π-donor center such as benzene or thiophene. So, the Si-Si bond is able to conjugate with π-systems.

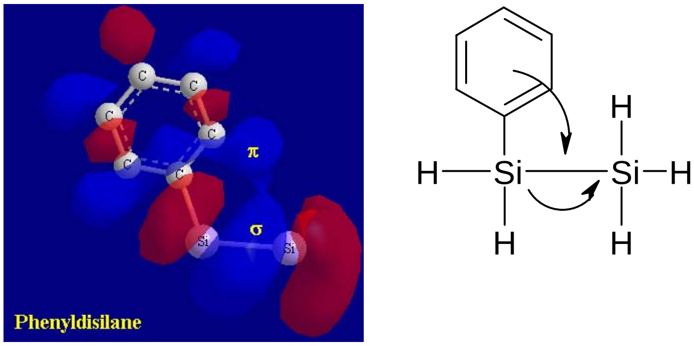


Figure 2. σ–π Conjugation in phenyldisilane.

Nonlinear optics (NLO) deals with the interaction of electromagnetic fields (light) with matter to generate new electromagnetic fields, altered with respect to phase, frequency, amplitude or other propagation characteristics from the incident field. A major advantage of the use of photonics is the possibility to increase the speed of information processes such as optical computing. One of the most intensively studied nonlinear optical phenomena is the second harmonic generation or frequency doubling. By this process near infrared laser light with frequency ω can be converted by a NLO material to blue light with frequency 2ω. The resulting wavelength is half the incident wavelength and hence it is possible to store information with a higher density.

It is obvious that the required properties of the NLO materials depend on the application that they are used for. The ease of modification of organic molecular structures makes it possible to synthesize tailor-made molecules and to adjust the properties to the desired application. In the case of second-order nonlinear optical processes, the macroscopic nonlinearity of the material is derived from the microscopic molecular nonlinearity in relation with the electronic structure and geometrical arrangement of the NLO-chromophores.

Organic molecules that exhibit second-order nonlinear optical properties usually consist of a delocalized π-system, enclosing either a donor or acceptor substituent or both. This asymmetry leads to a high degree of intramolecular charge-transfer interaction from the donor to acceptor, which generates a large second-order nonlinearity.[7,8]

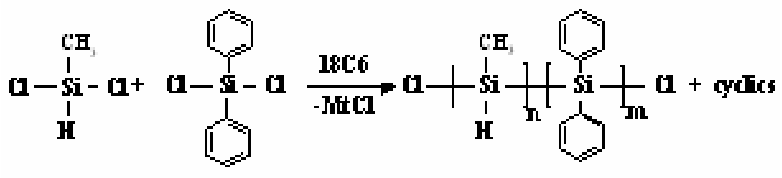
Most NLO compounds of this kind are absorbing in the visible spectrum. For a high-density optical storage, complete transparency in the visible is required. One approach to achieve this property is balancing the electro-active properties of the donor and acceptor substituents.[9] Another approach is the synthesis of molecules with a (σ-π)-conjugated frame.[10]

Polysilanes are promising materials for optoelectronics and their NLO properties are under consideration. Theoretical calculations made on simplified unit cells built using silicon atoms substituted only with hydrogens demonstrate clearly the formation of specific σ-chromophores.[11]

This work opens a new research field within the polysilane optoelectronics by taking advantage of new polymeric structures and concepts. Investigations of the electronic influences over the σ-chromophore formation in relation with various electroactive segments attached to the main chain were also presented.

Experimental

A soluble polydiphenylsilane (PSHDF) was obtained in homogeneous system by the reductive coupling of organodichlorosilanes in predetermined molar ratios using Na-crown ether 18C6 complex in solvent anhydrous toluene[12] (Scheme 1).



Scheme 1

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

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

^{13}C-NMR ($CDCl_3$): δ= -8.2, -0.8 (Si-CH_3), 126.5-135.7 (Si-C_6H_5).

UV-VIS ($CHCl_3$): λ_{max} (ε)= 285 (6500); 350 (14800 L $mol^{-1}\cdot cm^{-1}$).

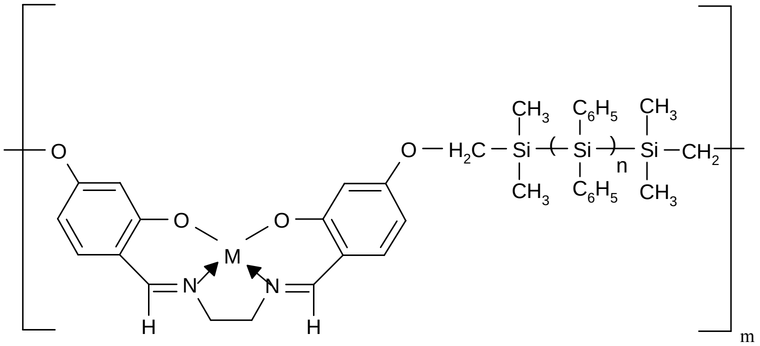
Mw= $32x10^3$ g.mol^{-1} and Mw/Mn= 1.50.

By taking advantage of the Si-H functionality new polysilanes could be obtained by enclosing of ligand fragments. Further complexation with various metal cations lead to polysilanes-metal complexes. Through this method both linear and pendent structures could be obtained.

A linear polysilane-metal complex structure was obtained using a chlorofunctionalized polysilane and N,N'-Bis(4-hydroxysalicylidene) ethylenediamine.[13]

The ligand synthesis and complex formation were made using a standard procedure involving first, salicylaldehide reaction with diamine and then the Ni (II) complex formation using an aqueous solution of nickel acetate.[14]

Linear polysilane-metal complex



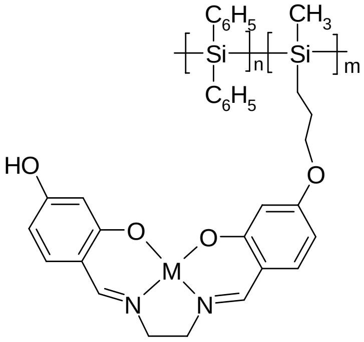
^{1}H-NMR spectrum (d ppm, DMSO): 3.80, s, 4H, -N-CH2-; 6.5-7.2, m, 6H (arom); 8.30, s, 2H, -CH=N-; 13.2, s, 4H, OH.

IR spectrum of polysilane-metal complex (λ, cm^{-1}): 3050, ν Car-H; 2830-2910, ν Calif-H; 1645-1650, ν C=N; 1530, 1460 ν C-C; 1250, ν, Si-CH_3; 1010-1100 overlapping (C-N, C-O-); 800, ν C-H; 435-500, Si-Si.

UV-VIS spectrum (λ, nm): 390 (π-d MLCT); 320 (σ–σ* or π–π* polysilane); 270 (π–π* phenyl).

TGA analysis: 100 ^{o}C - 200 ^{o}C water loss; 200 ^{o}C - 470 ^{o}C polymer decomposition; 41.63 % ash (SiO_2 + NiO) .

Pendent polysilane-metal complex was obtained by side-coupling of the poly[bromo-propyl-co-diphenyl]silane with N,N'-Bis(4-hydroxy salicylidene)ethylenediamine:[15]



^{1}H-NMR (DMSO-d$_6$): δ= 0.15 (m, -Si-CH$_3$), 1.5 (s, H^{10}), 2.01 (s, H^{9}), 3.62 (s, -N-CH$_2$-), 4.15 (s, H^{8}), 4.21 (s, Si-H), 6.2-7.05 (m, H$_{ar}$), 8.27 (s, H^{7}).

IR (KBr): 3050 (Car-H), 2830-2910 (C-H), 2150 (Si-H), 1645-1650 (C=N), 1530 1460 (C-C), 1250 (Si-CH$_3$), 1010-1100 overlapping (C-N, C-O-), 800 (C-H), 435-500 (Si-Si) cm^{-1}.

^{13}C-NMR (DMSO-d$_6$): δ= -2.5 (Si-CH$_3$), 64.81 (-CH$_2$-CH$_2$-), 69.52 (C^{8}), 113.40 (C^{3} and C^{5}), 129.27- 133.02 (Car), 162.12 (C^{7}).

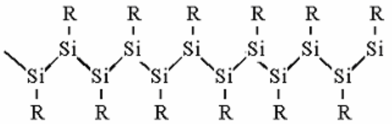
UV-VIS (DMSO): λ_{max} (ε)=206 (2500); 280 (600); 330 (1480 L·mol^{-1}·cm^{-1}).

Results and discussions

To obtain new materials with improved optoelectronic properties both the main polysilane chain and nature of attached substituents must be changed. The first step toward new polysilanes with NLO properties was to obtain a new structure of the main chain with extended s-electrons delocalization and a functionality which could be used to attach various electroactive groups.

Previous work[16] demonstrates the utility of the perfectly symmetric polydimethylsilane structure which, due to the optoelectronic properties is presently used in flat panels display devices.

This work presents a new polysilane built onto a highly symmetrical structure where the catenated silicon atoms are substituted only with phenyl groups. These polydiphenylsilanes are known as highly crystalline insoluble and infusible materials. Therefore it was decided to enclose within the main polymeric frame of small methylhydrosilyl- groups. This new structure, polydiphenylhydrosilane (PSHDF) presents entirely new and intriguing physico-chemical properties and due to its high stability to light irradiation should be considered as a potentially useful material for optoelectronics.[12]



- One-dimensional semiconductor (quantum wire)
- Luminescence with high quantum efficiency (30%)
- Photoconductivity with high hole mobility ($10^{-4} cm^2/Vs$)
- Wide band gap (3-4eV)

These electronic properties must be taken into account when discussing of optoelectronic properties of the synthesized polyhydrosilanes. Therefore important information could be draw from the electronic spectra of the materials.

The UV-VIS analysis of polydiphenylhydrosilane (PSHDF) shows the effect of the two aryl groups attached to the polysilane chain (Figure 3). In this case the interaction between the π-orbitals of the phenyls and the σ conjugated silicon chain lead to a decreased optical band gap, causing a bathochromic shift of the absorption maximum to around 350 nm. When alkyl groups are present like in homopolymers (polymethylphenylsilane, PSMF) the absorption maximum is located at 280 nm.

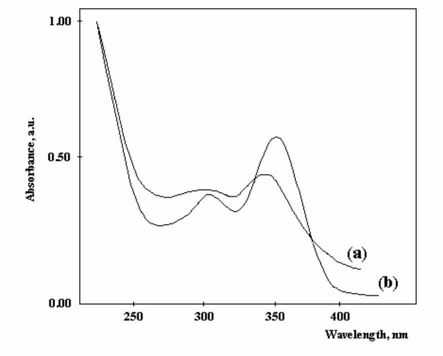


Figure 3. UV Spectrum of PSMF (a) ; PSHDF (b).

The PSHDF structure was investigated further by FL measurements and compared with the FL spectrum of PSMF (Figure 4).

The mirror-image relationship and the bandwidth between absorption and emission give information concerning the regularity of the main chain spatial conformation[18] (Figure 5).

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.[17] 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[18] 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.

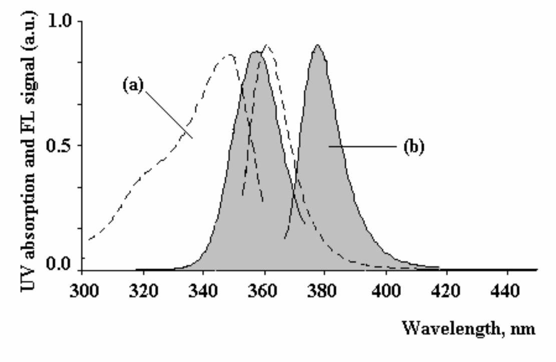
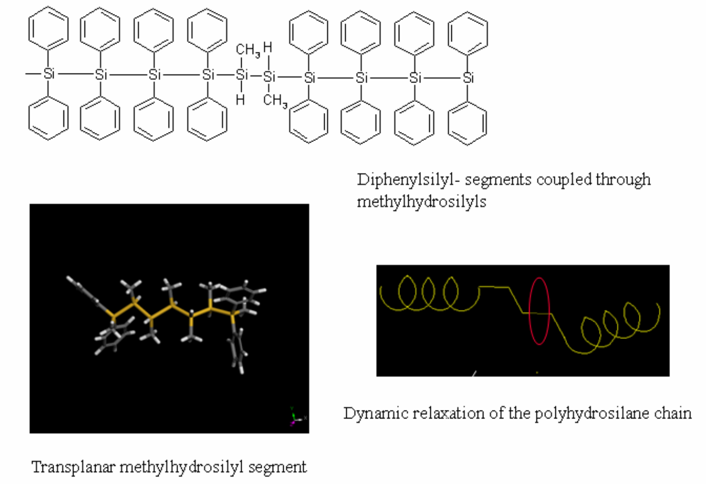


Figure 4. FL Spectra of PSMF (a) and PSHDF (b) in CHCl3 at room temperature.

Therefore, the electronic spectrum of PSHDF shows that the presence of the short methylhydrosilyl segments within the main polydiphenylsilyl chain has a "relaxing effect" of σ-chromophore by extending of the electrons delocalization around the flexible fragmentation points.



Diphenylsilyl- segments coupled through methylhydrosilyls

Dynamic relaxation of the polyhydrosilane chain

Transplanar methylhydrosilyl segment

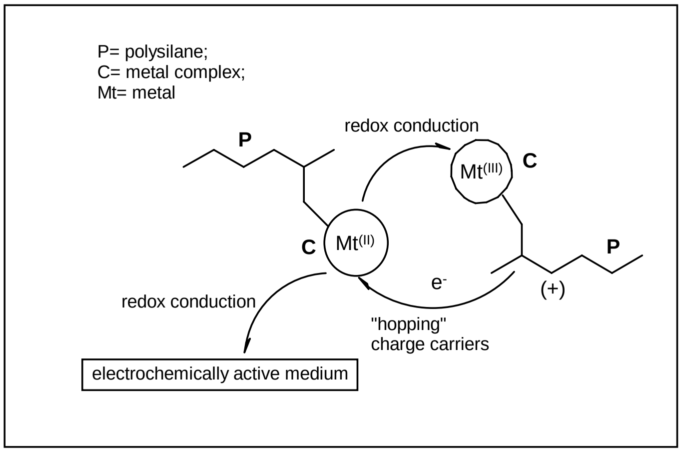
Figure 5. Main chain spatial conformation.

Using of this new structure opens the possibility to create new polysilane architectures by attaching of various groups to the Si-H reactivities.

These new polysilanic structures should overcome the presently organic NLO materials limits: poor efficiency, large operating voltages and short device lifetimes. To eliminate these disadvantages it is necessary to obtain new polymeric structures by increasing the molecular weight and extending of the σ-electrons delocalization; modifying the silicon substituents nature (replacing the methyls with phenyls increases σ–π conjugation effects); using electrons donor-acceptor systems (enclosing of π-electrons systems with specific properties).

Therefore, for a better exploitation of the NLO properties of polysilanes we realize that a new concept must be taken into account, a concept that combine the linear conjugative conduction of polysilane with the electronic properties of new electron- donor segments.

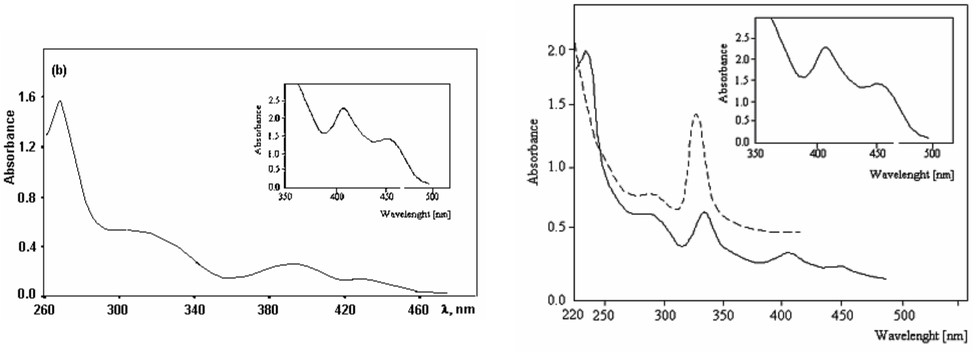
These new materials could be obtained by enclosing of metal complexes in polysilanes without the conjugative coupling of the Si-Si bonds with the metal complex.



Therefore, polysilanes, known as hole transporting materials (HTM), will carry electron acceptor metal complexes resulting in an ambipolar donor-acceptor polymer (p-n type). Moreover the redox character of the metal complex could function like an electronic relay when the material is in direct contact with electrochemically active media. When necessary, the interaction between the donor conjugated backbone and acceptor metal complex could be tuned by varying the chemical structure, substituents, nature of metal cation, length of the coupling bridge.

To investigate the electronic properties of the new polysilanes-metal complex we studied the UV-VIS spectra for both linear and pendant structures (Figure 6).

Both UV spectra show the specific $\sigma-\sigma^*$ transitions of polysilane at 320 nm in linear and 340 nm in pendant structure respectively. In addition absorption bands specific for salen-complex are present in the 380-460 nm and 400-480 nm regions respectively.



(a) (b)

Figure 6. (a) UV Spectrum of the linear structure: Polysilane-Ni complex; Salen-Ni complex (inset) λ σ–σ∗ : 320 nm; λ MLCT: 390; 430 nm; (b) UV Spectrum of the pendent structure: Polyilane (dashed); Polysilane-Ni complex; Salen-Ni complex (inset) λ σ–σ∗ : 340 nm;λ MLCT: 420; 450 nm.

The UV spectrum of the linear structure presents broad absorption bands at lower intensities than in the starting compounds. This suggests that the interferences between the conjugated σ-electrons delocalized in the polysilane segment and the metal-complex π-electrons system affect the conduction mechanism by increasing of the bandgap. The lower intensities of the absorptions bands are probably the result of the polysilane conformational changes within the range of 10 silicon atoms.

The UV spectrum of the pendant structure shows higher intensities for the σ–σ∗ transitions in polysilane at 340 nm. Also, the values of the wavelength remain almost unchanged comparing with the starting compounds. Therefore, we concluded that the pendant polysilane-metal complex is appropriate for a hybrid conduction mechanism study because in this case there seem to be no conjugative bridging with the metal complex moiety. The electronic properties of both segments remained unaltered by the coupling procedure and behave like separate entities, separating the electrono-donor character of the metal complex units from the main polymeric frame.

Conclusions

The chemical structure of polydiphenylsilane was modified to obtain both solubility in common solvents and to induce new properties by attaching of various organic segments. Thus, new polysilane structures were created by enclosing of electrono-donating metal complex fragments. The optical properties of these materials could be useful in obtaining of new optoelectronic devices.

Acknowledgements

To Romanian Ministry of Research and Education-MATNANTECH program, grant no. 36/2005 and no. 107/2006 for financial support.

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