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Computational Study of the Electronic Absorption Spectra of Polyhydrosilanes

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Abstract The UV absorption spectra of polyhydrosilanes are investigated with the purpose to obtain a model that correlates specific aspects of the electronic spectra to the polymer chemical structure. For this purpose polysilanes with a well defined chemical structure were synthesized in similar reaction conditions. UV investigations have been carried out to obtain the profile of the synthesized polysilane electronic spectra and identify the effects induced by both structural and conformational changes. Molecular modeling calculations were then correlated with the experimental results in order to connect the electronic system to the polysilane structure. Such a method is useful to study polysilanes with complex structures where parts of the polymeric architecture should have a specific influence on the conjugated electrons system.

1 Introduction

Polysilanes are a class of inorganic polymers that consists of linear chains of organically substituted Si atoms [1]. Such structures possess unique electronic, photoelectrical and non-linear optical properties [2]. Most of these are related to the σ-electrons delocalization along the chain which endows polysilanes with a directional conductivity [3–5].

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Among these polymers, polyhydrosilane copolymers containing R^1R^2Si and $RSiH$ structural units (where R, R^1, R^2 are identical or different organic substituents) revealed new and intriguing physico-chemical properties that could be taken into account when designing new materials for optoelectronics [6]. These copolymers often offer a number of advantages relative to the respective homopolymers because their physical, mechanical and electronic properties can be altered and adjusted in accordance with the properties of the monomeric components and further developed due to the presence of the Si-H reactive groups. Moreover, the presence of the methylhydrosilyl units even in small amounts induces solubility for the former insoluble homopolymeric structure [7].

All hydrogen substituted polysilanes absorb strongly in the UV spectral region. The absorption maxima are affected by the chemical nature of the substituents and by chain lengths [8, 9]. To the best of our knowledge, up to now, the information concerning the relation between the electronic structure of polyhydrosilane copolymers and their UV absorption spectra is more like formal. This work, is meant to show that, based on the UV profile of a polysilane, one could have important information concerning the chemical composition, conformation of the macromolecular chain, contribution of the substituents to the conjugated electrons system, dimension and ratio between the copolymer segments.

2 Materials and Methods

2.1 Materials

Diphenyldichlorosilane, $Cl_2Si(C_6H_5)_2$ (purum, >98%), methyl(H)dichlorosilane, $CH_3(H)SiCl_2$ (purum, >98%)

and methylphenyl-dichlorosilane, $C_6H_5Si(CH_3)Cl_2$ (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 and traces of benzophenone.

2.1.1 Polymethylphenylsilanes- PS

PS homopolysilane was prepared using the classical Wurtz coupling method, in heterogeneous system with molten sodium dispersion in toluene, at gentle reflux, according to a previously described procedure [10]. Fractionation of PS, 10% solution in toluene [11], resulted in a low molecular weight fraction (F1) and a high molecular weight fraction (F2); PS (F1)/PS (F2) = 7.2 gravimetric ratio.

^{1}H-NMR (CDCl$_3$, δ ppm): 0.94-0.97 (-Si-CH$_3$); 7.04-7.30 (-SiC$_6$H$_5$).

FT-IR (KBr, cm^{-1}): 3064 and 3045 (C-Harom.); 2953 and 2893 (C-Haliph.); 1424 and 1096 (Si-C$_6$H$_5$), 1243 (Si-CH$_3$); 695 (Si-C), 461 (Si-Si).

GPC: PS (F1): Mw = 7433 g /mol; Mw/ Mn= 1.66); PS (F1) Mw = 864755 g/mol; Mw/ Mn= 1.28

2.1.2 Poly[methyl(H)-co-diphenyl]silane copolymer (PS-H)

PS-H copolymer was prepared following several distinct temperature-dependent steps in order to avoid massive loss of the low boiling point monomer, methylhydrosilane [12]. The process started gradually at low temperature, 60-70 ^{o}C, with a low degree of conversion. At this point most of the resulted products are mainly low molecular weights linear and cyclic oligomers. When the reaction temperature reached 94 ^{o}C the sodium particles melted. At this point new reactive species occurred mainly by back biting and bond scission and the coupling reaction re-starts vigorously with a high exothermal effect. Most of the co-monomers were consumed during this stage. Thus, starting from an equimolecular mixture of diphenyldichlorosilane/methyl(H)dichlorosilane acopolymer with CH$_3$HSi/(C$_6$H$_5$)$_2$Si molar ratio, Mr = 1/1 was obtained. Usually this method leads to low molecular weight polyhydrosilanes.

^{1}H-NMR (CDCl$_3$, δ, ppm): 0.799-0.979 (Si-CH$_3$); 3.22-4.00 (Si-H), 6.93-7.26 (Si-C$_6$H$_5$).

FT-IR (KBr, cm^{-1}): 3065 and 3045 (C-Harom.); 2955 (C-Haliph.); 2085 (Si-H); 1482; 1426 and 1093 (Si-C$_6$H$_5$); 1257 and 869 (Si-CH$_3$); 695 (Si-C); 468 (Si-Si).

GPC: Mw = 1957 g/mol; Mw/ Mn= 1.72.

2.2 Instrumental Methods and Procedures

IR absorption spectra were measured with a FTS 40A Bio-Rad spectrometer at room temperature on KBr pellets. ^{1}H-NMR spectra were registered with a Bruker NMR instrument (Model DRX 400 MHz). All chemical shifts were referenced to TMS standard in CDCl$_3$. The measurements were run in CDCl$_3$ at room temperature. UV spectra were recorded in CHCl$_3$ solution using a Beckman Acta M4 UV-Vis-NIR spectrometer.

The molecular weight distribution of the polymers synthesized in this work were measured in THF, on a Spectra Physics 8800 gel permeation chromatograph with two PL-gel packed columns (103 Å and 500 Å). All molecular weights were reported versus polystyrene standard .

2.3 Computational Details

The molecular models of polysilanes were built using Hyperchem (v.8.0) software [13]. The geometry optimization was performed using first molecular mechanics, MM+ module followed by PM3 semiempirical algorithm.

All calculations including energy minimization and molecular dynamics referred to isolated molecule in vacuum. For the optimization of geometries, the conjugate gradient algorithm (Polak-Ribier) was employed using a gradient norm limit of 0.01 kcal / (Å mol). The geometry optimization was done by minimization of the potential energy of the molecule.

The optimized structure was further relaxed at T=298 ^{o}K, applying a molecular dynamics trajectory. In this study the dynamical simulations were performed for polysilanes in order to determine the trajectories of isolated molecules on the PM3 multidimensional potential energy surfaces for ground state S$_0$. In this respect, HyperChem program was employed for simulation, and the molecular dynamics options were as follows: 1) starting temperature, 0K; 2) simulation temperature, 298K (for equilibration); 3) temperature step, 30K; 4) heat time, 0.1 ps; 5) run time, 0.9 ps; 6) step size, $\Delta t=0.0005ps$ (0.5 fs); and 7) bath relaxation time, 0.1 ps. At the end of molecular dynamics we obtained the relaxed structures (at 298K) which were used for the calculation of the theoretical elctronic absorption spectra.

Thus, the molecular orbitals were calculated and the most probable electronic transitions were traced at ZINDO/1 – RHF/CIS semiempirical level of theory.

The programs have been running on Windows 7 operating system using a computer with the following characteristics: Intel Core i7, 2.4 GHz, 16GB RAM.

3 Results and Discussions

3.1 Experimental Investigations

Two different polysilane structures, i.e. polymethylphenyl-silane homopolymer, PS, and poly(methyl(H)silane -co-
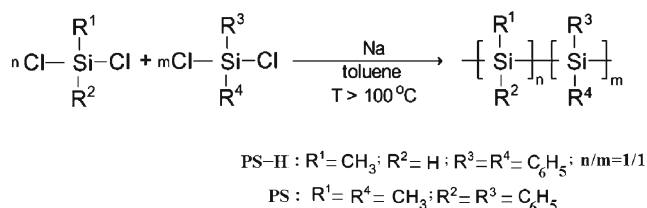
Scheme 1 Synthesis of polysilanes

Fig. 2 Polyhydrosilane helix conformation

diphenylsilane) statistical copolymer (PS-H) have been prepared using the classical Wurtz coupling method (Scheme 1).

All polysilanes absorb strongly in the UV spectral region. The literature [14, 15] mention that UV absorption of polysilanes containing aromatic groups directly bonded to the backbone is significantly red shifted due to the conjugative interactions between the phenyls and silicon chain's electronic systems. In our case both species of polysilanes have phenyl groups in the backbone but important differences should be observed in the case of copolymeric structures when each of the backbone components has its own UV absorption particularities (Fig. 1). The UV absorption profiles of PS(F1) and PS(F2) are quite identical. This suggests that the electronic properties of polysilanes are similar above certain values of their molecular weight. This could be explained by taking into account some already proved properties of polysilanes. It is common knowledge that the energy of the σ electrons transitions (i.e. the band gap) in polysilane strongly varies for linear chains up to around 30-50 Si atoms [16]. Another known fact is that the long polysilanes macromolecules are twisted following the helical model (Fig. 2) [17].

According to this model each coil of the helix is a collection of short linear segments (SLS). Since linearity is a principal condition for a conjugated electrons system to exist, it is logical to assume that only these SLS count finally for the electronic properties of the polymer.
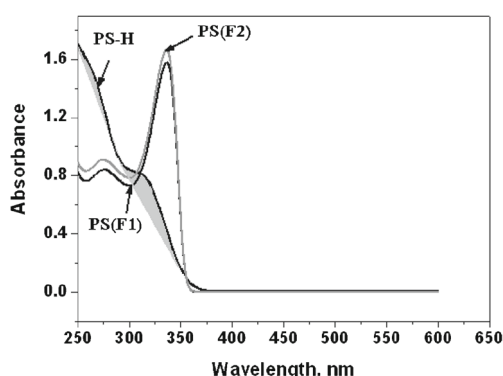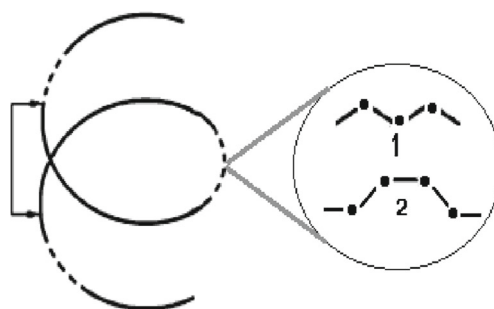
In the PS case, the similarity of the UV absorption spectra for both molecular weight fractions could be explained knowing that, the components of the described polymeric model are SLS with similar size and chemical structure. Two main UV absorption bands could be noticed for the synthesized structure, in perfect agreement with previously reported works [3, 18]. One, which is well represented, located at 335 nm and the second one more like a shoulder at around 275 nm. For the PS-H structures the UV spectrum has quite a different profile having a low represented shoulder at a higher wavelength and a higher maximum below 300 nm. This profile is quite representative for these kind of polysilanic structures [10]

These experimental results were correlated with calculated electronic absorption spectra determined for molecular models simulating the polysilane helical model.

3.2 Molecular Modelling of Polysilanes Chain

It is known that polysilanes containing aromatic substituents directly bound to the silicon atoms are characterized by the so called $\sigma - \pi$ conjugation [7]. In case of polysilane homopolymers the effects of such conjugation are relatively easy to identify. Much more difficult is the case of


Fig. 1 Absorption Spectra of PS-H, PS (F1) and PS (F2) in chloroform
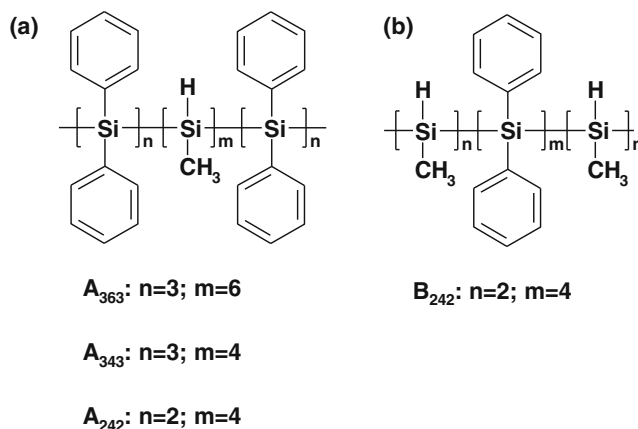
Scheme 2 Chemical structures of the copolymeric units used to generate the molecular models **a b**

polysilane copolymers where conjugated segments having different structures are connected. From this point of view an interesting example is represented by poly(methylhydro-diphenyl)silanes (PS-H). These structures are built like statistical copolymers where diphenylsilyl segments are coupled to methylhydrosilyls. The size of these two components can be controlled directly via the synthesis process. It is thought certain that the ratio of the two comonomeric units in the resulted linear structure is more like a statistical result. When studying the electro-optical properties of such structures one must know details on the way the two types of conjugated segments coupling influences the electronic spectrum. Therefore, while within the poly-diphenylsilane segment the $\sigma - \pi*$ conjugation is dominant, in the polymethylhydrosilane segment the $\sigma - \sigma*$ conjugation is major. The coupling of these two so different electronic systems generates a complex system where each component plays a particular role. Defining the characteristic aspects and identifying their effects on the electro-optical

properties of the polymer can be revealed by molecular modelling. Molecular modelling of PS-H was done by taking into account two cases: (a) copolymer chains where diphenylsilyl units are coupled statistically through methylhydrosilyl segments; (b) copolymer chains where methylhydrosilyl units are statistically coupled through diphenylsilyl segments (Scheme 2). Statistical coupling means that the ratio of the two comonomers, Mr, has an average value calculated for the entire chain. For example, Mr = 1 could result when two diphenylsilyl segments having 3 units each are coupled through a single methylhydrosilyl segment having 6 monomer units (A_{363}, Scheme 2). In this case the representative conjugated segment is poly-methylhydrosilane. On the other hand, the same value for Mr is obtained when two methylhydrosilyl segments having 2 units each are coupled through a diphenylsilyl segment having 4 diphenylsilyl units (B_{242}, Scheme 2). In this case, Mr = 1 but the representative conjugated segment is polydiphenylsilane. The molecular models of the

Fig. 3 Optimized structure of polysilane A_{343}-TP in trans-planar conformation (**a**); Relaxed structure of polysilane A_{343}-TG in trans-gauche conformation (**b**). Note that for A_{343}-TP the dihedral angle 4Si-5Si-6Si-7Si is of -175.926° (close to -180°), while for A_{343}-TG the torsion angle 4Si-5Si-6Si-7Si is about -62.319° (close to -60°)

(a)

(b)
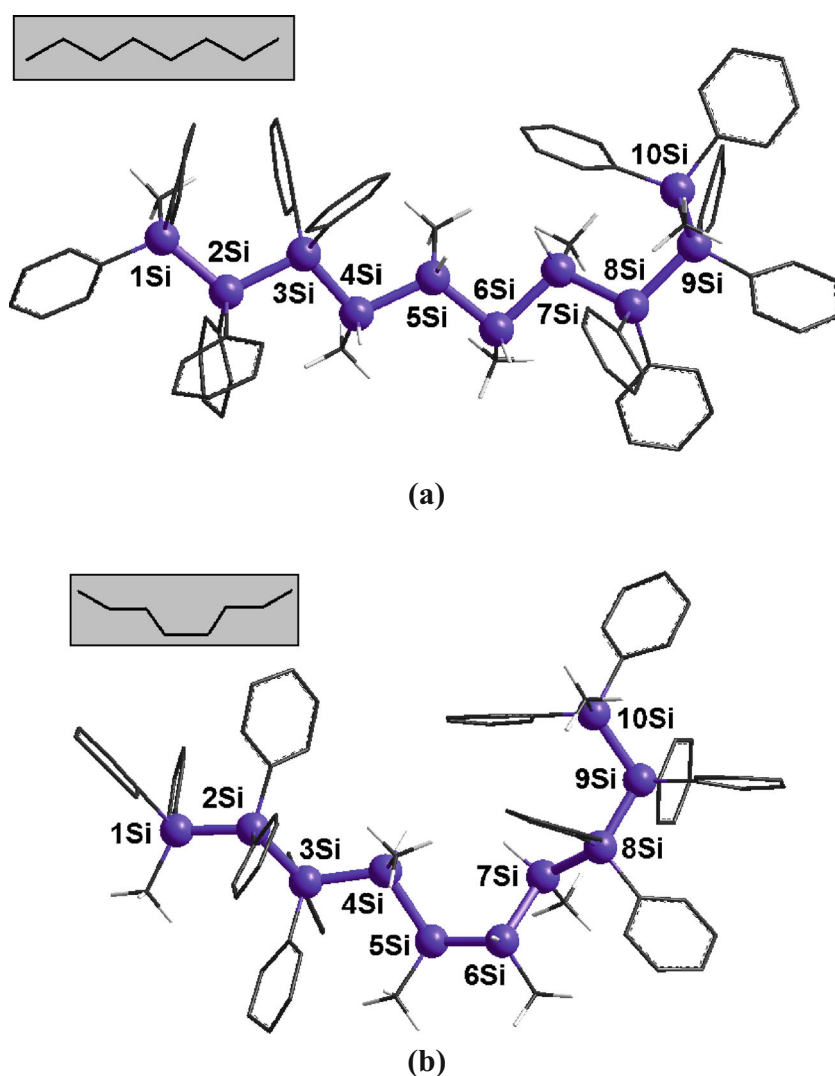
studied polysilanes were built knowing that the electronic absorption spectrum of polysilanes changes dramatically for shorter linear Si chains [16]. These models should simulate the statistical segments with the purpose to evaluate the electro-optical properties of the whole structure. Two specific conformations have been considered for each segment, trans-planar (TP) and trans-gauche (TG). The molecular models have been built first for copolymeric structures with diphenylsilyl units connected through methylhydrosilyl segments (Scheme 2a) and calculated for both TP and TG conformations (Fig. 3).

UV spectra calculated within 250-500 nm for A_{363}-TP and A_{363}-TG show multiple electron transitions involving both the π system of the diphenylsilyl groups and the σ electrons within the methylhydrosilyl segments (Fig. 4).

Two main UV absorption bands could be noticed for both conformations. One, which is well represented, located over 300 nm and the second one at lower wavelength. According to the model described above, these two absorption bands could be described using the two possible conformations of SLSs. So, substitution of the silicon atoms with relatively small groups like methyls and/or hydrogens increases the flexibility within specific regions of the SLS. This allows switching of the methylhydrosilyl segments from TP to TG conformation which cuts the σ electrons delocalization. However, due to minimal energy requirements, most of the remaining parts of the SLS keep the stable trans-planar conformation and maintain a high degree of the σ electrons delocalization. These assumptions were confirmed by simulation of the electronic spectra for a SLS segment containing methylhydrosilyl units coupled with diphenylsilyl short segments. Comparing the UV profiles for both TP and TG
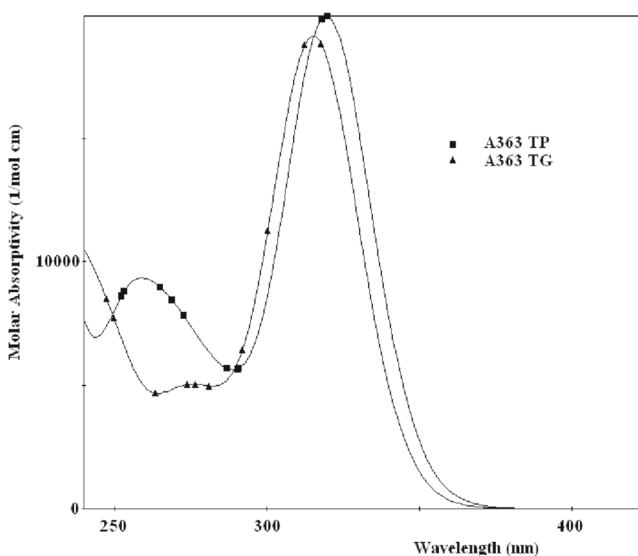

Fig. 4 Simulated electronic absorption spectra of PS-H: (■)A_{363}-TP (optimized structure); (▲)A_{363}-TG (relaxed structure)

conformation one can observe quite important modification related to the second absorption band bellow 300 nm. Therefore, TP-TG switching of the flexible methylhydrosilyl segment reduces the intensity of this peak to that of a barely visible shoulder (Fig. 4).

Further, molecular models of PS-H structures having different lengths of the methylhydrosilyl and diphenylsilyl segments in TP conformation were built and the corresponding electronic absorption spectra have been generated.

For the PS-H model structures with Mr = 1, the calculated electrons transitions simulate absorption bands that emerge in almost the same range of the spectrum (Fig. 5). Slight differences are reflected only by the intensity values, lower for the shorter conjugated segments in A_{242}. On the other hand, for PS-H having shorter methylhydrosilyl segments and Mr $\neq$ 1 like in A_{343} the peak bellow 300 nm became a barely visible shoulder. A similar approach was taken for copolymeric structures with methylhydrosilyl units connected through diphenylsilyl segments (Scheme 2b). The molecular model for a B_{242} structure have been built and calculated according to the already described general procedure. This time the extended $\sigma - \pi*$ conjugation typical for polydiphenylsilane leads to a consistent decrease of the HOMO-LUMO band gap causing electronic transition at higher wavelengths (Fig. 6). Also, the short conjugated methylhydrosilyl segments produce only a weak shoulder bellow 300 nm.

An overall analysis of both (A) and (B) cases reveals several important characteristics. Both the experimental measurements and simulations showed that two main UV absorption maxima are present. Let us consider these two bands as the contributions of electron transitions grouped into two components: one with mainly $\sigma - \sigma*$ transitions, the sigma component (C_σ) and the second one with mainly $\sigma - \pi*$ transitions, the π component (C_π) (Scheme 3).

A quite clear correspondence between the above defined components and the UV absorption bands in the simulated spectra is obvious. Therefore, in any of the presented (A) models the peak bellow 300 nm reflected in a highly sensitive manner any change in shape (conformation) and length of the methylhydrosilyl segment. A reasonable conclusion is that this absorption is representative for the C_σ component. The peak at higher wavelengths will be assigned to the C_π component.

Also, one should notice that the C_π component is much better represented in the spectrum. A possible explanation is the amplification of the sigma conjugation effect due to the electrono-accepting character of the phenyl groups. This so called $\sigma - \pi$ conjugation is not possible in the methylhydrosilyl segments where there is only the "pure" sigma conjugation.

Fig. 5 Electronic absorption spectra simulated for PS-H structures: (●) A$_{242}$; (■) A$_{363}$ (▲) A$_{343}$ (relaxed structures)
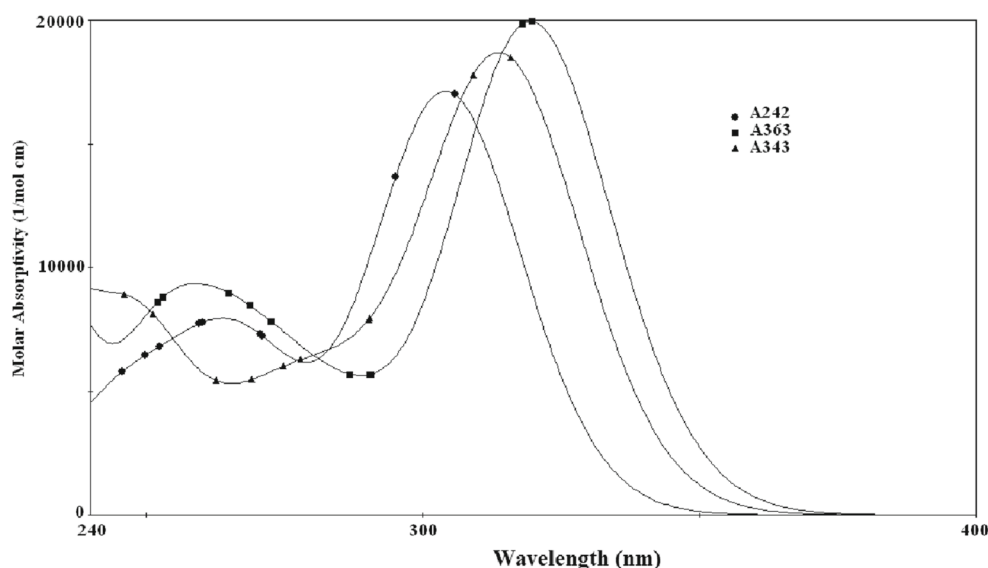
Applying these considerations to the model structures is further used to explain the profile of the simulated electronic spectra.

The model A$_{363}$ shows the contributions to the simulated electronic spectrum of both C$_\sigma$ and C$_\pi$. Decreasing the relative contribution of C$_\sigma$, like in A$_{343}$, leads to a severe lowering of the corresponding peak intensity. By ratio of the intensities relative to C$_\pi$ the peak resulted from the C$_\sigma$ contribution is barely visible. This is a normal effect due to the unbalanced Mr. Decreasing proportionally both C$_\sigma$ and C$_\pi$, and well balancing Mr like in A$_{242}$ produces a proportional decrease of both simulated absorption bands.

The model B$_{242}$ shows a spectrum profile with a well represented C$_\pi$ contribution producing a large absorption band stron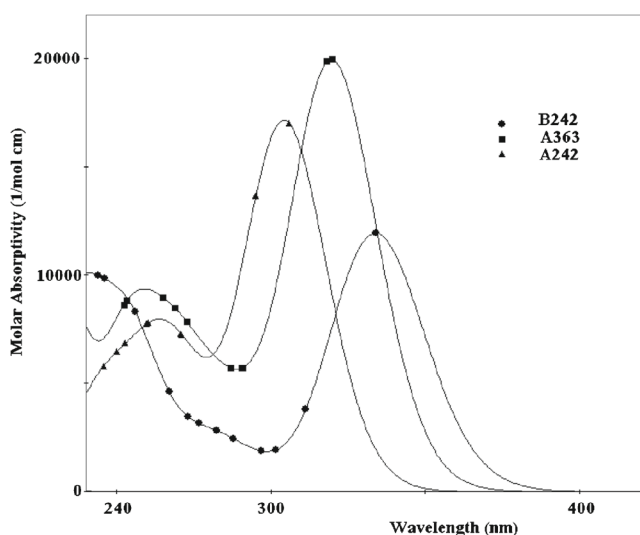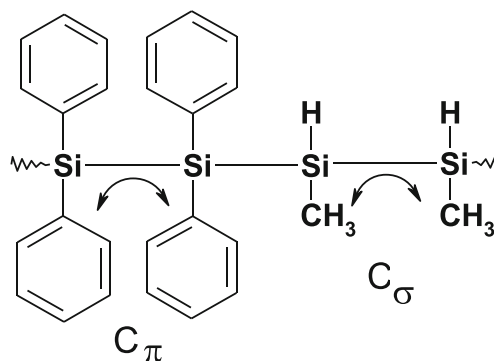gly red shifted. As expected, the short methylhydrosilyl segments have a low C$_\sigma$ contribution like a barely visible shoulder located at less than 300 nm.

Further, the analysis was further applied to various polysilanes both as presented in previous published works and also to the synthesized copolymers.

A total substitution at the silicon atoms with phenyl groups leads, as already mentioned to the presence of a single UV absorption maximum, well defined and with considerable intensity [19]. According to the presented approach, this profile is the result of the C$_\pi$ unique contribution to the electrons transitions.

When the silicon atoms are substituted with phenyl and alkyl groups, like in PS, the electronic spectrum shows both the C$_\sigma$ and C$_\pi$ contributions. Therefore, the electronic spectrum displays a weak peak at lower wavelengths and the strong maximum produced by the C$_\pi$ major contribution (Fig. 1 and Scheme 4).

When the silicon atoms are substituted with alkyl groups only, like in polydihexylsilane, the UV spectrum will show a profile with only one single absorption maximum due this time to the unique contribution of C$_\sigma$ [20].

Fig. 6 Electronic spectra simulated for PS-H structures: (■) A$_{242}$; (●)A$_{363}$ (▲) B$_{242}$ (relaxed structures)

Scheme 3 Representation of the C$_\pi$ and C$_\sigma$ components and their influence on the σ conjugated electrons system in PS-H
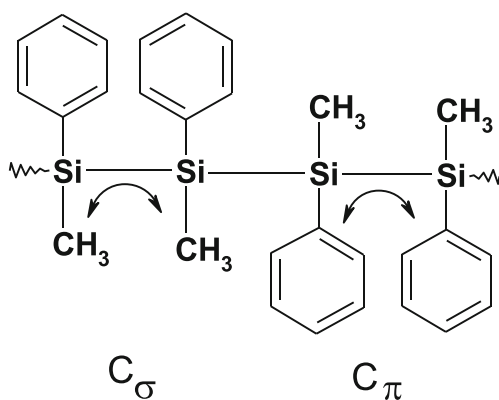
Scheme 4 Representation of the C_π and C_σ components effects on the sigma electrons conjugated system in a homopolymer like PS (the components were represented separately for a clear understanding; however both effects work simultaneously)

Applying the procedure to PS-H copolymeric structures reveals the characteristic UV spectrum profile where both C_σ and C_π show their contribution (Fig. 1). So, one can observe an absorption maximum at longer wavelengths that confirms the contribution of C_π to the electronic transitions. The appearance of this maximum is more like a broad shoulder and results from the participation of multiple C_π generated by each local conformation in conjugated chains of various lengths. The UV absorption signal due to the C_σ contribution is mostly overlapped by the specific strong phenyl rings absorption and, therefore, it is barely visible.

4 Conclusions

This study is meant to provide a theoretical approach useful to reveal details concerning the relationship between the polysilanes structure and their electronic absorption spectra. For this purpose both poly[diphenylsilane-co-methyl(H)silane] and polymethylphenylsilane have been synthesized using the same experimental approach. Further the UV analysis was done in order to collect information on the main electrons transitions and spectrum profile. Then, molecular models of representative structures were built and their corresponding electronic absorption spectra were simulated. Comparison between the theoretical results and experiments was used to identify the contribution of the main electrons transitions to the general spectral frame. This information was used further to describe particular aspects of the UV profile in relation with the chemical nature of the substituents that decide their contribution to the conjugated electrons system by taking into account possible conformations of the macromolecular chain, the dimension and ratio between the copolymer segments.

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