Polysilanes. A New Route Toward High Performance EL Devices

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Summary: The discovery of a remarkable class of plastics that can conduct electricity has opened a new era of plastics science and technology that has just been recognized by the award of the 2000 Nobel prize for chemistry. They can be used to make a wide range of electronic devices such as transistors, light-emitting diodes, solar cells and even lasers, through much simpler manufacture than conventional inorganic materials, increasing flexibility, reducing cost, and opening up new markets. Polysilanes are subject of an intensive research work aiming to various optoelectronic applications. Through this work 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.

Keywords: optoelectronic properties; polyhydrosilanes; polysilane metal-complex

Introduction

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

Electroluminescent devices based on thin conjugated polymer films[1] and/or sublimed thin oligomer[2] layers are very attractive because of their application in flat, large-area displays.[3] In such devices, light emission is the result of the recombination of singlet excitons formed by the mixing of the negative and positive polarons,[4] injected from the cathode and the anode, respectively, under the applied electric field. To obtain equal numbers of positive and negative charge carriers in the emissive region a well balanced charge carrier injection[5] and good charge carrier transport[6] must be achieved. In case of an unbalanced charge carrier injection, the majority of carriers will each the counter electrode leading to a faster device degradation due to Joule heating.[7] The combination of electron transporting layers (ETL) and/or hole transporting layers (HTL) together with an emissive layer is responsive for improvement of the device performance.[8] These layers possess smaller barriers at the electrode/transport layer interface and gain better charge carrier transport due to higher charge carrier mobility. Additionally, the layers combination leads to a band offset at the interface to the emitting layer, where charge carriers accumulate. The excitons generated at this interface are protected from the quenching processes at the electrodes.[9]

Polysilanes with σ-conjugated Si main chains have been investigated in several EL configurations.[10] In these materials, the hole mobility have been estimated to be in the order of 10^{-4} cm^2 V^{-1} s^{-1}.[11] The charge carrier transport within the polysilanes is a thermally activated hopping process involving states associated with the σ-conjugated silicon backbone. In this case

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the hole mobility along a polysilane chain is strongly influenced by the conformational arrangement of the silicon backbone due to the presence of various substituents at the silicon atoms. Also these substituents determine the film forming properties, solubility and morphology of the polymer.[12]

From this point of view polysilanes are promising materials for optoelectronics and their EL and NLO properties are under consideration. Theoretical calculations made on simplified unit cells built using silicon atoms substituted only with hydrogen demonstrate clearly the formation of specific σ-chromophores.[13]

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 Part

To obtain new materials with improved optoelectronic properties both the main polysilane chain and nature of attached substituents must be changed.

This work presents a new polysilane build 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.

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[14] (Scheme 1)

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.

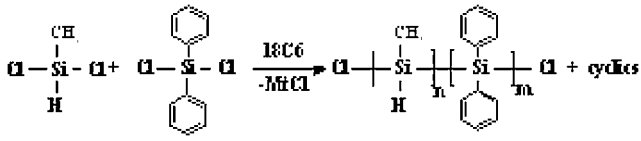
A linear polysilane-metal complex structure (Figure 1) was obtained using a chlorofunctionalized polysilane and N,N′-Bis(4-hydroxysalicylidene) ethylenediamine.[15]

Pendent polysilane-metal complex (Figure 2) was obtained by side-coupling of the poly[bromo-propyl-co-diphenyl]silane with N,N′-Bis(4-hydroxysalicylidene) ethylenediamine[16]:

Results and Discussion

Polysilanes are a specific class of conjugated polymers with intriguing optoelectronic properties originating from an unexpected σ-conjugation.[17,18]

A σ conjugation which suggests an interaction and delocalization of σ-electrons, although formally the backbone is saturated.[19] The σ-delocalization can be adequately described by molecular model-



Scheme 1.
Synthesis of polydiphenylsilane.

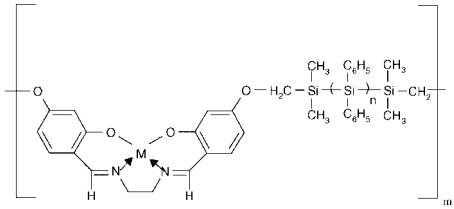


Figure 1.
Linear polysilane-metal complex.

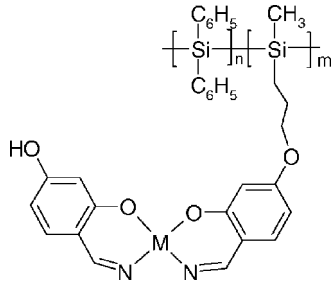


Figure 2.
Pendent polysilane-metal complex.

ing theoretical approach (Figure 3). 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

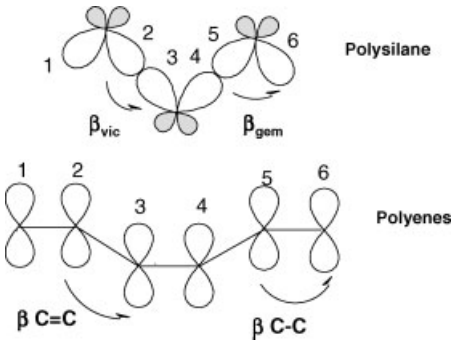


Figure 3.
Electronic structure of polysilanes.

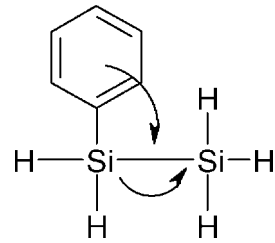


Figure 4.
σ–π Conjugation in phenyldisilane.

into account. The transition in polysilanes is of the 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 s symmetry (LUMO).[20,21]

Another interesting fundamental problem in spectroscopic studies of polysilanes, but also of copolymers having silarylene 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 (Figure 4).

The UV-VIS analysis of polydiphenylhydrosilane (PSHDF) (Figure 5) shows the effect of the two aryl groups attached to the polysilane chain. 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

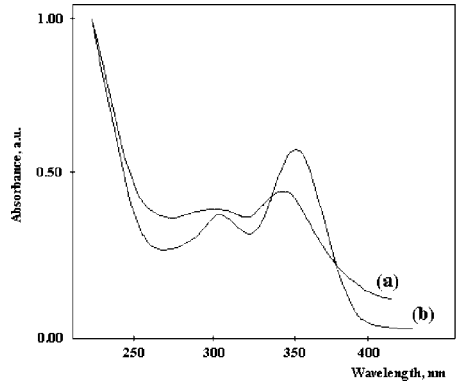


Figure 5.
UV Spectrum of PSHMF (a); PSHDF (b).

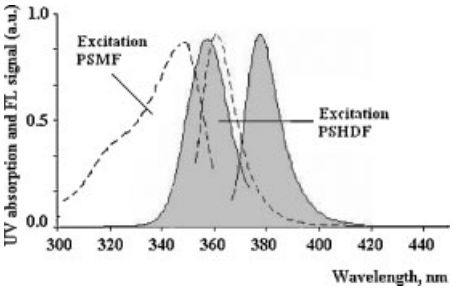


Figure 6.
FL Spectra of PSMF (dotted) and PSHDF (continuous) in $CHCl_3$ at room temperature.

are present like in homopolymers (polymethylphenylsilane, PSMF) the absorption maximum is located at 280 nm.

The PSHDF structure was investigated further by FL measurements and compared with the FL spectrum of PSMF (Figure 6).

The mirror-image relationship and the bandwidth between absorption and emission give information concerning the regularity of the main chain spatial conformation[22] (Figure 7).

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.[22]

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[23] 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.

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 (Figure 8) 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.

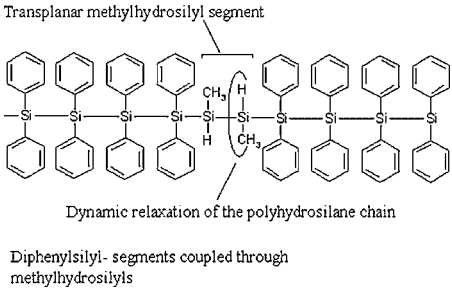


Figure 7.
Spatial conformation of the main chain.

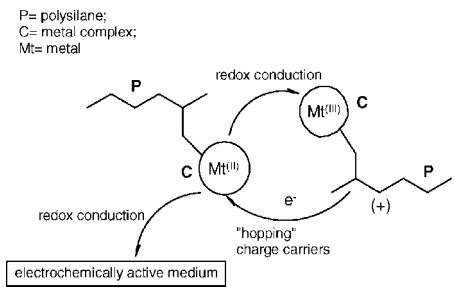


Figure 8.
Polysilane-metal complex.

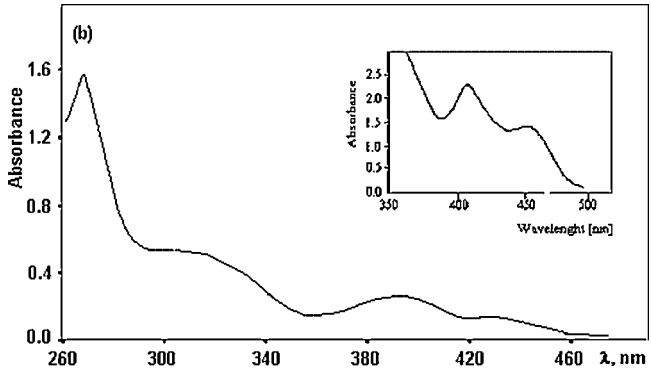


Figure 9.
UV Spectrum of the linear structure: Polysilane-Ni complex; Salen-Ni complex (inset) λ σ–σ^*: 320 nm; λ MLCT: 390;430 nm.

To investigate the electronic properties of the new polysilanes-metal complex we studied the UV-VIS spectra for both linear and pendant structures (Figure 9, 10).

Both UV spectra show the specific σ–σ^* 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.

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.

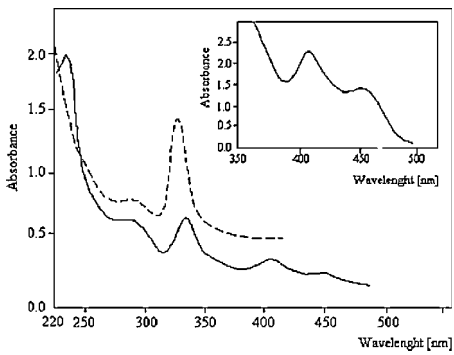


Figure 10.
UV Spectrum of the pendent structure Polysilane (dashed); Polysilane-Ni complex; Salen-Ni complex (inset) complex; Salen-Ni complex (inset) λ σ–σ^*: 340 nm; λ MLCT: 420; 450 nm.

Conclusions

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.

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