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Thickness dependent structural ordering,  
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A photoluminescence study on representative  $\sigma$ -  
conjugated polymers

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## ABSTRACT

We present a fundamental experimental study based on the fluorescence investigation of thin  $\sigma$ -conjugated polymer films, where the dependence of optoelectrical properties and UV degradation on film thickness ranging from nano- to microscale was studied. Such extensive and detailed study was performed for the first time and observed spectral shifts in emission and excitation spectra and UV degradation retardation point towards the conclusions that there exists a threshold thickness where the material degradation behavior, electron delocalization and structure suddenly change. The development of well aligned polymeric chain structure between the nano- and micrometer thickness (on the mesoscale) was shown responsible for the manifested phenomena. The material thicker than critical 500 nm has extremely small Stokes shift, maximum extended  $\sigma$ -delocalization along the silicon polymer backbone and exhibits remarkable UV degradation slowdown and self-recovery ability. On the contrary, the electronic properties of thin films below 80 nm resemble those of random coils in solutions. The films of moderate thickness show relatively steep transition between these two modes of structural ordering and resulting properties. Altogether, we consider this complex phenomenon as a consequence of the mesoscale effect, which is an only recently introduced concept in polymer thin films.

**KEYWORDS** Mesoscale; photoluminescence; polysilanes; weak bond; dangling bond; selfhealing; metastability

## 1. Introduction

Linear polysilanes, called polysilylenes (PSis), are a group of  $\sigma$ -conjugated polymers with the backbone consisting entirely of silicon atoms. PSis are polymer materials applicable in many electrical, optical and optoelectrical applications due to their electronic and photoelectrical properties caused by the effect of  $\sigma$ -electron delocalization along the main chain [1, 2]. However, a single bonded linear chain is more vulnerable than a double bonded one which makes the material more susceptible to UV degradation [3, 4]. UV degradability is a very important yet peculiar property for any application of PSis. It can be desirable in the use of polysilanes as resists in lithography or as UV macroinitiators of chemical reactions. On the other hand, the UV instability of PSis limits the development of devices using their electronic properties, for instance light emitting diodes operating in the UV and the visible light region, where it is important to prolong the durability of the active layer over the whole expected device lifespan [3]. Hence, the improvement of the UV radiation stability of PSis is one of the main challenges for their further research.

Intrinsic photoluminescence (PL) is a characteristic feature of PSis and it is strongly dependent on the structure of the material. A PL emission spectrum of a real polymer material - poly(methylphenylsilane), PMPSi, deposited as a thin film, is composed of two distinctive features as exemplified in Figure 3a): a very intensive main sharp PL band situated at the wavelength 360 nm and two merged weak broad emission bands manifested in the region from 420 to 520 nm. The sharp band in UV is attributed to the  $\sigma^*$ - $\sigma$  exciton radiative recombination which is an intrachain transition. The chromophore responsible for the absorption of a light quantum is a conjugated segment of the main silicon chain of PSis. The energy of this  $\sigma$ - $\sigma^*$  transition depends straightforwardly on the conjugation length of the delocalized  $\sigma$ -orbital

system [5]. Once formed, the exciton travels along the main chain until it is trapped on the longest segment, which has the smallest band gap and lowest energy, where a radiative recombination occurs and a photon is emitted [6]. The broad emission band at 420 nm is related to the radiative recombination of charge-transfer states or to the recombination of excitons trapped on chain imperfections or other impurities generated by the photolysis of the polymer, for example cross-link points etc. It was also shown, that a constrained conformational disorder can result into the distortion-related localized states which are the centers of radiative recombination emitting at 420 nm too. However, this behavior of conformational defects was observed only on polysilanes introduced into small pore (about 2.8 nm) mesoporous silica whereas this was not observed in 5.8 nm pores and on homogeneous silica substrate or on relaxed molecules in solutions which can be explained by strong host-guest interactions that substantially affect and stabilize the distorted conformation of the polymer chain [7]. The other broad band emission at 520 nm is a manifestation of exciton recombination on so called weak bond (WB). A WB is a Si-Si bond of inferior quality having a longer bond distance between silicon atoms than regular Si-Si bonds in the PSis' main chain. These WBs are formed in the material structure due to the photodegradation. The WB is stabilized by the surrounding polymer matrix; however, it is amenable to the thermal annealing. Exciton diffusion, free electron-hole pair formation, their trapping in WBs and their subsequent radiative recombination by tunnelling are responsible for the weak emission at 520 nm [8, 9].

Excitation spectra show two maxima in Figure 4 (curve 1), one at 330 nm (due to  $\sigma\text{-}\sigma^*$  transition) and another one at 275 nm due to  $\pi\text{-}\sigma^*$  transition as there is a strong  $\pi^*\text{-}\sigma^*$  mixing which is a manifestation of the phenyl side group presence in the polymer structure [10]. The PL of PSis is strongly related to their structure and responds sensitively to polymer degradation by

a change of the UV emitted light intensity and by manifestation of several emission broad bands in the visible region of the spectra. Moreover, the excitation spectra can be collected as well and interpreted in terms of structural changes too. PL has been already shown as a useful and extremely sensitive tool for structural investigation of PSis [11, 12].

The photodegradation of polysilanes by the UV radiation deteriorates the  $\sigma$ -conjugation and thus decreases the intensity of the exciton PL band. Two basic degradation mechanisms dependent on the energy of incident photons are accepted in the recent literature and confirmed by our previous observations too [8]. The scission of the PSi's backbone chain results into a creation of two silyl radicals (as chemists would normally say) which are at the ends of the two newly released shorter chains. This kind of radical is called pertinently a dangling bond (DB) in physical terminology. Another possible result of incident photon absorption is the formation of a WB. The creation of DBs and WBs in polysilanes depends selectively on the wavelength of the radiation [13]. Electrons and holes keep their original orbital symmetries in WBs and thus an optical transition is possible between them what means that a WB is allowed to act as a radiative centre with a luminescence as described above. In contrast to that, a DB is a non-radiative centre and suppresses PL of the Si-Si chain. With respect to the selectivity of degradation process in alkyl-aryl substituted PSis, the high energy photons can be considered as those having wavelength lower than 300 nm, typically in the range between 250 nm and 290 nm, which correlates with  $\pi$ - $\sigma^*$  transition. The low energy photons are considered to have the wavelength longer than 300 typically between 330 and 355 nm which correlates with  $\sigma$ - $\sigma^*$ . In PMPSi, the silicon chain is broken and DBs are formed by high energy photons at the incident place of absorption so that no blue shift is observed in the absorption spectra in the  $\sigma$ - $\sigma^*$  excitation of the Si-Si chain region [14]. On the other hand, low energy radiation creates excitons of lower energy

in PMPSi which travel to longer chain segments of lower energy and cuts them predominantly at the defects and WB in the Si–Si chain [14, 15]. This fact is manifested by the blue shift of the absorption spectrum maximum in the  $\sigma$ – $\sigma^*$  region with the progress of degradation [8, 12, 14 and 15]. Nevertheless, the recovery of the material was observed under certain conditions instead of a progressive deterioration of the material structure. Such “selfhealing” effects observable due to postdegradation annealing at higher temperatures or just after some relaxation time are referred to as metastability [16, 17]. This concept originally developed for glassy materials was adopted for PSis in solid phase. The polymer recovery is based on the formation of WBs followed rather by their relaxation than by scission during annealing. The hypothesis of weak bonds of inferior quality temporarily stabilized by the polymer chain lattice were mathematically modeled and experimentally verified. These processes were shown to be thermally activated and dependent on the external conditions (air, inert atmosphere or vacuum) and on the energy of incident photons [8, 9]. On the other hand, chain scission is expected to lead to non-reversible processes [11]. Similar observation of two types of degradation induced defects was presented by Kobayashi [18] and explained by two subsequent types of DB differing in energy configuration diagram.

Generally, the radicals on polymer chain (DBs in our case) formed during irradiation can cause further propagation of the degradation and allow this reaction to continue for long periods of time even after radiation has ceased. This post-degradation is very severe problem which is evidently related to the creation of DBs and a valuable lesson can be drawn from a successful yet empirical only invention that was found, patented and introduced in the field of radiative sterilization of medical plastics made from semicrystalline polymers (like polypropylene for example). It is based on addition of so called mobilizers, which increase the free volume and thus

the mobility of polymer chains. The photolytic and photooxidative degradation of the polymer having the mobilizer incorporated therein is suppressed so that the irradiated polymer is not embrittled, does not become embrittled subsequent to the irradiation and even after storage for a long period of time has its initial flexibility [19]. Hence, it has been practically demonstrated at least in some cases, that under certain circumstances the structure of the polymer may support radical termination or recombination. In other words it means that even the DBs may be healed if the microstructure of the polymer is appropriate towards these ends.

However, the above described picture of PSis degradation present state of knowledge is not sufficient to cover all experimentally observed features. There is a discrepancy between the behavior of thin and thick films in the photodegradation process. The fundamental PL studies were measured on thin films (thickness about tens of nanometers) and the degradation studies were carried out on thick films (one and more  $\mu\text{m}$ ) and the self-recovering effects were observed on thin [16, 17] films in vacuum only and on thick films [8] under oxidative atmosphere without the issue of thickness being discussed at all. On the other hand, the rarely observed phenomena of PL decay retardation in thick films were explained by photo- and prephotobleaching mechanisms, suggesting that the scission of Si-Si bonds is slowed down by the thermal consumption of the absorbed energy by Si-Si segments in thick films and, moreover, a sponge-like structure of degraded material with a diminished absorption of UV light arises, formed with the degradation beam penetration, and the front of such zone propagates through the thickness of the material until reaching the substrate, thus making the degradation of PSis virtually slower [6, 20 and 21].

It is widely accepted that the conformation of polymer chains is different in the closest proximity (several average bonding lengths) of the substrate surface and in the bulk material in



case of thick films. On the other hand, according to a few rare recent studies, the thickness influences the properties of thin polymer films in a very non-trivial way. The same material in films shows different properties in dependence on its thickness. Isolated chains on the substrate surface resemble a diluted solution with the random coil conformation of chains and, with an increased surface coverage a structure of thin film is developed. But in case of thin films of low or moderate thickness, the chains are affected by the substrate on a short distance and the main part of the material does not manifest bulk properties. Moreover, if the thickness of films is sufficient and the polymer chains can build a supramolecular structure, then they can be aligned rather than entangled and, thus, in the first place, optoelectrical properties [22, 23] and the polymer structure [24, 25, 26] are influenced. Evidences for thickness threshold of structural ordering in thin poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) films have been already published [27]. According to the aforementioned studies on MEH-PPV, poly(*t*-butyl)acrylate and polystyrene, and to our preliminary observations on PSis [3], we hypothesize that such behavior might be more general phenomenon. It is not obvious that the structure and properties of the thin film depend incrementally on the film thickness but they can suddenly change and even could emerge beyond a certain dimension limit, whereas the threshold lies between the nano- and microscale as demonstrated in the following experimental study on PSis.

## 2. Experimental

PMPSi (with  $M_w=27\ 600$  g/mol and  $M_n=8\ 500$  g/mol) and copolymer poly(dimethylsilane-methylphenylsilane) - P[DMSi-MPSi] (with  $M_w=82\ 027$  g/mol and  $M_n=18\ 610$  g/mol), were obtained from Flourochem Ltd., UK. Films for UV/VIS and PL measurements were prepared by

the spin coating method using spin coater Laurell WS-650-MZ-23NPP and by drop-casting from the solution in toluene. Quartz glass and undoped single crystal silicon wafers were used as substrates. The absorption spectra were measured by the UV/VIS Spectrometer Cary 100 (Varian) and by Lambda 1050 UV/VIS/NIR spectrometer from Perkin Elmer. The fluorimeter FSL 920 from Edinburgh Instruments (UK) was used for the measuring of PL spectra. The thickness of films varied from 10 to 1000 nm, depending on process conditions. The thickness was measured by using the profilometer Talystep (Taylor Hobson, USA). PL spectra and decay curves were taken in a vacuum (pressure less than 1 Pa) ensured by the cryostat Optistat DN-V (LN2), Oxford Instruments at room temperature.

### 3. Results and discussion

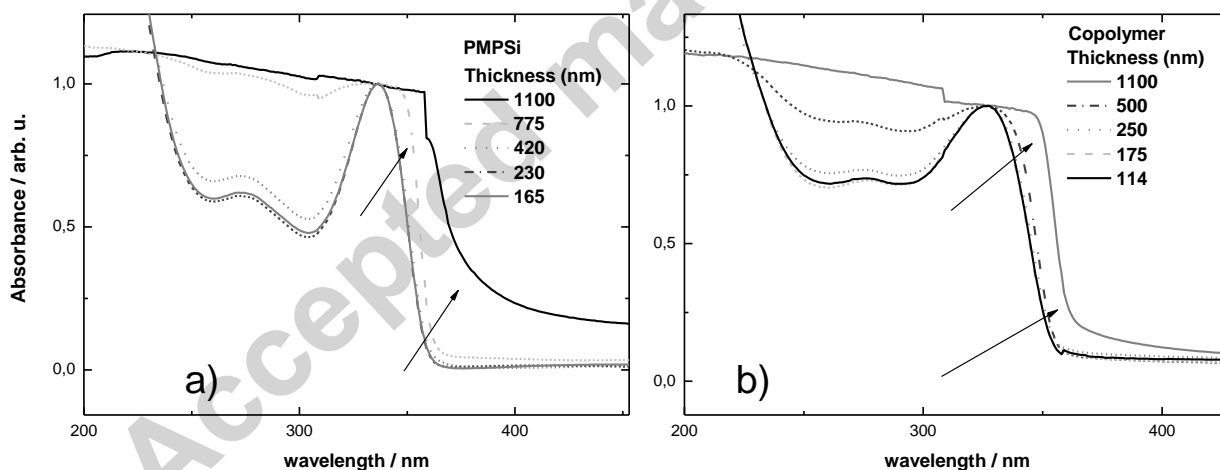


Figure 1 Normalized absorption spectra of thin film with various thickness a) PMPSi b) P[DMSi-MPSi].

Figure 1 shows the absorption spectra of investigated polysilanes. The long wavelength electronic transition at 330 nm arises mainly from delocalized  $\sigma$ - $\sigma^*$  transition on the silicone backbone. The peak at 275 nm is related to  $\pi$ - $\pi^*$  transition in the benzene ring. The spectra are

normalized to the value at the wavelength of  $\sigma$ - $\sigma^*$  absorption maximum. Nevertheless, the absorption measurement of the thickest films (thickness 1100 nm and to lesser extent for thickness 775 nm) was overloaded in that region and resulted in truncated shape of absorption peaks. Therefore, it was not possible to find exactly the maximum of absorption and the spectrum is shown for the purpose of completeness. However, it is evident that the position of the maxima is most likely not changed with the thickness of the film, only the long wavelength tails of the absorption spectra are more populated and the absorption edge is shifted from higher to lower energies with increasing layer thickness for both polymers. Such shift towards lower absorption energies with increasing thickness testifies for increasing conjugation length of polymer segments as well as for their increasing population in thicker films, which can be interpreted [28] as a manifestation of better organized polymer structure.

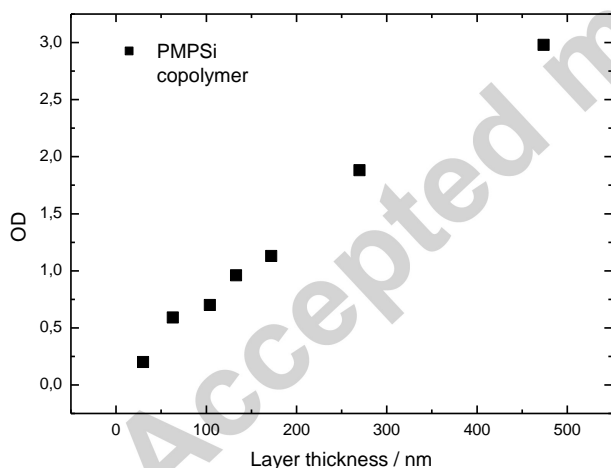


Figure 2 Dependence of optical density (OD) on the film (PSi's layer) thickness.

Absolute value of optical density (OD) is very important for luminescence studies on thin solid films as well. Figure 2 shows the dependence of OD on the thin film thickness for both materials. It is evident, that the materials is highly absorbing and that films under investigation in this study having thickness from tens through hundreds up to thousands nm are far from the critical range

of 0.2-1 OD where a strong dependence of the spectrum shape on thickness is expected due to the reabsorption effect. Generally, the spectra are expected to be independent on the thickness until optical density reaches about 0.2-0.5. Strong dependence has been reported in the range of about 0.2-1 OD and no dependence should be again at higher densities [29].

PL study is the most sensitive and highly selective method for structural investigation of PSi's backbone chain dimensionality, conformation and defects [12]. The microstructural interpretation framework of emission and excitation spectra can be summarized (and justified) as follows: The wavelength of the maximum in UV emission peak depends directly on the length of the conjugated segment where the radiative recombination of the exciton takes place, i.e. the longer segment, the longer wavelength. Defects of the polymer structure influence crucially the PL of the material. Conformational defects which can be defined as any deviation from ideal all-trans conformation cause shortening of the conjugation length. The smallest conformational defect can be defined as a kink on the polymer backbone and indeed it decreases the conjugation length although it does not restrain the exciton from travelling along the chain [6, 21]. Imperfections or deviations from purely linear covalent polymer chain structure as branching or crosslinking points dramatically decrease the intensity of the UV emission and change the ratio between UV and visible emission intensity. Fujiki [30] found a correlation of NMR signals occurring on introduction of branching points with the defect luminescence at 450 nm at a level in excess of 1% of such bonding configurations. Introduction of branching to 5 % silicon atoms in the polymer diminishes the UV emission to nearly negligible values [31]. The ratio between UV and visible luminescence intensities is therefore highly indicative for analysis of the PSi's dimensionality [12]. Analysis of the visible part of emission spectra allows distinguishing between the polymer chain structural defects and weak bonds as discussed above. However the

peaks in visible region are quite broad, overlap to a reasonable extent and thus make the interpretation more difficult in this issue. Excitation spectrum resemble to some extent the absorption spectrum, actually it is its subset in some sense. The absorption of a photon is a fast (vertical) process therefore the excitation spectrum gives information about the conformation at the site of light quantum incidence with the chromophore [32] although only those absorption events that lead to a radiative recombination are recorded. Thus it is possible to investigate the microstructure of the PSis material at two distinguished sites i.e. at the absorption site and at the recombination site and the distance of these two sites in space (and in time too) is simply due to the exciton diffusion. Though one might argue that this interpretation framework is simplified and limited to one-dimensional approach only and that there are strong interchain interactions in conjugated polymers this is not appropriate in this case. Interchain aggregation influences significantly electronic structure of  $\pi$ -conjugated polymers [33 and 34], through interaction of the delocalized  $\pi$ -electron systems in case of so called  $\pi$ -stacking. Slightly similar situation can be observed just in non-substituted  $\sigma$ -conjugated PSis. Creation of two or three dimensional structures from  $(SiH_2)_n$  chains gives rise to the interchain interactions which significantly influence the electronic properties of the material. On the other hand, methyl and phenyl substituted PSis show signs for very weak interchain hydrogen bonds in two or three dimensional structures only while the stability of the solid phase is due to cooperative effects of such weak bonds. Consequently, the electronic structure of the polymer backbone chain in comparison with the one dimensional structure is hardly influenced [35].

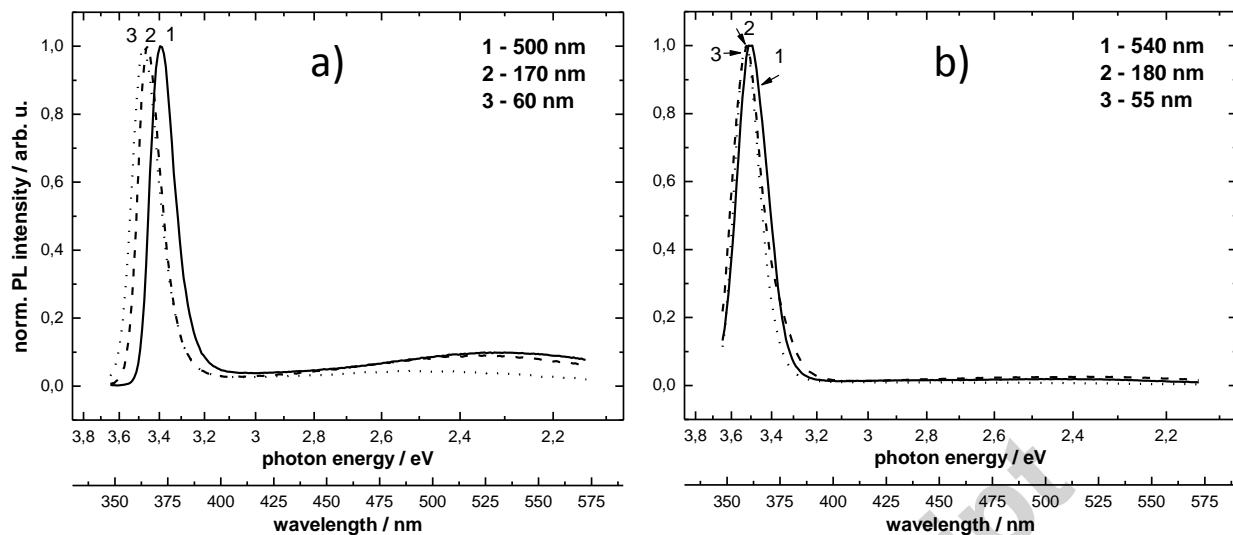


Figure 3 Emission spectra of polysilane thin films with a different thickness,  $\lambda_{\text{ex}}=330$  nm, graph window notation a) PMPSi, b) P[DMSi-MPSi].

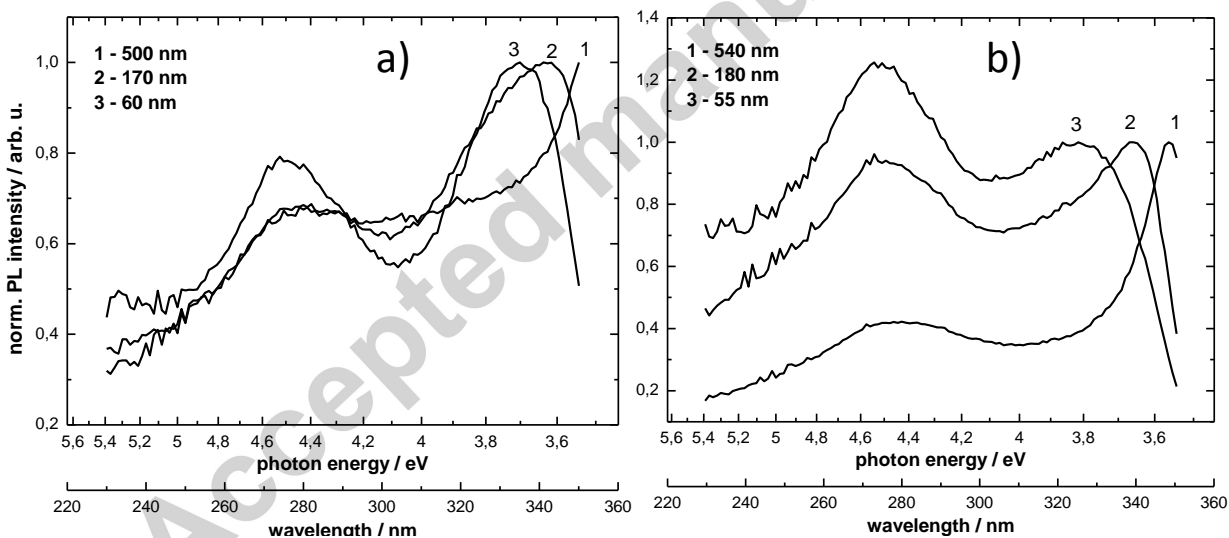


Figure 4 Excitation spectra of polysilane thin films with a different thickness,  $\lambda_{\text{em}}=360$  nm, graph window notation a) PMPSi, b) P[DMSi-MPSi].

Thus the microstructure of alkyl and aryl substituted PSis can be successfully understand and interpreted in terms related to polymer chains as quasi one dimensional structures that keep such character even in solid phase and this approach is relevant for the whole context discussed above.

The observed emission spectra of PMPSi and copolymer P[DMSi-MPSi], are shown in Figure 3 exemplified on three selected films. In case of PMPSi, a small shift of emission maxima depending on the film thickness is clearly seen. The thicker the film is the more the UV emission peak is shifted towards lower energy due to the increasing length of the polymer chain segment at the site of recombination. However, the effect is pronounced only a little and, in case of P[DMSi-MPSi], the shift of emission maxima cannot be clearly observed at all. The exciton diffusion along the polysilane chain and its selective recombination on the longest conjugated segment [6] impedes the manifestation of the emission peak maximum dependency on the PSi's backbone chain conformation. Broad bands of the low intensity at 420-450 nm and 520-530 nm, as mentioned above, are caused by imperfections and by the WBs formation [8], however their low intensity indicates high quality of the polymer material. The slightly pronounced dependence of visible luminescence at 520-530 nm on PMPSi film thickness that is seen in Figure 3a) can be explained by the stabilizing effect of the polymer matrix on WBs. If the film is too thin, WBs cannot be stabilized hence they cannot be present as recombination centers in the film structure and manifested by visible luminescence. On the other hand, the luminescence at 420-450 nm is much less intense and thickness independent which both testifies for very good linearity of polymer chains in the source polymer material. The luminescence in the visible region for P[DMSi-MPSi] (Figure 3b) is relatively less intensive in comparison with the strong UV emission than it is observed in case of PMPSi. A plausible explanation for the relatively much weaker visible luminescence of P[DMSi-MPSi] in comparison with PMPSi is that the copolymer material formed even better developed structure than the homopolymer. This behavior correlates with the more pronounced self-recovery ability of P[DMSi-MPSi] observed in the degradation study discussed below.

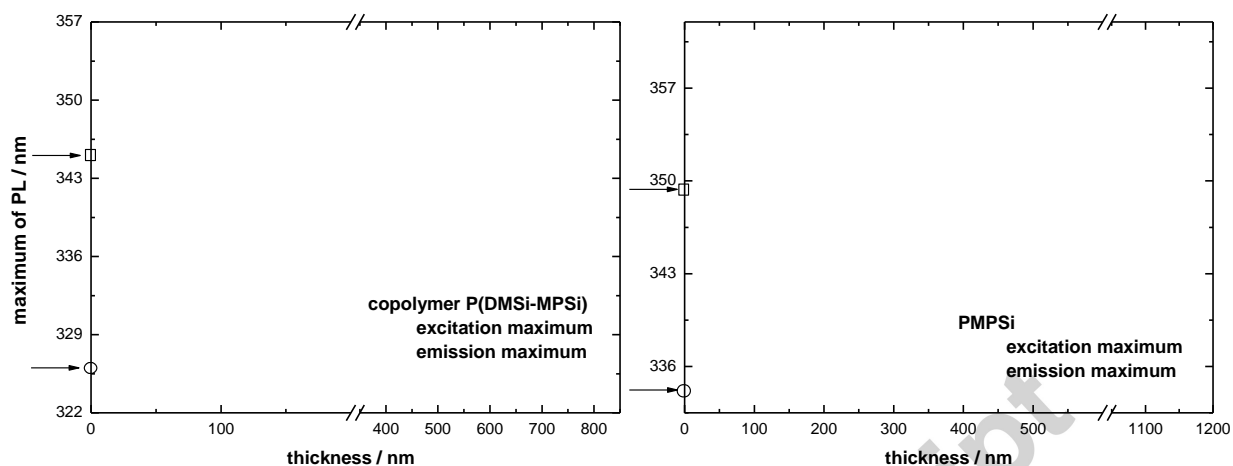


Figure 5 Emission and excitation maximum wavelengths in dependence on the sample thickness. Arrows show values observed in toluene solutions, data points are virtually attributed to the zero thickness, graph window notation a) P[DMSi-MPSi], b) PMPSi.

The dependence of emission peak maximum wavelength on sample thickness was investigated systematically and the results measured for the whole set of samples is shown in Figure 5. A small gradual increase of the wavelength value (i.e. decrease in energy) can be observed for P[DMSi-MPSi] while in case of PMPSi the increase is very small if observable at all. Although the two materials have very similar absorption and emission spectra, the observed emission maximum shift is different. If the origin of this effect is in reabsorption, both materials will exhibit the same dependence on thickness as reabsorption typically causes long wavelength shifts of the fluorescence bands with the increase of the optical density of the sample. In fact, they exhibit different behavior. The PMPSi reaches saturation at 360 nm, the copolymer P[DMSi-MPSi] at 356 nm. Graphs contain also the emission peak wavelength measured for solutions virtually attributed to zero thickness. It was observed 345 nm for P[DMSi-MPSi] and 347 nm for PMPSi. The polymer random coils in toluene solution shows the shortest conjugation lengths



which fact is obviously in accord with the notion that any solid phase of the polymer will be more ordered than the solvated coil in solution. It can be deduced from the relative weakness of the maximum position dependence on the thickness that there are always present some of the very long or longest-possible conjugated segments in the distribution of the conjugation lengths of polymer chain segments in the solid state. It seems that the conformational structure of PMPSi is slightly more sensitive to the film thickness than it is manifested for P[DMSi-MPSi]. Similar phenomena were observed in [36].

On the other hand, in both cases, PMPSi and P[DMSi-MPSi], large shifts of excitation maxima related to the  $\sigma$ - $\sigma^*$  transition in the region at about 330 – 350 nm are manifested in Figure 4 and the structural sensitivity of PL investigation method in excitation spectra is not smeared by the above discussed exciton diffusion. Moreover, although the emission spectra could be influenced by a reabsorption effect, it does not play any considerable role in the study of excitation spectra, which are independent on this phenomenon because the measured PL wavelength is constant while the excitation wavelength is changed. Similarly to emission, the data are plotted in Figure 5. The wavelength at the maximum in excitation spectrum is 334 nm for PMPSi and 326 nm for P[DMSi-MPSi] so the copolymer has larger Stokes' shift. This suggest that P[DMSi-MPSi] has shorter conjugation length of segments in average in solution, and that the increase of conformational order is relatively bigger for P[DMSi-MPSi] than for PMPSi during formation of the solid thin film. The thinnest PMPSi film in our study was 20 nm thick and its UV emission maximum was at 335 nm which suggest that not much changed between solution and thin film. Similarly, the wavelength 326 nm was observed for P[DMSi-MPSi]. This value remains practically constant up to the sample thickness of approximately 80 nm for both materials. It can be assumed, that a relatively unordered structure prevails in thin films below 80 nm with

conformations similar to that of the coils in solution. It can be ascribed to certain rigidity of the PSis molecules which are relatively short (usually having the polymerization degree about only few hundreds or thousands [10] and have probably broken rod-like shape of molecules [37] resembling in some way the popular Rubik's Snake. On the other hand, it can be observed, that the emission maximum wavelength slightly rises which testifies for presence of longer conjugated segments with increasing film thickness. In other words, the distribution of the conjugation length of PSis chain segments extends to higher range and enriches by longer segments while keeping its center still at the position as in solutions. With the thickness of films increasing over 80 nm, the excitation maxima for  $\sigma$ - $\sigma^*$  shift markedly to a lower energy, i.e. to higher wavelengths. It means that much more ordered phase is formed and that the distribution of the segmental conjugation length shifts towards higher values and the Stokes' shift becomes smaller for both polymers. Taking the exciton travelling mechanism to the longest available conjugated segment into account, the distribution of the conjugation length not only shift but most likely becomes also much narrower, similarly to the FWHM of the  $\sigma$ - $\sigma^*$  peak in excitation spectra in Figure 4. These shifts are accompanied by a change of the ratio of the PL intensity between two main excitations bands (peaks). Considering the excitation peak at 275 nm associated mostly with the phenyl side groups localization, in other words  $\sigma$ - $\pi^*$  absorption remaining relatively unchanged, it can be concluded that the intensity of the  $\sigma$ - $\sigma^*$  transition band strongly increases with the film thickness, hence the concentration of longer conjugated polymer segments with perfect conformation increases extremely with the thickness as well and the amount of non-radiative recombination events decreases complementary. Saturation can be observed in all these dependencies at the film thickness above 500 nm. Films thicker than 500 nm have constant emission and excitation maxima and very small Stokes' shift about 5 nm.

To summarize, the structural ordering in thin PSis films has two stable regions and a transition or threshold region in dependence on the film thickness. Films that are thinner than 80 nm resemble the polymer in solution to some extent. Films which are thicker than 500 nm show marks of well-developed structure with high share of linear polymer segments in ideal conformation maximizing thus the  $\sigma$ -conjugation length of the segments. The range between 80 and 500 nm shows transitive behavior with strong dependency of the micro-structure on the thickness.

According to the paragraph above, we performed a set of degradation experiments with the film thickness as the varied parameter. Figure 6 shows that the intensity of PL emission bands at 360 nm decreases with the photodegradation time for spin cast films (both PMPSi and P[DMSi-MPSi]), whereas the excitation beam of the wavelength 330 nm was employed directly as the degradation agent. The non-trivial dependence of PL decay on the thickness of the film is clearly seen. The thicker is the film, the slower is the degradation.

Observations shown in Figure 6 might be still explained by the theories of progressive frontal deterioration during [20, 21]. The same observation may be explained by the immediate manifestation of the recovery mechanism which works instantaneously against the deterioration. Figure 7 shows degradation curve recorded for a P[DMSi-MPSi] drop cast film with a thickness of about 1000 nm.

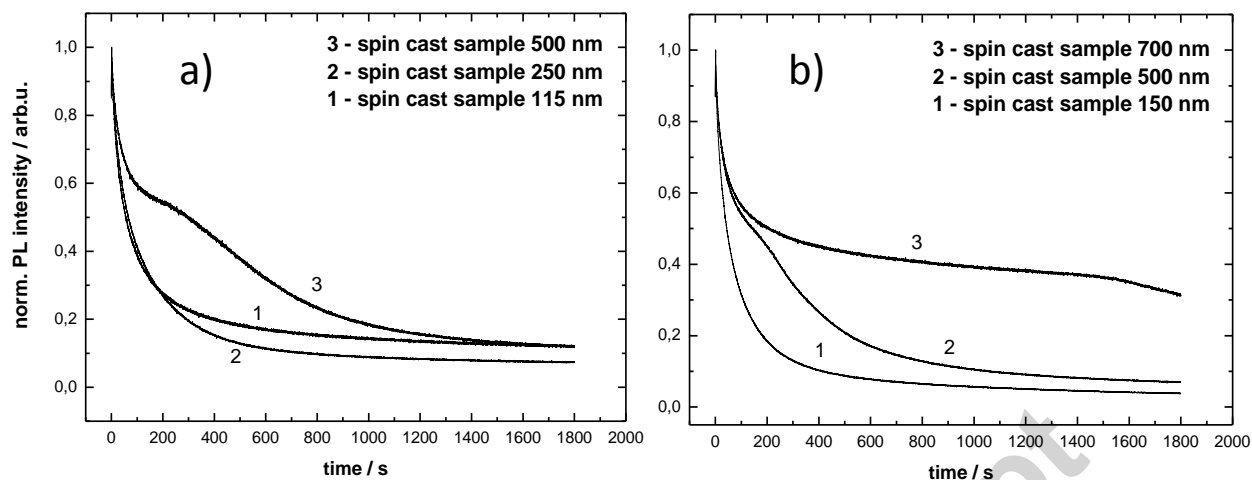


Figure 6 PL decay of a) PMPSi, b) P[DMSi-MPSi]. Used wavelengths  $\lambda_{em}=360$  nm,  $\lambda_{ex}=330$  nm.

The shape of the curve with a minimum unambiguously testifies for two processes working against each other. At the beginning, the degradation prevails and the self-recovery effect slowly increases. At the curve minimum, those two antagonistic processes become to be comparable and after that a dynamic equilibrium and saturation is reached.

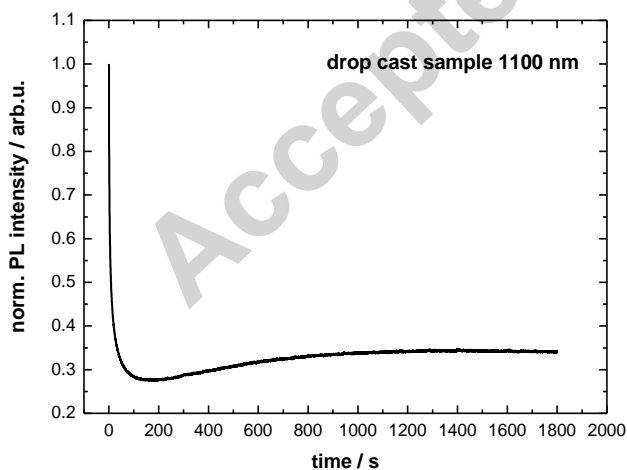


Figure 7 PL decay of a thick P[DMSi-MPSi]. Used wavelengths  $\lambda_{em}=360$  nm,  $\lambda_{ex}=330$  nm.

The self-healing mechanism can be of surprising efficiency as documented in Figure 8 where a degradation curve for P[DMSi-MPSi] is shown. It seems that initial degradation can induce the self-healing process and moreover that this process can prevail over the degradation and even the defects present in the material from its preparation can be erased from the material structure and higher luminescence intensity than at the beginning of the degradation can be achieved.

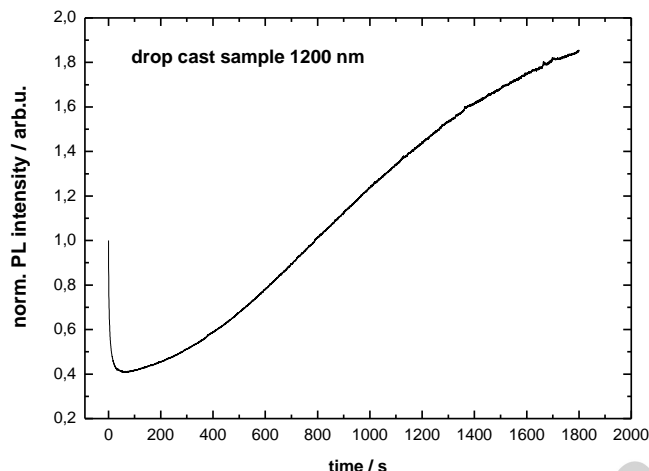


Figure 8 The self-recovery of the material P[DMSi-MPSi] cast from solution in toluene observed at  $\lambda_{em}=360$  nm,  $\lambda_{ex}=330$  nm.

Again in degradation experiments, three typical features can be identified with respect to the sample thickness. (i) If the structure of the material is poorly developed in very thin films, a rapid double exponential degradation curve is observed. (ii) If the material has the thickness in the transition region, one can observe significant slowdown of degradation and prolongation of the material performance. (iii) Finally, if the film is thick enough and the structure of the material is well developed, a self-recovery process of the material manifests itself even during the action of the degradation agent and stabilizes the material.

The correlation between structural ordering and stabilization and recovery of WBs is evident. A WB is a defect which is only possible if stabilized by its surrounding [38]. The more perfect

stacking of the polymer chain segments is in its proximity, the higher probability of its healing arises. Besides WBs, it cannot be neglected that DBs can be created during degradation of PSis too. It must be emphasized that the mobility of polymer chain ends is limited but still possible in glassy polymers and that it must be dependent on the free volume. It can be expected that the more ordered the structure of the polymer is, the smaller the mobility of such free chain ends is. The strongest limitation of the segmental movements appears in crystalline state, as obvious. If the structure of the polymer film is perfect enough such that almost no movement of the two radicals at the freshly scissored chain ends is possible due to a strong cage effect of surrounding well stacked chains, it is only a radical recombination which remains to happen to the two radicals. Nevertheless, a more detailed and extensive study is still needed to obtain deeper insight into the interplay between degradation and self-recovery mechanisms in PSis. PSis were considered as typically unstable and highly degradable materials suitable mostly as resists for lithography, ceramic precursors or macroinitiators [39, 40 and 41] in real life applications. It can be hypothesized on the base of the last experiment (see Figure 8 again), that PSis could be prepared in a relatively well-ordered state which would not be susceptible to degradation at all.

#### **4. Conclusion**

The non-trivial dependence of properties on thickness is typical for thin films made from both PSi polymer materials. Two thickness thresholds were observed. Thin films below 100 nm have unordered structure resembling the polymer in solution. Thicker films show remarkable trends of prolongation of the segment conjugation length with increasing thickness directly manifested in PL spectra. Films thicker than 500 nm show very small Stokes shift and have extremely extended segment conjugation length due the increased linearity of polymer chains. Thus, the observed PL

shifts unambiguously testify to the presence of a well aligned structure of polymer chains with maximized conjugation length of segments which can explain the stabilization and promotion of the self-healing of the material. Stabilization and recovery of WBs is best plausible in the highly ordered 3D structure. For the thinnest films, a simple double-exponential UV degradation decay is observed. With the increasing thickness over 80 nm, the exponential decay of PL displays a substantial slowdown above the thickness of 500 nm. Moreover, in case of 1  $\mu\text{m}$  thick film made from the copolymer, the PL decay exhibits a minimum at 27 % of the initial PL intensity followed by a PL enhancement until the saturation is reached at 34 %. If the film is thick enough, the self-healing mechanism can promote such material recovery that even the initial imperfections can be healed (vanished) and the PL intensity of the material can overcome the initial value. Such behavior was demonstrated to emerge on mesoscale (between nano- and micro-dimensions) and was not observed for nanoscale thin films.

Although the presented study is based on only yet superiorly powerful PL study, it may invoke a revision of the recent knowledge on thin film structure with thickness range from tens to thousands nanometers using both experimental and theoretical [42] approaches. We believe that our observations may be very helpful not only in the field of  $\sigma$ -conjugated PSis but also for much broader scientific interest given to  $\pi$ -conjugated polymers and that the correlation between the thickness and microstructure ergo optoelectronic properties of various  $\pi$ -conjugated polymers will be elucidated in the near future while seeing first achievements so far.

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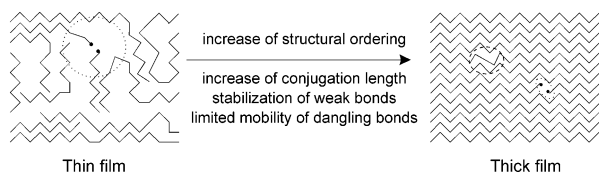
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## Table of Content – Graphical Abstract



### Highlights:

- Photoluminescence was used as a tool for structural investigation of polysilanes
- Primary study of strong dependence of thin polymer film structure on mesoscale
- A mesoscale effect observed for the first time on sigma conjugated polymers
- Conjugation length is dramatically extended in thicker films than in nanoscale
- Self-recovery effect was shown to be dependent on the mesoscale as well