ROMANIAN ACADEMY
„PETRU PONI” INSTITUTE OF MACROMOLECULAR CHEMISTRY- IASI

CONJUGATED POLYMERS FOR APPLICATIONS IN OPTOELECTRONICS

Ph. D. Thesis Abstract

Scientific supervisor:
Dr. Valeria Harabagiu

PhD Student:
Marius Soroceanu

Iasi
2015

ROMANIAN ACADEMY
„PETRU PONI" INSTITUTE OF
MACROMOLECULAR CHEMISTRY IASI

No. **2159/27.V.2015**

Mr/Ms. ....

We bring to your knowledge that on July 1st, 2015, 12:00 am, in the library of the Institute of Macromolecular Chemistry "Petru Poni" Iasi will be publicly presented the Thesis "**CONJUGATED POLYMERS FOR APPLICATIONS IN OPTOELECTRONICS**" by author, physicist Marius Soroceanu for conferring the scientific title of Ph.D.

The doctoral committee has the following members:

CHAIRMAN:
Dr. Anton Airinei, Director of the "Petru Poni" Institute of Macromolecular Chemistry - Iasi
SCIENTIFIC SUPERVISOR:
Dr. Valeria Harabagiu, "Petru Poni" Institute of Macromolecular Chemistry - Iasi.
REVIEWERS:
Dr. Mariana Pinteala, "Petru Poni" Institute of Macromolecular Chemistry - Iasi.
Prof. Dr. Ovidiu Caltun, „Alexandru Ioan Cuza" University -Iasi, Faculty of Physics.
Prof. Dr. Nicolae Hurduc, „Gh. Asachi" Technical University -Iasi, Faculty of Chemical Engineering and Environmental Protection.

In accordance with the Regulation of the Romanian Academy on the organization of doctoral studies for granting scientific degrees , we send you the abstract of the PhD thesis with the request to inform us in writing on your feedback and comments. On this occasion we invite you to attend the public presentation of the thesis.

DIRECTOR,

Dr. Anton Airinei

INSTITUTUL DE CHIMIE MACROMOLECULARĂ "PETRU PONI"

Acknowledgments

Deep consideration and thanks with all my gratitude to Ms. **Dr. Valeria Harabagiu** for continued support, understanding that showed, total confidence, constant advice and guidance throughout doctoral thesis program.

All my gratitude and profound respect to Dr. **Liviu Săcărescu** for support, help, guidance, advice and ideas generously provided, trust and patience throughout the period of the realization of the scientific research of the thesis.

Thoughts of gratitude goes to Mr. **Dr. Anton Airinei**, Ms. **Dr. Mariana Pinteala**, Mr. **Prof. Dr. Ovidiu Caltun** and to Mr. **Prof. Dr. Nicolae Hurduc** who have honored me, as president, respectively reviewers, in the doctoral committee, for their patience in analysing the thesis and the suggestions made.

I also thank **all colleagues** from the "Petru Poni" Institute of Macromolecular Chemistry for open and honest collaboration and for their efforts to characterize the compounds investigated in the thesis throughout the research program.

Thanks to Romanian Academy for financial support during the training period of the PhD thesis (2010-2014).

In particular I want to thank **my family** for unconditional love, moral support, understanding and encouragement offered permanently throughout these years.

Table of contents

This summary contains the main original results obtained. The numbering of chapters, figures, tables and bibliographical references correspond to that found in the thesis.

Keywords: Polysilanes, σ conjugation, optoelectronics, alignment layers, displays.

Part II: Original results

Introduction

In recent years, efforts by scientists to find new suitable materials for electronic and optoelectronic applications led to increased interest in the research of photoelectronic and electrical properties of conjugated polymers with semiconducting properties.

Polysilanes are a class of polymers whose backbone chain is composed of silicon atoms, substituted mainly by alkyl or aryl groups. One may also find silico-functional polysilanes containing other atoms than the carbon linked to the main chain, such as hydrogen, halogen, oxygen, sulfur, nitrogen, etc. Polysilanes form a separate group due to their specific properties and applications covering technology areas of micro- and nanoelectronics. These polymers are promising in view of their ability to be casted in films with good mechanical properties, which is added to the high-potential electrical properties of use. The latter are due to the delocalization of the σ electrons along the macromolecular chain, as a result of the relative position and distance between adjacent sp^3 orbitals of silicon atoms. This phenomenon leads to special physical properties - strong electronic absorption, conductivity, photoconductivity, photosensitivity - that are crucial for many technological applications of polysilanes.

Research purpose

The main purpose of the activity in the thesis was to identifify the effects induced by different substituents and chemical structure of polysilanes on their morphology, and thermal, , electrical and optical properties in view of their use in obtaining various optoelectronic devices.

Objectives of the study

- evaluation of behavior in dilute solutions of polysilane copolymers containing segments with different degrees of rotational freedom;
- show the influence of the substituents on the optical properties in solution and in solid form, with identification of effects induced by chemical structure and conformational changes;
- correlation of experimental and simulation data of thermo-scission process;
- investigation of electrical properties of polysilanes in undoped and doped states ;
- surface morphology analysis under the action of UV radiation for polysilane films with small amount of methylhydrosilyl units;
- identify potential applications of polysilanes like nanostructured materials or alignment substrates for liquid crystals to beused in LCD technology.

Structure of the thesis

PhD thesis entitled "**CONJUGATED POLYMERS FOR APPLICATIONS IN OPTOELECTRONICS**" is divided into two main parts. *The first part* consists of three chapters and includes a study of literature that describes methods of polysilane preparation, their electronic structure, the influence of substituents on the crystallinity, chain conformations and solubility properties and their optical and electrical properties. This Part alsosummarizes some possible applications. *Part II - Original contributions* is structured into eight chapters debuting with the objectives of the thesis that were formulated after critical analysis of existing data in the literature and identification of lees or unexploredaspects .

CHAPTER IV is dedicated to structural characterization of polymers using ^{1}H NMR and FTIR spectroscopy.

CHAPTER V consists in the study of the behavior of the dilute solution of low molecular weight diphenylsilane copolymers containing segments with different degrees of rotational freedom, showing the dependencies induced by the copolymer composition and the chemical structure of the second comonomer.

CHAPTER VI includes a study that targeted thermal stability of polydiphenyl-methylphenyl and poly[diphenyl-methyl(H)]silane copolymers and showed that thermal stability of the copolymers is dependent on the content of phenyl and methyllhydrosilyl units. Also the value of glass transition temperature is affected by the ratio of the two comonomers. Thermal cleavage studies were conducted for linear polysilanes with different content of diphenylsilylene and methylhydrosilylene or methylphenylsilylene units. The experimental data obtained by thermogravimetric analysis in tandem with FTIR analysis of the decomposition gases were correlated with theoretical data derived from molecular modeling perform with the help of semi-empirical methods for the calculation of the molecular orbitals (PM3, AM1 and MNDO/d). The correlation of the theoretical and experimental results allowed detailing the cleavage mechanism specific to Si-Si bond in polyhydrosilanes. The possibility of using these polymers to produce ceramic composites based on silicon carbide at lower temperatures was evidenced

CHAPTER VII includes the presentation of optical properties of polysilanes in solution.

Thus, UV studies of polysilanes have been conducted with the aim to show the influence of the substituents on the optical properties. To reveal details of the relationship between polysilane structure and electronic absorption spectra a theoretical modeling of optical properties was performed yielding information about the main electronic transitions and spectra profiles. Comparing the results of theoretical and experimental electronic transitions the main contributions of different species could be identifyed. This information was used to describe a procedure able to highlight important structural and conformational features. The method could be applied to build specific structures and predict the electro-optical properties of polysilanes. and The photoscindation of poly[diphenyl-co-methyl(H)]silane has been also investigated in this chapter. Important differences were observed in terms of the rate of photodegradation of the polyhydrosilanes according to the ratio of the two comonomers.

CHAPTER VIII describes the results on the electrical conductivity of investigated polysilanes. It was found that the electrical conductivity of polymers in undoped state are very low in both pill and film. Following the iodine doping was an increased conductivity for all polymers investigated.

CHAPTER IX followed the morphological changes of films deposited by spin-coating on glass substrate under the action of UV radiation for oligohydrosilanes containing small amounts of methylhydrosilyl units. AFM analysis of film surface shows that this type of polymer composition tends to form worm-like morphology, which become different when the polymer film is exposed to UV irradiation with the excimer XeCl laser. Increased fluency of 122-366 mJ/cm^2 induces growth of conical structures. The study shows that laser irradiation may be used to control the surface morphology of the polysilanes thin films, in particular polyhydrosilanes. This method is of interest in micro-optoelectronic properties of semiconductor material which have small dimensional controlled at high accuracy.

CHAPTER X presents a study on the possible use of polyhydrosilanes for aligning liquid crystals used in LCD technology. It was highlighted that the introduction methylhydrosilyl units in the polymer chain improves transparency of the films. The films surfaces were structured by rubbing with various textile fabrics and found to be appropriate carriers for aligning liquid crystals, as proved by polarized light microscopy. The results are of interest to technology electronic displays.

CHAPTER XI contains the experimental part of the thesis and presents materials used, synthesis and characterization methods.

The thesis ends with conclusions and presenting the bibliography consulted.

The original results presented in this thesis have been the subject of six publications and were also presented as posters at five different scientific events.

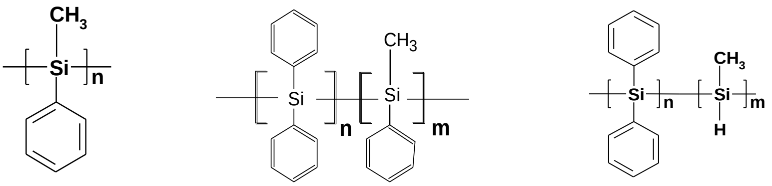
Part II: Original contribution

CHAPTER IV. CHARACTERIZATION OF STRUCTURE AND FLEXIBILITY OF POLYSILANE MACROMOLECULAR CHAINS

The thesis considered as conjugated polymers homo- and copolysilanes having various substituents (methyl, phenyl and hydrogen in various combinations) attached to the silicon atoms of the main chain. By Wurtz reductive coupling in heterogeneous process (sodium dispersion in organohalogen silanes solution in toluene) three classes of polysilanes were prepared:

- polymethylphenylsilanes (MP): homopolymeric structures composed of methylphenylsilane units; they were extensively studied in the literature and are used in this study for comparison purposes;

- poly(diphenyl-methylphenyl)silanes (DPMP): copolymers with statistical distribution of the structural units;
- poly[diphenyl-methyl(H)]silane (DPMH), which have different proportions of methylhydrosilane units.



(a) MP **(b) DPMP** **(c) DPMH**

Figure IV.1. The chemical structure of the investigated polysilanes: a) polymethylphenylsilane (MP), (b) poly(diphenyl-methylphenyl)silane (DPMP), (c) poly[diphenyl-methyl(H)]silane (DPMH)

The chemical structures of the synthesized polysilanes is shown in **Figure IV.1** and physico-chemical properties are recorded in *Table IV.*1. To follow the influence of the structural characteristics on their properties, the samples belonging to each of the classes differ not only by the nature of the silicon substituents, but also by their molecular weights and / or ratios of differently substituted structural units.

Table IV.1. Sinthesis[a)] and physico-chemical properties of polysilanes

Sample code	**The initial reaction mixture**		**(Co)polysilanes**			
	Monomers[b)]	**M1/M2**[c)] **(molar)**	**M1 units/M2 units**[d)] **(molar)**	**Mw**[e)]	**Mw/Mn**[e)]	**Tg**[f)] **(^{o}C)**
MP	DCMFS	-	-	7400	1.6	68
DP$_1$MP	DCDPS+DCMPS	1/1	0.8/1	5200	1.2	71
DP$_7$MP	DCDPS+DCMPS	7/1	6.7/1	4600	1.2	87
DP$_1$MH	DCDPS+DCMHS	1/1	1/1.1	3200	1.5	49
DP$_2$MH	DCDPS+DCMHS	2/1	2/1	3200	1.5	54
DP$_3$MH	DCDPS+DCMHS	3/1	2.7/1	4300	1.3	64
DP$_7$MH	DCDPS+DCMHS	7/1	6.7/1	4100	1.2	82

[a)] Reaction conditions, temperature, 100-110 ^{o}C; solvent, toluen;

[b)] DCMPS – dichloromethylphenylsilane; DCDPS – dichlorodiphenylsilane; DCMPS – dichloromethylphenylsilane; DCMHS – dichloromethyl(hidrogen)silane

[c), d)] M1 - structural diphenylsilylene units; M2 methylphenylsilylene or methyl(hidrogen)silylene or structural units from them

[e)] Mw – weight average molecular weight; Mw/Mn – polydispersity index; determined by gel permeation chromatography (GPC) in chloroform

[f)] Tg – the glass transition temperature determined by differential microcalorimetry (DSC)

CHAPTER V. HYDRODYNAMICS AND MOLECULAR CHARACTERISTICS

The study was conducted as a result of the major influence of polysilane chains flexibility the on the optoelectronic properties. Until now, only a few studies concerning the physical properties of polysilanes in highly diluted solutions are available and most of them are related to homopolymers [36,37]. Thus the study conducted in this chapter is meant to add information on silane copolymers. To evaluate the behavior of polysilane copolymers containing segments with different degrees of rotational freedom in dilute solutions, the DP$_2$MH, DP$_3$MH and DP$_1$MP silane copolymer samples were considered. They are composed by different contents of rigid diphenylsilylene connected through more flexible methylhydrosilylene and methylphenylsilylene units. *Table V.2* shows their hydrodynamic properties. In poor solvent solution (chloroform), for all oligohydrosilanes relatively low critical concentrations were revealed, above which supramolecular clusters were found in solution, while DP_1MP more rigid copolymer presents these agglomerations throughout the range of concentrations.

From partial specific volume values, $\bar{v}$, and hydrodynamic radii, R_h, correlated with the molecular weights, a compact structure of DP_1MP chains in solution, compared to a better solubility and a less dense structure of oligohydrosilanes was identified.

Table V.2. Hydrodynamic and molecular characteristics of polyorganosilane copolymers in chloroform solutions [111]

Sample	[η] cm^3/g	K'	$\bar{v}$ cm^3/g	$s_0 \times 10^{13}$ S	$D_0 \times 10^7$ cm^2/s	MSD	$A_0 \times 10^{10}$ erg/grad/mol 1/3	R_h^c nm	R_h^{rapid} nm	R_h^{lent} nm	dn/dc cm^3/g	c_{cr} g/dl
DP_2MH	3.8	0.3	0.85	-1.4	29	4500	2.9	1.4	1.4	50	0.22	~4
DP_3MH	3.1	0.7	0.84	-1.4	37	3700	3.2	1.2	1.1	60	0.32	~2
DP_1MP	2.2	2.2	0.80	-0.8	54	2100	3.5	0.9	0.7	60	0.26	-

CHAPTER VI. THERMAL PROPERTIES

The thermal behavior of polymers is of particular importance in optoelectronic applications. A using problem that arises is linked to the durability of the polymer over time, which is dependent on its thermal stability. The crystallization or melting of the material caused by Joule effect and the shorting current (films can contain small discontinuities, goals) could result in changing of the film structure/morphology. The material must allow continuous, uniform and heat-stable films [120]. Therefore, a comparative study was performed by thermogravimetric analysis for homopolymer and silane copolymers, in order to highlight the differences in thermal stability. Calculations of molecular orbitals and molecular dynamics simulations based on semi-empirical theory were also performed and the data were compared with those obtained experimentally, defining the pecularities of the thermo-scission of polysilane as a function of their structure.

VI.1. Thermal stability of polysilanes

Thermal stability of polysilanes was investigated by thermogravimetric analysis (ATG). MP, DP_7MP, DP_1MH and DP_7MH samples (see molecular characteristics in chapter IV, *table IV.1*) were studied. The MP homopolymer was analyzed for comparison and the samples of the selected copolymers differ in nature and proportion of the more flexible methylphenyl- or methyl(H)silane units, interconnecting the more rigid diphenylsilane units or sequences. *Table VI.1* collects the thermal decomposition data for the four polysilanes samples.

As shown in *Table VI.1*, the thermal stability of polysilanes is strongly dependent on their chemical structure that influences all the parameters of the decomposition process: starting decomposition temperature, rate of decomposition, the residual mass. Depending on the start value of thermal decomposition temperature, polysilanes studied enroll in the following order of thermal stability, a direct consequence of their chemical structure: MP > DP_7MP > DP_7MH > DP_1MH. In the ranges T_{onset} and T_{end}, MP homopolymer and DP_7MP copolymer have the highest rate of decomposition (lose 12 %/min by weight of the initial weight) and shows the smaller residual mass at 700 ^oC. Replacement of methylphenylsilane units with diphenylsilane or methyl(H)silane units, not only reduces the onset temperature,, but, surprisingly, also determines a lower rate of the thermo-degradation (7 %/min for DP_7MP; 8 %/min for DP_7MH; 6 %/min for DP_1MH), and the residual masses are higher than that recorded for homopolymer.

Table VI.1. Results of thermo-scission process for polysilanes (TGA-DTG)

Sample code	T_{onset} (°C)*	T_{pic} (°C)*	T_{end} (°C)*	Residual mass (%)
MP	362	424	476	25.03

DP_7MP	341	477	522	30.87
DP_1MH	258	365	515	34.53
DP_7MH	332	393	482	35.62

- *T_{onset} is the temperature the thermal decomposition starts; * T_{pic} is the temperature corresponding to the maximum peak of the predominant thermal decomposition proccess; * T_{end} is the temperature at which the thermal decomposition substantially ceases.*

•

VI.2 An assessment of the decomposition gases

The gases evolved from the thermal decomposition of the samples subjected to TG analysis were continuously analyzed by IR spectroscopy, providing information on both the gas composition at a particular temperature and the variation in composition with increasing sample temperature.

The thermal decomposition of the samples was carried out under an atmosphere of nitrogen. Since all the spectra indicate the presence of oxygen gas in the molecule, this can be explained only by the adsorption of large amounts of oxygen in the initial samples, so that the thermo-scission of polysilane chains is accompanied by *in situ* thermal oxidation processes at a small scale.

The FTIR spectrum profile of gases resulted from thermo-scission of DP_7MP is presented in **Figure VI.5**.

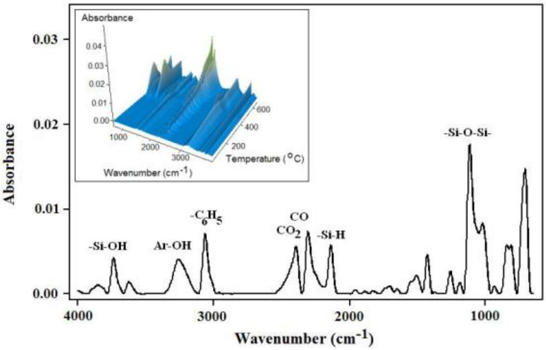


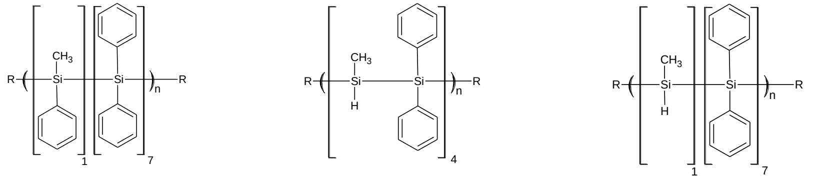
Figure VI.5. FTIR spectrum profile of gaseous compounds evolved from thermo-scission of DP_7MP at the temperature level of T_{peak} = 477 °C; inset image: 3D TG-FTIR diagram of gases evolved from thermal degradation of DP_7MP [121]

The FTIR spectrum of the gases from thermo-scission, measured at T_{peak} = 477°C shows the Si-O-Si absorption band at 1100 cm^{-1}. Also, the Si-H bond stretching is present at 2100 cm^{-1}, close to the characteristic bands of CO_2 and CO (2300 - 2400 cm^{-1}), which pleads for the emergence of some radical processes involving the replacement of silicon substituents by hydrogen atoms, followed by cleavage of macromolecular chain with the formation of hydrosilane oligomers. Interesting, the aliphatic C-H stretching absorption at 2800-2900 cm^{-1} is missing, meaning that these groups are most likely absent in the gaseous composition. Instead, the IR spectrum displays at 3060 cm^{-1} the absorption band of the aromatic C-H stretching. Thus, it is reasonable to assume that most of the gaseous chemical species will have structures combining $–C_6H_5$, -Si-H and –Si-O-Si- moieties. Usually these are low molecular siloxanes or silanols with phenyl or hydrogen substituents at the silicon atoms. The content of oxygen-containing compounds (carbon oxide, siloxanes, silanols, phenols) in the decomposition gases increases with increasing temperature as can be seen from the evolution of their characteristic bands as a function of temperature.

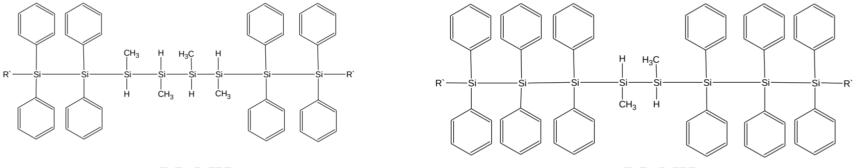
VI.3. Simulation of the thermo-scission process by molecular modeling

The synthesized copolymer structures were considered to construct the molecular models. Each molecule model was built based on linear chains having eight silicon atoms in the repetitive structure and final ethoxy groups (*Table VI.2*). The simulated structures - DP$_7$MP$_S$, DP$_1$MH$_{S,a}$ and DP$_7$MH$_S$ – show ideal sequencing that could result in the synthesis of DP$_7$MP, DP$_1$MH and DP$_7$MH copolymers, accordingly to the co-monomers ratios in the initial reaction mixtures. DP$_1$MH$_{S,b}$ (1/1 ratio between differently substituted units and having a symmetrical arrangement of units with a block of four central methyl(H)silane units linked with blocks of two end diphenylsilane units) and DP$_3$MH$_S$ structures (characterized by a 3/1 ratio between differently substituted units and a symmetrical arrangement of units, with a block of two central methyl(H)silane units linked to blocks of three diphenylsilane units) were also simulated. The last two structures contain terminal methyl units.

Table VI.2. Chemical structure and notation of oligosilanes considered for modeling and experimental investigation [121]



DP$_7$MP$_S$ **DP$_1$MH$_{S,a}$** **DP$_7$MHs**



DP$_1$MH$_{S,b}$ **DP$_3$MH$_S$**

R = -OCH$_2$CH$_3$; R' = CH$_3$

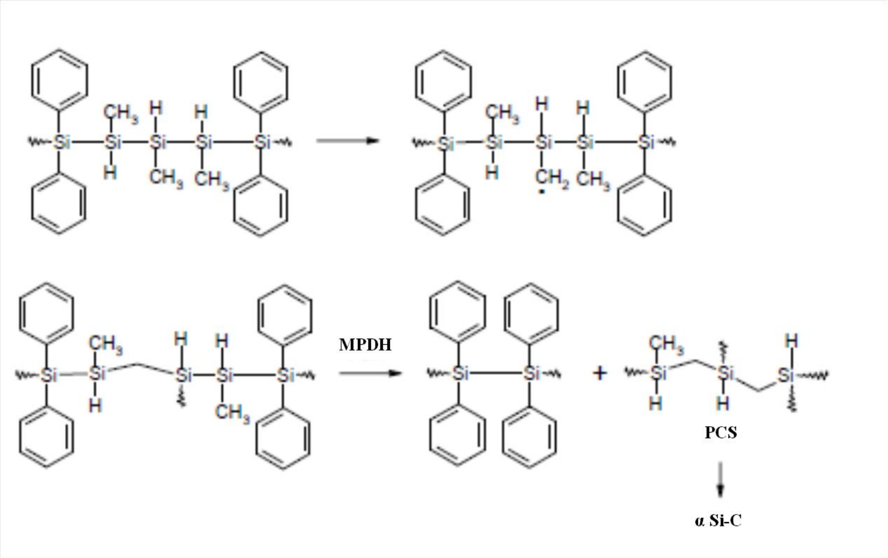
From the values of the bond energies and formation heats for oligosilanes and optimized structures of cleaved fragments, important conclusions on the possibilitis of chaincleavages were withdrawn.

VI.4. Thermo-scission mechanism of polysilanes

Combining experimental data with the results of the simulation a thermal decomposition mechanism has been proposed for studied copolysilanes.

The oxidation processes occurs as side reaction, which produces low molecular weight siloxanes, silanols and similar gaseous products observed in the decomposition gases. The main silicon backbone is quite resistant to thermal breaking and Kumada like rearrangements of the methyl groups with formation of the methylene bridge and polycarbosilane networks. During this process, the hydrogen radicals could attach also to silicon giving thermoresistant Si-H groups leading to chain scission and formation of low molecular weight hydrosilanes found in the combustion gases. However, the low content of hydrosilanes the gas mixture than indicates that such effects are quite rare.

In case of polyhydrosilane copolymers, the diphenyl segments are resistant to thermal scission, since it is known that a polydiphenylsilane structure is infusible. Thus, the thermal decomposition could involve first only the methylhydrosilylene units. In this case, the Kumada rearrangements and the intermediate polycarbosilane phase (PCS) will produce a solid containing both a α-Si-C ceramics and polydiphenylsilane residues (*Scheme VI.3*) [125].



Scheme VI.3. Thermal scission of polyhydrosilane by conversion of the methylhydrosilylene segments into polycarbosilane and ceramic material [121]

Correlation of both theoretical and experimental results was used to have details on the specific mechanism of the Si-Si bonds breaking in polyhydrosilanes. Unlike their homologues homopolymers, polyhydrosilanes thermo-scission takes place at lower temperatures producing larger amounts of ceramic material and polycarbosilanes.

CHAPTER VII. OPTICAL PROPERTIES

As a result of σ delocalization of electrons, polysilanes show strong absorptions of σ-σ* type in near UV between 250-400 nm. The excitation corresponds to a transition from bonding backbone orbital σ (HOMO) to the most stable antibonding backbone orbital σ* (LUMO).

From UV-Vis spectroscopy studies we can say that the substituents, but also their nature have a very strong effect on the conformation of macromolecular chain and the conjugation of sigma electrons, due to the changes of the relative position and of the distance between adjacent sp^3 orbitals [1,41,126,127].

VII.1. Absorbtion in UV-Vis

The UV absorption spectrum of polymethylphenylsilane (MP) contains two absorption maxima [1] (**Figure VII.1**). Absorption band at λ_{max} =275 nm is assigned to the π-π* transition of the phenyl, and the one at λ_{max} = 337 nm is characteristic to σ-σ* transition specific for σ delocalization of the electrons of the polymer chain. We may note that the band attributed to σ-σ* transition is two times greater than π-π* transition band assigned to phenyl groups. As mentioned above, σ-π conjugation resulting from the interaction between Si-Si polymer chain and π conjugation orbitals of the aromatic ring strongly influences the conjugation of the polysilane chain.

In the case of poly(diphenylmethylphenyl)silane with 7/1 ratio between diphenylsilane and methylphenylsilane units (DP_7MP) in UV spectrum (**Figure VII.2**) one may observe an absorption maximum located at λ_{max} = 260 nm assigned to π-π* transition of the phenyl groups and an absorption band at λ_{max} = 328 nm assigned to σ-σ* transition from polysilane chain. The introduction of the diphenylsilylane units in the silane polymer chain shifts hypsochromically the absorption maximum of the characteristic band assigned to polysilane chain with 9 nm and with 15 nm the the band attributed to the transition of the phenyl groups as compared with the polysilane homopolymer.

We can also say that the introduction of a larger number of phenyl units has a hypsocromic effect on the characteristic absorption band of the polysilane segment and a hyperchromic effect of the absorption band attributed to the transition of phenyl groups, which suggests a decrease in the conjugative interactions between phenyl substituents and the polysilane skeleton. This process is due to the conformational constraints induced by the steric hindrance of the phenyl groups.

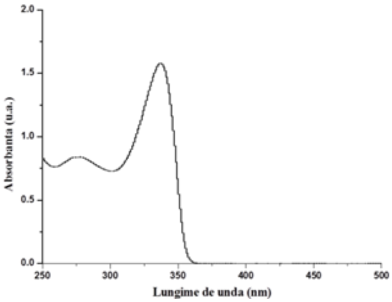


Figure VII.1. UV absorption spectrum of polymethylphenylsilane (MP) in $CHCl_3$ solution

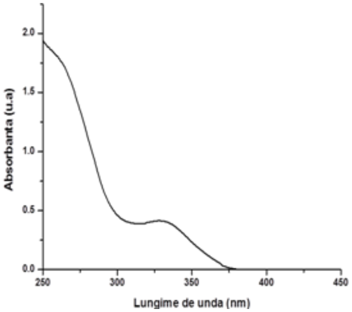


Figure VII.2. UV absorption spectrum of poly(diphenyl-methylphenyl)silane (DP_7MP) in $CHCl_3$ solution

VII.3. Fluorescence

It is well known that polysilanes have good fluorescence properties [139]. Luminescent polymeric materials represents an area extensively studied in recent years due to applications targeting optoelectronic devices [140]. Another aspect that should be noticed about the synthesized polysilanes is the fact that they are soluble and are able to forme thin transparent films recommends for optoelectronic applications. The change of substituents causes changes in emission levels, so we can consider this as an advantage because it can make polymers with emission in the areas of interest. *Table VII.2* presents the maximum emission of the four polymer samples studied.

Table VII.2. Maximum emission of the investigated polymers

Polymer	**Maximum emission (nm)**
MP	353
DP_7MP	376
DP_7MH	369
DP_1MH	370

Fluorescence spectra of the polymers confirmed the influence od the polymer structure of on their fluorescent properties.

VII.4. UV irradiation behavior in solution

In order to investigate the behavior of the polymers in solution under UV irradiation poly[diphenyl-co-methyl(H)]silane (DP_1MH, DP_7MH) having two ratios between methylhydrosilyl and diphenylsilyl units, and a homopolymer of reference: polymethylphenylsilane (MP) were considered. UV irradiation uindergoes with the cleavage of the polymer chain, resulting in lower molecular weight fragments and the formation of new crosslinked structures with emission in the visible region of the spectrum.

In this study, diphenylsilyl long chains ensures a high degree of sigma electrons delocalization and methylhydrosilyl units provide solubility [136]. The optical properties of these types of structures have been studied for the purpose of their application for optoelectronic devices [141].

UV absorption profiles of MP and DPMH in solution as functions of the time of irradiation are shown in **Figure VII.15 a, b, c**.

Before irradiation, the UV spectra show the σ-σ* transitions at 310 nm for DP_1MH and at 334 nm for DP_7MH, while MP displays this signal at 335 nm (**Figure VII.15 a, b, c**). Exposure to UV irradiation produced decreasing the intensity and a hypsochromic shift of the absorption maxima due to Si-Si bonds scission in all polysilane structures.

An important difference is related to the decomposition rate (**Figure VII.15 d**). While MP absorption intensity decreased with 42% in 8 s, for DP_1MH the intensity decreased with 6 % and for DP_7MH with 24 % in the same interval of time. This confirms that photo-scission takes place faster for MP than DP_1MH and DP_7MH.

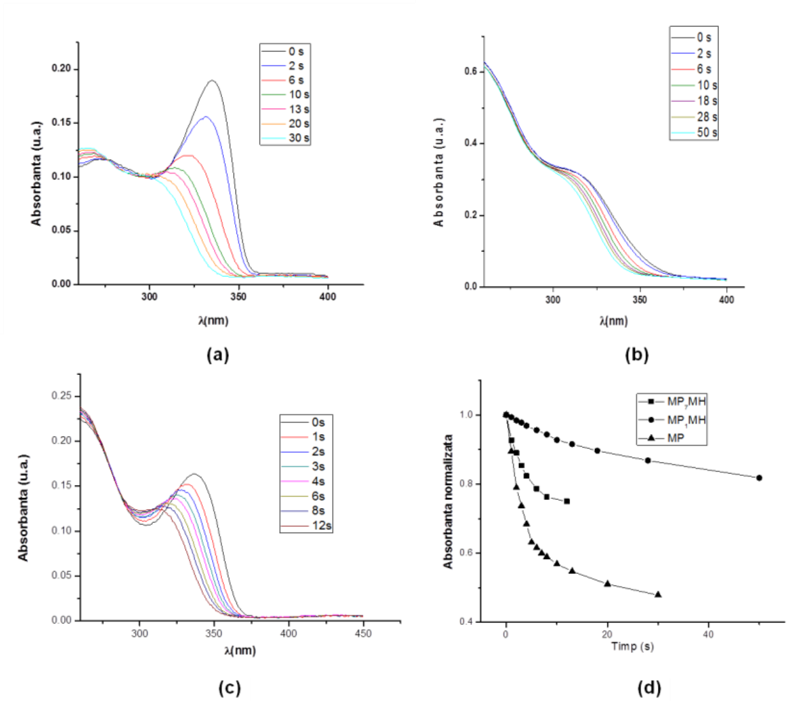


Figure VII.15. Absorption spectra of MP (a), DP_1MH (b) and DP_7MH (c) in chlorofom during UV irradiation. Curve 0 before irradiation, the curves 1-8 after exposure to UV light (365 nm) for increasing duration, (d) the change in absorbance versus time of exposure

CHAPTER VIII. CONDUCTIVITY OF POLYSILANES

The values of the electrical conductivities of the polymer in the initial state (undoped) showed very low values in both the pellet and the film. The introduction of a higher content of the phenyl units in the polymer chain results in higher conductivity in undoped state. In the case of polyhydrosilanes we can say that a higher content of methylhydrosilyl units lead to a decrease in the conductivity as compared to polyhydrosilane of lower content of methylhydrosilyl units.

Following the doping with iodine vapor an increased conductivity for all polymers was observed. Comparing the doped samples of DP$_7$MP and MP, one may say that the homopolymer conductivity was somwhat higher than that of the copolymer. The explanation could consist in the higher content of the phenyl groups of the homopolymer as compared to the copolymer, as phenyl groups lead to a stiffening of the chain impairing electrons transfer from the polymer to iodine, to form I_3^- ions; thus the gaps along the polysilane chain can not be generated, these ones being considered the true carriers of conductivity after doping with I_2 [149].

Table VIII.1. Conductivities of doped and undoped polysilanes

Sample	**Undoped pill ($S\cdot cm^{-1}$)**	**Doped pill ($S\cdot cm^{-1}$)**	**Undoped film ($S\cdot cm^{-1}$)**	**Doped film ($S\cdot cm^{-1}$)**
DP$_7$MH	$9x10^{-13}$	$7.1x10^{-8}$	$6x10^{-9}$	$8.9x10^{-6}$
DP$_1$MH	$7x10^{-13}$	$4.3x10^{-9}$	$5x10^{-10}$	$2.6x10^{-6}$
MP	$4.2x10^{-12}$	$9.6x10^{-8}$	$8x10^{-9}$	$5.4x10^{-7}$
DP$_7$MP	$9x10^{-11}$	$4.7x10^{-9}$	$1.2x10^{-8}$	$1.1x10^{-7}$

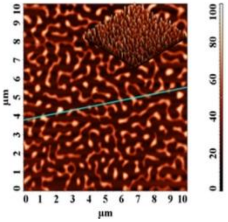
The doping of polyhydrosilane with iodine also led to an increase of their conductivity as compared with the other two polymers. The results suggest the association of electrical conductivity of polysilanes with specific electronic properties of Si-Si main chain. Thus less bulky groups (Si-H) allow the dopant to diffuse throughout the polymer chain and thus the conductivity of the polymer is increased.

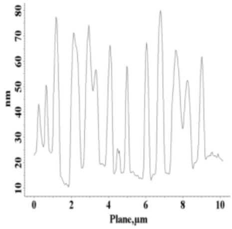
CHAPTER IX. STRUCTURING OF POLYSILANE FILMS UNDER LASER IRRADIATION

The modifications of the polysilane thin film surface exposed to coherent UV laser irradiation were investigated by AFM in order to determine the evolution of the surface morphology in relation to the process parameters. For this purpose 2-D and 3-D AFM images and height profiles were collected for each sample, before and after irradiation with different fluence/pulse numbers (**Figure IX.1 a-g**).

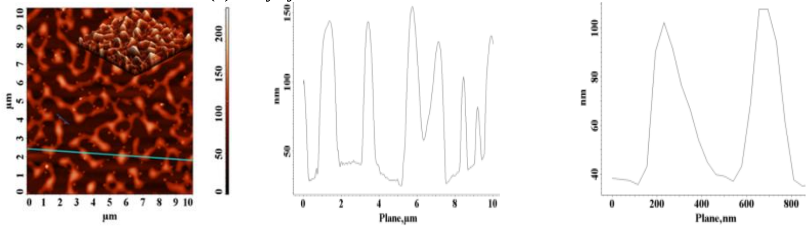
As one may see from **Figure IX.1a**, before irradiation the copolymer film surface shows a wormlike morphology. The breadth and height of the wormlike structure are about 200–250 nm and 60–80 nm, respectively, as seen from height profile for the untreated sample.

Figure IX.1(b-g) illustrates the coherent UV irradiation effects induced on the DP$_7$MH films' surface morphology in terms of increasing laser dose. It is obviously seen that the polymer surface undergoes the formation of a large number of cones in the wormlike microstructure at higher UV doses. Cones began to appear from almost the beginning of the irradiation process at random locations on the DP$_7$MH copolymer surface. In order to estimate the dimensions of the surface formations, the grain size analysis method available in the Nova software was used. A typical cone possesses a base diameter of 78 nm and a height from 100 to 130 nm when the film was irradiated at 366 mJ/cm^2. UV dose, where a cone vertex is obviously seen. The average diameters of the conical structure formations versus UV dose were constant at about 78 nm, for the last two samples (**Figure IX.1 f, g**).

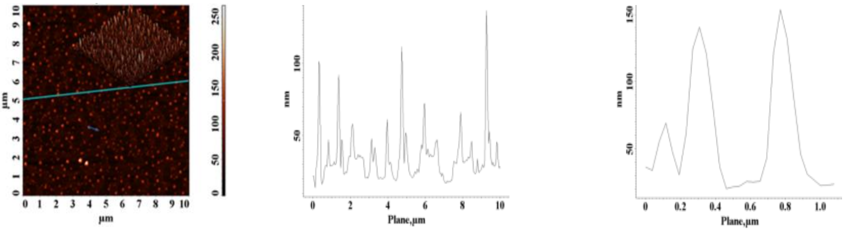




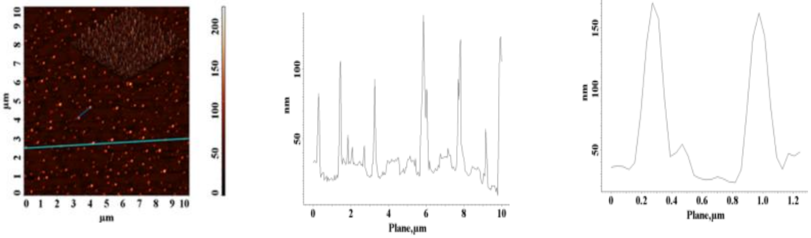
(a) Polyhydrosilane film surface before irradiation



(b) Fluence, 122 mJ/cm^2, 11 mJ/pulse (5 pulse numbers)



(f) Fluence, 366 mJ/cm^2, 33 mJ/pulse (10 pulse numbers)



(g) Fluence 366 mJ/cm^2, 33 mJ/pulse, (15 pulse numbers)

Figure IX.1. Polyhydrosilane films irradiated with 308 nm laser. Morphology changes at different laser fluence/pulse numbers. From left to right: 2-D and 3-D (inset) AFM topography images, overall height profile, and height profiles of the cone structures. [163]

The cones grow at higher doses in a great number density to represent the dose effect damage on the DP$_7$MH film surface. The number of cones varies with the number of laser shots. For the last two samples the number varies from 147 to 259. The conical heights were measured in terms of UV dose; the cone height grows dramatically at higher doses to 100–130 nm at 366 mJ/cm^2.

CHAPTER X. ALIGNMENT OF LIQUID CRYSTALS ON POLYSILANE SUBSTRATE

This study is focused on investigating different polysilane structures as possible candidates for liquid crystal alignment layers produced by conventional technology of friction. Four polysilanes having methyl, phenyl and hydrogen side groups in various combinations were considered. Thin films have been casted onto quartz glasses and their optical properties like energy gap or other energies describing the absorption edge were analyzed in connection with the polymer chemical structure. The surface morphology was studied first and subsequently adapted by rubbing with two types of velvet.

The surface features are discussed in relation with both chemical structure of the polysilane and patterning conditions. The alignment capacity of polysilane films was further tested using a nematic LC (5CB). The results were recently published [182].

X.1 Correlation with optical properties

The transparency of the polysilane films was studied within the 200–1100 nm spectral range. The UV-VIS spectra presented in **Figure X.1** reveal that samples do not absorb visible light, having a transmittance of about 90% in the domain starting from 450 nm to near infrared domain. One may observe that the transparency band can be extended to the UV region depending on polysilane substituent nature. The introduction of specific side groups could influence the position of the cut-off wavelength (the wavelength at which the transmittance becomes less than 1% in the spectrum). Therefore, polysilanes containing rigid methylphenyl segments present higher cut-off wavelengths (**Figure X.1**).

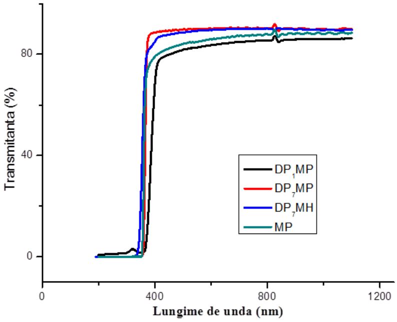


Figure X.1. The UV-VIS spectra of the studied polysilane films [182]

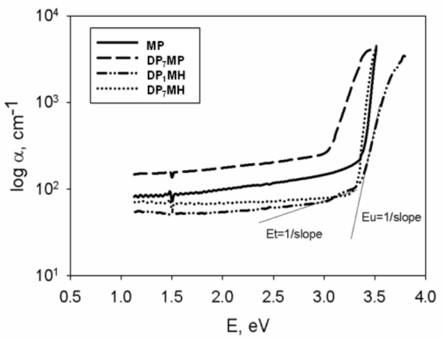


Figure X.2. Absorption coefficient dependence on photon energy for the investigated polysilanes [182]

The transmission characteristics of the investigated films in the visible domain are optimal for LC alignment. Moreover, the sharp fall in the UV region can offer information on the band gap. This parameter and the energies describing the absorption edges are determined using the approach of Tauc [183] and Davis-Mott [184].

Figure X.2 shows the absorption coefficient as a function of incident photon energy, E, for the studied polysilanes. It can be noticed that the shape of the obtained curves is similar to that proposed by Tauc for a typical amorphous compounds [183]. Each of the absorption edges from **Figure X.2** exhibits two different domains, characterized by different slopes.

The values of Eu and Et of the polysilane films are obtained from the reverse of the slope of the dependence of absorption coefficient on photon energy in the two domains depicted in **Figure X.2**. It can be noticed that the results displayed in *Table X.1* are influenced by the substituent type and the copolymer composition. The different absorption capacities of the samples in the low-energy absorption domain can be explained by considering the fact that in this energy region take place transitions involving defect states in the tails of the states density. Thus, the presence of structural defects, like the break or torsion of polymer chains, determines the occurrence of the optical absorption processes. The combination of the flexible methyl or bulky phenyl side groups into polysilane backbone could favor structural disorder and hence the increase of the Et and Eu values. In the sample DP_7MP where the diphenylsilyl segments are connected through bulky methylphenyl units, significant distortions can be produced leading to defects and higher values for Eu and Et energies. When the coupling of the diphenylsilyl is made through an elastic segment, such as methyl(H)silyl (DP_1MH and DP_7MH), all tensions are dissipated by local modification of the polymer conformation, resulting in lower values for the width of the tails of localized states.

Table X.1. The values of Tauc energy, Et, Urbach energy, Eu, and optical band-gap, Eg, of the studied polysilanes [182]

Sample	The average thickness of the film, μm	Et, eV	Eu, eV	Eg, eV
MP	15 ± 0.35	3367.1	127.6	3.37
DP$_7$MP	10 ± 0.31	4310.3	319.4	3.21
DP$_1$MH	20 ± 0.21	2173.9	277.3	3.29
DP$_7$MH	10 ± 0.28	1785.7	121.2	3.35

The Tauc plots for the investigated polysilanes, displayed in (**Figure X.3**), present a saturation domain at high energies followed by an exponential one in the low energies range, from which were extracted the values of the optical band-gap energy (*Tabel X.1*). Therefore, the different types of chain conjugation affect the Eg values. In DP$_7$MP containing diphenylsilyl segments linked through methylphenilsilyl there is a synergetic effect on Eg caused by both σ-π and σ-σ conjugations, leading to a reduction of the optical bandgap. In DP$_7$MH only σ-σ conjugation has continuity since the σ-π one is interrupted by the short chain of methylhydrosilyl. This results in slightly higher values of Eg. The same tendency is noticed for DP$_1$MH which contains methyl(H)silyl units, where the lower probability of electrons' delocalization eliminates the possibility of optical absorption processes. Nevertheless, all samples exhibit optical band-gap energy higher than 3.21 eV, which is a good indicator of transparent polymer films [189].

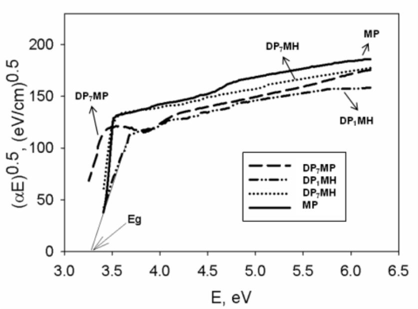


Figure X.3. The Tauc dependence for the investigated polysilanes [182]

The above observations show that all investigated polysilane films have a good optical transparency, prerequisite for use as liquid crystal alignment layers.

X.2. Surface morphology of the polysilane substrate

The investigations continued with morphological analysis of polysilane films in order to check their surface organization ability (after rubbing) and implicitly their LC alignment properties [190]. For a better understanding of the effects created by the rubbing velvet fibers, a comparative analysis between the pristine films and the patterned ones was performed. The changes occurring in the polysilane surface features were closely examined by AFM investigations.

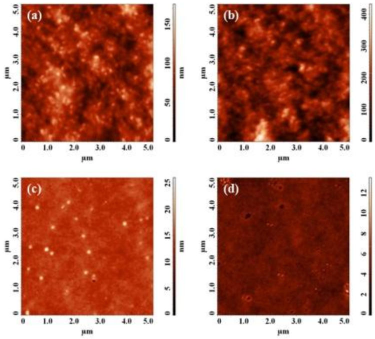


Figure X.4. The 2D-AFM images of the pristine polysilane films: (a) MP, (b) DP_7MP, (c) DP_1MH and (d) DP_7MH [182]

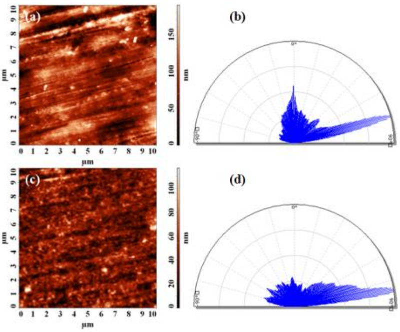


Figure X.7. 2D-AFM image (a, c) and the corresponding Fourier angular spectra (b, d) for MP film rubbed with velvet with short fibers (Vsf) and velvet with long fibers (Vlf), respectively [182]

Figure X.4 reveals that the topography of the unrubbed polymers is determined by the structural peculiarities. Thus, the morphological aspects can be associated with the different packing abilities of the studied polysilanes, due to the side groups, which induce a different flexibility for each macromolecule. The presence of bulky and rigid methylphenyl units in the MP and DP_7MP polymer structures favors the conformational disorder, thus the chain packing is diminished and the surface roughness increases resulting in granular formations of nanometric dimensions.

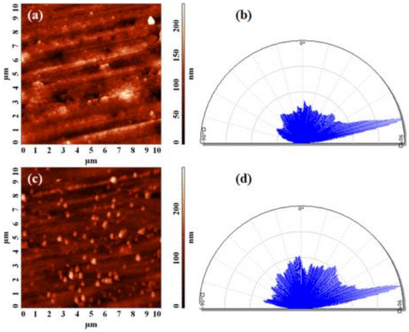


Figure X.8. 2D-AFM image (a, c) and the corresponding Fourier angular spectra (b, d) for DP_7MP film rubbed with velvet with short fibers (Vsf) and velvet with long fibers (Vlf), respectively [182]

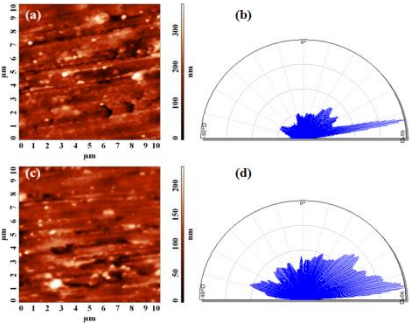


Figure X.9. 2D-AFM image (a, c) and the corresponding Fourier angular spectra (b, d) for DP_1MH film rubbed with velvet with short fibers (Vsf) and velvet with long fibers (Vlf), respectively [182]

In DP_1MH and DP_7MH samples, the introduction of non-bulky and flexible methyl(H)silyl segments enhances the chain mobility and conformational order. This leads to a closer chain packing, with lower free volume as reflected by smaller root mean square roughness. There were thus obtained roughnesses of 19 nm for the MP homopolymer, 52 nm for DP_7MP and only 0.9 and 0.6 nm for DP_1MH and DP_7MH respectively (*Table X*.2).

The changes resulted in the morphology of the investigated samples might be explained by considering the chemical structure of the polymer, which determines through its organization a specific deformation response of the film surface during processing. In other words, when the chain conformation determines denser packing it can be assumed that the hardness increases producing only weakly developed structure at the surface, while a more ductile polymer is deformed more easily, producing relatively well-developed structure. The linking of rigid methylphenyl units leads to a reduced chain packing resulting in a less organized structure, which allows deeper penetration of the velvet fibers (**figurile X.7** and **X.8** for samples MP and DP$_1$MP respectively).

Conversely, the presence of the flexible methylhydrosilyl coupling segments (methyl groups) results in a more compact polymer structure and this generates a smaller depth of the formed microgrooves (**FigureX.9**).

X.3. Testing of LC alignment ability

The alignment behavior of 5CB on polysilanes, rubbed with the two types of velvet, is tested by PLM. The employed approach provides preliminary indications on the quality of nematic orientation. The method is based on recording the changes in light intensity when rotating the sample (placed under crossed polarizers). For all films, dark regions are recorded at 0 and 90° rotation of the LC director with respect to the crossed polarizers, revealing that it is aligned parallel to the polarizers' transmission direction. Further rotation of the polymer film from this position at 45 and 135° relative to the crossed polarizers, bright states are observed since the electric field components passing through the easy direction of 5CB have the highest resultant on the analyzer transmission direction. This behavior is characteristic for a homogeneous alignment of a nematic LC.

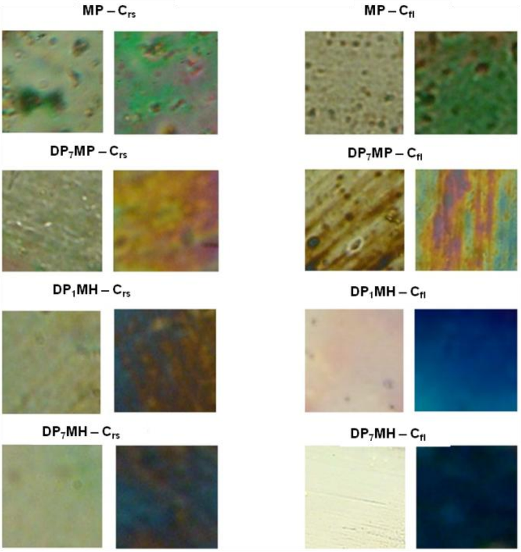


Figure X.11. Polarized light images revealing dark and bright states as result of 5CB orientation on rubbed polysilane films with velvet having short (Vsf) and long fibers (Vlf), respectively [182]

Given the regularity of the induced grooves it can be noticed that the higher uniformity of the surfaces rubbed with Vlf leads to a higher contrast between the dark and bright states (**Figure X.11**). This is an indicative that the 5CB orientation is more uniform in the case of Vlf., The ability to align more flexible copolymers containing methylhydrosilyl units is superior to that outlined for stiffer polysilanes. Considering the transparency and surface morphology of polyhydrosilanes after rubbing surface structure one may conclude that these copolymers meet the requirements of the liquid crystal alignment layers.

General conclusions

Thesis entitled "**Conjugated polymers for applications in optoelectronics**" is divided into two main parts and contains 11 chapters. *The first part* consists of a literature study on σ-conjugated polymers. Due to the interaction of sp^3 orbitals of Si atoms, these polymers show a σ electron delocalization. This phenomenon leads to specific physical properties: strong electronic absorption, conductivity, photoconductive, photosensitivity, and so on, which are crucial for many technological applications of polysilanes.

The main method for obtaining polysilanes (mostly used) is Wurtz coupling. This method remained the most viable process for preparing high molecular weight linear polysilanes. The substituents of polysilanes affect optical properties and the conductivity being thus possible the preparation of polymers which can be exploited as high performance materials, for example, in electronic devices such as photoreceptors, light-emitting diodes and displays.

The second part is divided into eight chapters and contains original contributions in this area.

The polymers were investigated using ^1H NMR and FTIR spectroscopy. The absorption bands from IR spectra characteristic to vibration frequency of specific silane bonds and signals with characteristic displacement from ^1H NMR spectra confirme the proposed structures of the investigated polysilanes.

The molecular and hydrodynamic properties of low molecular-weight diphenylsilane copolymers proved to be dependent on their composition and the chemical structure of the second co-monomer. Including the hydrogen as side groups instead of phenyls (DP_2MH and DP_3MH) leads to larger molecular weights, M, and hydrodynamic radii, $R_{h,}$ and higher ‘‘critical’’ concentration, c_{cr}, methylhydrosilyl groups, better solubility in chloroform and higher M. Though no ccr was observed for DPMP solutions, supramolecular structures were registered all over the concentration range studied with DLS. The polymers DPMP and DP_3MH contain approximately the same molar proportion of phenyl groups in the chain. However, DPMP chain holds at least one C_6H_5-group in each monomer unit that can introduce more steric hindrances than less bulky H-group. On the contrary, in the DP_3MH copolymer the blocks of diphenylsilane alternate by methylhydrosilyl fragments allowing the chain to more freely rotate. DPMP molecular chain reminds a cylindrical brush-like macromolecule, where conformation is controlled by steric repulsion of densely grafted side chains. A lower value of specific partial volume, $\bar{\nu}$ for DPMP as compared with DP_2MH and DP_3MH indirectly confirms the denser DPMP structure.

Thermo scission of linear polysilanes with different content of diphenylsilylene and methylhydrosilylene or methylphenylsilylene units has been studied. For this purpose, molecular models of the copolysilanes were built first. Then, semi-empirical molecular orbital methods such as PM3, AM1 and MNDO/d were employed to calculate the potential energy surfaces. Following, the possible paths of Si-Si bond breaking were calculated based on the enthalpy change of the scission reactions and heats of the formation computed at the level of every generated model. The theoretical results indicated a different path for braking of the Si-Si bonds when methylhydrosilyl segments are part of the main silicon backbone. Synthesis of copolysilanes having structures similar to the computed molecular models has been performed. The resulted polymers were then submitted to TG-FTIR analysis in inert atmosphere. Correlation of both theoretical and experimental results was used to have details on the specific mechanism of the Si-Si bonds breaking in polyhydrosilanes. Unlike to their homologues homopolymers, polyhydrosilanes thermo-scission takes place at lower temperatures producing large amounts of ceramic material and polycarbosilanes. Such materials could be used further to produce ceramic silicon carbide composites at low temperatures.

Has been studied optical properties modeling aimed at proving a useful theoretical approximation to reveal details of the relationship between structure of polysilanes and electronic absorption spectrum. Subsequently UV analysis was carried out to obtain information on main electronic transitions and spectra profile. Then were constructed molecular models of representative structures and absorption spectra were simulated corresponding electronic. Comparing the results of theoretical and experimental electronic transitions could identify the main contribution in general spectrum. This information was used to describe a procedure able to highlight important structural features and conformational. This method could be applied to build and to predict electro-optical properties of polysilanes. Studies have shown that fluorescence emission polymers present in the UV-Vis and emission maximum is influenced by the different nature of the substituents.

It was investigated the photoscindation process of the soluble copolymer poly[diphenyl-co-methyl(H)]silane. For reasons of comparison the polymethylphenylsilane (MP) homopolymer was used for this study. Exposure of poly[diphenyl-co-methyl(H)] silane (DP_1MH) on UV irradiation with λ = 334 nm in solution, lead to further branching structures / cross-linked with visible emission spectrum at 407 nm. Also significant differences were observed in the rate of photodegradation of the polyhydrosilanes to the homopolymer. Therefore, it was revealed that the Si-Si bond cleavage occurs faster in MP than in DP_1MH due branched structures / crosslinked results that are more resistant to UV exposure.

Electrical properties were investigated for polysilanes studied showing that initial electrical conductivity values of the polymers in the undoped state are very low in both pill and in film. Following the doping with iodine vapor was an increased conductivity for all investigated polymers.

Oligohydrosilane with a low content in methylhydrosilyl units was studied in order to follow the surface morphologycal changes under UV irradiation of its thin films spin-coated on glass slides. AFM analysis showed that this polymeric structure has a high tendency to generate wormlike structures all over the film surface. The morphology changed dramatically when the polymer film was exposed to coherent UV irradiation of the XeCl laser, i.e., cone microstructures emerged over the entire surface. Increasing the fluence from 122 to 366 mJ/cm^2 induced growth of the conical structure. Through this work it was proved that laser irradiation could be used to control the morphology of the thin film surface of a particular polyhydrosilane structure. The method has high potential in micro optoelectronics where the properties of the semiconducting material should be controlled at a low dimensional level with high accuracy.

A series of polysilanes films was prepared in order to investigate their optical and morphological properties for LC alignment purposes. The influence of the specific chemical structure over the optical properties of the polylsilane was investigated resulting that introduction of less polarizable methylhydrosilyl units into the polymer backbone improves the transparency. All samples present a transmittance of about 90% in the range of 450–1100 nm. The Urbach energy tends to increase for the samples with rigid methylphenyl segments, MP and DP_7MP, which facilitate less chain packing and implicitly a more disordered structure. Optical bandgap is higher than 3.21 eV revealing a low probability of optical absorption processes, thus sustaining the suitability of the samples as alignment layers from the point of view of lack of absorption in the visible domain. The morphology of the pristine polysilanes is constituted from isotropically distributed granular formations. In order to obtain a proper alignment of a nematic LC the surface of the samples was adapted by rubbing with two different velvets: one with short fibers and other with longer fibers. The polymers containing methylhydrosilyl units present a more compact structure. Hence, finer grooves are formed at the polymer surface, leading to a better orientation of the 5CB nematic. Also, the velvet with longer fibers generates surfaces with higher uniformity facilitating a positive contribution to the LC alignment. This is supported by the higher contrast between the bright and dark states recorded by PLM. Considering the transparency and surface morphology of the samples containing more methyl substituents, it can be concluded that this type of polyhydrosilane are good candidates as alignment layers for LCDs.

The original results presented in this thesis made subject to the following national and international publications (**six** publications) is also presented as **five** different scientific posters, as follows:

Papers published in national and international journals

1. *Study of piezoelectrycity in structures based on nanofibrous ZnO layers and polysilane,* L. Ghimpu, V. Cojocaru, **M. Soroceanu,** L. Sacarescu, A. Katashev, V. Harabagiu, I. Tiginyanu, Proceedings of the International Semiconductor Conference (**2012**), CAS, 2, 6400780, 295-298.

2. *Hydrodynamic and molecular characteristics of organosilane copolymers of low molecular weight,* E. Tarabukina, A. Krasova, A. Filippov, L. Sacarescu, M. Simionescu, G. Sacarescu, **M. Soroceanu,** V. Harabagiu, High Performance Polymers (**2013**), 25 (1), 79-86 (f.i. = 1,090, SRI=0,656).
3. *Thermodegradability of soluble polydiphenylsilane copolymers*, L. Sacarescu, C. Cojocaru, G. Sacarescu, M. Simionescu, **M. Soroceanu**, V. Harabagiu, Polymer Degradation and Stability (**2014**), 107, 82 (f.i. = 2,633, SRI=2,291).
4. *Morphological Investigation of Poly[methyl(H)silane-co-diphenylsilane] Irradiated by XeCl Excimer Laser*, **M. Soroceanu,** L. Sacarescu, E. G. Hitruc, C. Ursu, V. Harabagiu, International Journal of Polymer Analysis and Characterization (**2014**), 19(6), 482-488 (f.i. = 1,230, SRI=0,589).
5. *Computational study of the electronic absorption spectra of polyhydrosilanes*, L. Sacarescu, M. Fortuna, **M. Soroceanu**, C. Cojocaru, G. Sacarescu, M. Simionescu, V. Harabagiu, Silicon (**2014**) - Acceptat (f.i. = 0,704, SRI=0,627).
6. *The influence of polysilane chemical structure on optical properties, rubbed film morphology and lc alignment*, **M. Soroceanu**, A. I. Barzic, I. Stoica, L. Sacarescu, V. Harabagiu, eXPRESS Polymer Letters (**2015**), 9(5), 456–468 (f.i. = 2,953, SRI=2,033).

Papers presented at scientific manifestations

1. *Effect of Iodine Doping on Absorption Edges of Polysilanes*, **M. Soroceanu**, A. I. Barzic, C. Cojocaru, L. Sacarescu, V. Harabagiu, International Conference on Physics of Advanced Materials (ICPAM-10), 22-28 Septembrie 2014, Iași, România.
2. *Proprietăţi optice ale polisilanilor: studiu comparativ*, **M. Soroceanu**, M. Fortuna, L. Săcărescu, G. Săcărescu, V. Harabagiu, A XXIV-a Sesiune de comunicări ştiinţifice a Institutului de Chimie Macromoleculară „Petru Poni" Iaşi, Progrese în ştiinţa compuşilor organici şi macromoleculari, 3 - 5 Octombrie 2013, Iaşi, România.
3. *Photo-decomposition mechanism of polyhydrosilanes*, **M. Soroceanu**, V. Harabagiu, L. Sacarescu, 4th Bilateral symposium on functional heterocyclic and heterochain polymers for advanced materials, 2 – 7 Septembrie 2012, Iași, România.
4. *Polysilane-based fluorescent nanostructures*, **M. Soroceanu**, L. Sacarescu, I. Atudosie, V. Harabagiu, A XXIII-a Sesiune de comunicări ştiinţifice a Institutului de Chimie Macromoleculară „Petru Poni" Iaşi, Progrese în ştiinţa compuşilor organici şi macromoleculari, 29 Septembrie - 1 Octombrie 2011, Iaşi, România.
5. *Rubbed Polysilane Films as Liquid Crystal Alignment Layers*, **M. Soroceanu**, A. I. Barzic, I. Stoica, L. Sacarescu, V. Harabagiu, Seventh Cristofor I. Simionescu Symposium Frontiers in Macromolecular and Supramolecular Science, Institutul de Chimie Macromoleculară „Petru Poni", 4 – 5 iunie 2015, Iași, România.

Selected references

1 Michl J., R. D. Miller, Polysilane High Polymers, *Chem. Rev*. 89, 1359, 1989.

36 Cotts P. M., Miller R. D., Trefonas III P. T., West R., Fickes G. Dilute solution physical properties of organosilane polymers *Macromolecules* 20(5), 1046-1052, 1987.

37 Cotts P.M., Miller R.D., Sooriyakumaran R. In Zeigler JM and Fearon FWG (ed) Silicon-Based Polymer Science A Comprehensive Resource. Washington, DC: Advances in Chemistry Series 224, ACS, 397–412, 1990.

41 Navratil K., Sik J., Humlitek J., Nespurek S. Optical properties of thin films of poly(methyl–phenylsilylene), *Opt. Mater*. 12, 105-113, 1999.

111 Tarabukina E., Krasova A., Filippov A., Sacarescu L., Simionescu M., Sacarescu G., **Soroceanu M**., Harabagiu V. Hydrodynamic and molecular characteristics of organosilane copolymers of low molecular weight, *High Perform. Polym.* 25(1), 79-86, 2013.

120 Murata H., Fujiyama T., Sato S., Tsuitsui T. *Eur. Pat. Appl. Ep* 622, 975, 1994.

121 Sacarescu L., Cojocaru C., Sacarescu G., Simionescu M., **Soroceanu M**., Harabagiu V. Thermodegradability of soluble polydiphenylsilane copolymers, *Polym. Degrad.Stabil*. 107, 82-90, 2014.

125 Jones R.G., Benfield R.E., Cragg R.H., Swain A.C., Webb S.J. Evaluation of the synthesis of polysilanes by the reductive-coupling of dihaloorganosilanes, *Macromolecules* 26, 4878-4887, 1993.

126 Sun Y.-P., Miller R., Sooriyakumaran R., Michl J. Fluorescence of poly(di-n-alkylsilane)s in roomtemperature solution, *J. Inorg. Organomet. Polym.* 1(1), 3-35, 1991.

127 Watanabe H., Kato M., Okawa T., Kougo Y., Nagai Y., Goto M. Crystal and molecular structure of [i-Pr2Si]4 and [(Me3SICH2)2Si]4 and some structural properties of cyclopolysilanes, [R1R2Si]n (n = 3-6), *Appl. Organomet. Chem.* 1(2), 157-169, 1987.

136 Sacarescu L., Bockholt A., Siokou A., Simionescu M., Sacarescu G. Structural and Optical Properties of Polyhydrosilanes, *Macromol. Chem. Phys.* 210(23), 2015–2021, 2009.

139 Zhao L., Lei Y., Li S., Huang S.Preparation of amorphous ter-polysilane bearing vinyl side groups and its fluorescent property, *Materials Letters* 60(17-18), 2175–2178, 2006.

140 Vyprachticky D., Cimrova V. New synthesis, electroluminescence, and photophysical properties of poly [(formylphenyl)methylsilanediyl] and its derivatives, *Macromolecules* 35(9), 3463-3473, 2002.

141 Sacarescu L., Mangalagiu I., Simionescu M., Sacarescu G., Ardeleanu R. Polysilanes. A New Route Toward High Performance EL Devices, *Macromol. Symp*. 267(1), 123–128, 2008.

149 Nakayama Y., Hirooka K., Oka K., West R. Hole transport in oriented polysilane films, *Solid State Communications* 109, 45–49, 1999.

163 **Soroceanu M.,** Sacarescu L., Hitruc E. G., Ursu C., Harabagiu V. Morphological Investigation of Poly[methyl(H)silane-co-diphenylsilane] Irradiated by XeCl Excimer Laser, *Int. J.Polym. Anal. Charact*. 19(6), 482-488, 2014.

182 **Soroceanu M**., Barzic A. I., Stoica I., Sacarescu L., Harabagiu V. The influence of polysilane chemical structure on optical properties, rubbed film morphology and LC alignment., *eXPRESS Polym. Lett.*, 2015.

183 Tauc J. Optical Properties of Solids, Plenum, New York, 1969.

184 Mott N.F., Davis E.A. “Electronic Processes in Noncrystalline Materials”, Clarendon, Oxford, 1979.

189 Hamciuc V., Pricop L., Marcu M., Ionescu C., Sacarescu L., Pricop D.S. Reaction conditions study in linear H-functional polysiloxane synthesis. *J. Macromol. Sci. Pure Appl. Chem.* A35, 1957-1970, 1998.

190 Berreman D.W. Alignment of liquid crystals by grooved surfaces *Mol. Cryst. Liq. Cryst*. 23, 215–231, 1973.