THE INFLUENCE OF THICKNESS AND USED SOLVENT ON LUMINESCENCE AND PHOTODEGRADATION OF POLYSILANE THIN FILMS

Pavel URBÁNEK 1,2, Ivo KUŘITKA 1,2, Michal URBÁNEK 3

1 Centre of Polymer Systems, University Institute, Tomas Bata University in Zlín, Nad Ovčírnou 3685, 760 01 Zlín, Czech Republic

2 Polymer Centre, Faculty of Technology, Tomas Bata University in Zlín, Nam. T. G. Masaryka 275, 762 72 Zlín, Czech Republic

3 Institute of Scientific Instruments of the ASCR, v.v.i., Academy of Sciences of the Czech Republic, Královořepolská 147, 612 64 Brno, Czech Republic

Abstract

Analysis of the influence of processing parameters on the photoluminescence (PL) of a homopolymer poly(methylphenylsilane) (PMPSi) and a copolymer - poly[dimethylsilane-methylphenylsilane] (P[DMSi-MPSi]) is presented. The influence of solvent type and effect of thickness of prepared thin films were investigated by the fluorescence spectrometry. There are fundamental differences between thin film and thick film. In thick films, the $\sigma$-conjugation length of polymer chain segments is reasonably longer approved by strong bathochromic shift in the excitation spectra. Moreover, degradation of both polysilane materials was observed as photoluminescence decay measured at two different degradation wavelengths 285 and 330 nm in vacuum. Two patterns of degradation behaviour dependent on film thickness were observed with transition at about 500 nm as in fluorescence spectra too. The degradation and metastability phenomena described in previous papers were observed on thick drop cast films only, which means that they are not general effects, but dependent on film thickness. Hence, the new facts are discussed and the interpretation is extended in terms of mesoscale confinement effects on thin films.

Keywords: polysilane, photodegradation, photoluminescence, thin film, metastability

1. INTRODUCTION

Polysilanes (PSis) attract attention as a very interesting group of polymeric material because of their nonlinear optical and photoelectronic properties. In contrast to $\pi$-conjugated carbonaceous materials, PSis are an example of a rare group of polymers that have $\sigma$-conjugated bonding orbitals along the main chain, which is responsible for their unique properties. However, a single bonded linear chain is more vulnerable than double bonded one what makes the material susceptible to degradation by UV radiation. In the field of application of polysilanes, it is a very important property, e.g. it is desirable in use of polysilanes as resists in lithography or as UV sensitive macrorinitiators of chemical reactions. On the other hand, UV degradability limits the development of devices using electronic properties of PSis, for instance light emitting diodes operating in UV light region, where it is important prolonged the durability of the active layer. Stability of PSI is one of the main challenges with respect to their prospective applications. UV degradation of PSIs has been studied by array of methods and theoretical models. It is assumed that the excitone travels along the main chain until is trapped on the longest segment, which has lowest potential energy and one of the sigma bonds dissociates, as the non-radiative $\sigma^*-$$\sigma$ transition leads to scission of the Si-Si bonds. On the other hand, recovery of the material was observed under certain conditions instead of chain scission. Such “selfhealing” effects are referred as metastability. This concept was developed for polysilanes in solid phase and is based on the formation of "weak" bonds, and their scission or relaxation. Weak bonds were modelled for regular lattice of polymer chains and experimentally verified. These processes were shown to be dependent on the external conditions (air, inert atmosphere or vacuum; temperature) and on degradation agents, i.e. energy of incident photons. Similar metastability phenomena were observed also for e-beam degradation. [1-5]
Intrinsic photoluminescence (PL) is the characteristic feature of PSi’s and depends strongly on the structure of the material. According to recent knowledge, typical representative polymer – poly(methylphenylsilane) (PMPSi) has a strong and narrow emission peak at (355±5) nm which is attributed to radiative exciton recombination (σ*-σ transition) and weak and broad emission in the region from 420 to 520 nm that is attributed to radiative recombination on structural defects. Excitation spectra show two maxima, one at 330 nm (due to σ-σ* transition) and the second at 275 nm due to π-σ* transition as there is a strong π*-σ* mixing. Excitation spectrum corresponds to the absorption spectrum. The spectra of poly(dimethylsilane) (PDMSi) are simpler, since there are no aryl side groups attached to the chain, thus, only a σ-σ* and σ*-σ transitions are manifested in single peaks. Copolymer - poly[dimethylsilane-methylphenylsilane] (P[DMSi-MPSi]) shows spectral features of both homopolymers, so its spectra are very similar to that of PMPSi. Fluorimetry proved to be a suitable sensitive tool for observation of PSi degradation and subtle changes in their structure induced by UV radiation. Behaviour of PSi’s under illumination by excitation light manifest in emission, thus, PL allows to observe degradation in time as changes of emitted light intensity as well as probe the structure of material by collection of emission and excitation spectra [4-9]

In this paper, the attention is focused on the influence of thickness on photoelectronic properties of PMPSi and copolymer P[DMSi-MPSi] both in terms of spectral features as well as UV degradation. The influence of used solvent type on the PL characteristic is investigated as well.

2. EXPERIMENTAL

PMPSi and copolymer P[DMSi-MPSi] were delivered by Flourchem Ltd., UK (Batch 060033-1, 060032-1 respectively). Films for PL measurements were prepared from two different solutions – firstly in toluene and next time in mixture of toluene and tetrahydrofuran (THF). Two methods were used for casting of thin films – drop casting and spin coating as well. Quartz glass and undoped single crystal silicon wafers were used as substrates. Fluorimeter FSL 920 from Edinburgh Instruments was used for the measuring of PL spectra. The thickness was measured by profilometer (Talystep). „Thin” films were about 50 nm and „thick” films thickness was below 1000 nm. PL spectra and decay curves have been taken in vacuum (pressure 1 Pa) ensured by cryostat Optistat DN-V (LN2), Oxford Instruments at room temperature.

3. RESULTS AND DISCUSSION

3.1 Excitation spectra

The results of excitation spectra analysis are summarised in Table 1. The thickness influences the position of peaks in excitation spectra of PMPSi significantly and it is possible to observe bathochromic shifts of these peaks with increasing thickness of the films, as shown in Fig.1. Small bathochromic shift of excitation peaks is apparent in position 1 (about 275 nm) in size of one to three nanometres. The bathochromic shift is much more pronounced in the position 2 (from 330 to about 350 nm). In this case, the shift to higher wavelength is about more than 20 nm. The position of the maximum in the position 2 for thick films was only estimated since was not possible to collect signal in such intimate proximity of emission line due to very small Stoke’s shift between excitation and emission spectra. The range of excitation spectra measurement was set from 230 to 345 nm. The upper limit was chosen to protect single photon counting detector against overloading by scattered excitation light. Hence, the accuracy of ± 5 nm is given by the limit of 345 and the position of emission maximum at 354 nm. The differences between thin and thick films are clearly evident from the excitation spectra for the copolymer P[DMSi-MPSi] as well as it can be seen in Fig. 2. Similar positions of peaks and trend in their shift with increasing thickness of films are confirmed.
Up to now, it was generally accepted that PMPSi and, in general sense all aryl substituted Psis, have excitation maximum at 330 nm at the same position as the maximum observed in absorption spectrum. (See the introduction and references therein.) However, the absorption was always measured for thin films or polymer solutions due to limitations of UV-VIS absorption spectrometers and similar samples were used for subsequent excitation measurements. The similarity between thin film and solution spectra testifies for low alignment of chains in the thin film. Although the thick films were used for many studies, according to our best knowledge, it was never registered that their spectra are principally different from those recorded on thin films. On the other hand, the relation between conjugation length and emission maximum wavelength is well known. The longer is the length of conjugated segments, the higher the wavelength of excitation maxima in the position 2 is expected [5, 7 and 8].

The observed phenomena could be explained in terms of different structure development during preparation of thin and thick films. In this sense, it is reasonable to assume that spin coating of thin films does not lead to formation of organised supramolecular structure and the polymer chains are caught on the substrate in
random form and directions. Due to fast evaporation of solvent arises film with significantly shorter length of conjugated polymer chain segments than in thick films while the evaporation proceeds slower and polymeric chains are better aligned thus achieving large degree of conjugation. This is clearly seen from difference between the positions of excitation maxima in the position 2. Thin films do not allow formation of a defect free material layer. The polymer chains are in near proximity or even in direct contact either with the substrate or with the surface of the film. Macromolecules in thick films could form a mesoscale layer of several hundreds nm between subsurface and substrate adjacent layers and can be confined in energetically favoured conformational states, i.e. in all-trans conformation connected with the highest level of $\sigma$-orbital delocalization.

The next factor playing an important role in forming of films is the choice of used solvent. There are substantial differences in excitation spectra by both materials in both thin and thick films. The positions of maxima in excitation spectra are slightly affected but their intensities are influenced strongly. The thin films formed from THF containing solution exhibit higher efficiency of PL excited by the light of wavelength 330 nm. This could be due to better alignment of aryl side groups and rests of polar solvent caught in the structure thus supporting the photoinduced electron transfer and stabilises the charge transfer (CT) states. [3] On the other hand, this effect becomes of minor importance in thick films, as THF does not specifically support formation of all-trans conformation, thus overbalanced by the effect of mesoscale layer formation.

![Degradation curves of PMPSi](image.png)

**Fig. 3.** Degradation curves of PMPSi. In first row (Graphs a, c) are presented curves for thin films, Graphs b, d present curves for thick films, whereas left column (Graphs a, b) are degradation curves at $\lambda_{ex}=285$ nm and $\lambda_{em}=354$ nm and right column (Graphs c, d) present deg. curves at $\lambda_{ex}=330$ nm and $\lambda_{em}=354$ nm. Full black line denotes films of PMPSi from solution in toluene and dashed line from mixture in toluene and THF.

### 3.2 UV degradation

Degradation curves for PMPSi are shown in Fig. 3 and for P[DMSi-MPSi] in Fig. 4. As degradation agent, the excitation beam was employed directly. Two wavelength were used – 285 and 330 nm. Graphs a and c in
both Figures shows degradation process for thin films. The exponential decay of PL intensity during first 100 s of irradiation of thin films is faster for thin films made from solution in toluene. The rest of degradation (second part, after 100 s) proceed similarly for both types of solvent but one case of copolymer cast from THF mixture slightly more intensive degradation at 330 nm. In all cases, the degradation process ends in total damage of the thin layer for both used photon energies.

Fig. 4. Degradation curves of copolymer P[DMSi-MPSi]. In first row (Graphs a, c) are presented curves for thin films, Graphs b, d present curves for thick films, whereas left column (Graphs a, b) are degradation curves at $\lambda_{ex}=285$ nm and $\lambda_{em}=354$ nm and right column (Graphs c, d) present deg. curves at $\lambda_{ex}=330$ nm and $\lambda_{em}=354$ nm. Full black line denotes films of P[DMSi-MPSi] from solution in toluene and dashed line from mixture in toluene and THF.

Another degradation pattern was observed for thick films. In case of PMPSi, slower degradation compared to thin films occurs by irradiation at the excitation wavelength 285 nm. This can be caused by the metastability mechanism, which is competitive to degradation, similarly as in case of laser degradation studies reported earlier [5, 7]. Tetrahydrofurane contributes to retardation of the decay as well. However, these mechanisms are not able to overwhelm the deterioration process under used condition and resulted just in slowdown of the decay. A stronger effect was observed for excitation wavelength of 330 nm. Thick PMPSi film cast from toluene solution undergoes slow degradation, moreover, the film cast from THF containing solvent exhibits a reasonable slowdown at 40 % at about 200 s followed by second decay above 300 s, although even here, self healing and PL enhancement during degradation was not observed. Much stronger effect was observed for copolymer P[DMSi-MPSi] (see Fig. 4 Graphs b and d). The degradation process is more complicated for both excitation wavelengths (285 and 330 nm). After certain time (200 – 400 s) a break point is observed and PL intensity arises, again thus the degradation curve has a broad minimum. Similar curve shape as in Fig. 4 Graph b was observed in previous work where PMPSi was excited by a laser beam at 266 nm. [5, 7] At used excitation wavelength 285 nm, the return starts at 18 % of initial PL intensity for THF mixture cast sample and at 22 % for toluene cast sample. At excitation wavelength of 330 nm (Fig. 4, Graph d), the expression of return is very strong. The minimum of degradation curve is very sharp, located at time about 20 s and reaches saturation at nearly 100% for the sample cast from THF mixture. Moreover, for the sample cast from
toluene solution, the saturation even exceeds the initial PL intensity. It seems that THF has opposite role than in PMPSi.

Generally, the degradation shows different behaviour with increasing thickness of the film and it is slower for thicker films. Moreover, in case of copolymer, the increased thickness results not only in retardation of degradation but also to recovery having breakpoint on degradation curves. In case of degradation at 330 nm, observed patterns resemble more annealing than degradation as PL intensity is recovered to 100 % or even improved up to nearly 140 % of its initial value. As well as in spectroscopic study, the degradation correlates with film thickness and, as possible explanation, the mesoscale polymer phase with better conformational structure of polymer chains is suggested. Better alignment of chains would lead to lower free volume in polymer phase which supports weak bond creation and their relaxation into regular bonds. In next, denser polymer packing reinforces the cage effect of surrounding chains hindering movements of chain ends with free radicals after eventual scission, thus inducing their recombination in oxygen free environment. This could be also the underlying mechanism of PL increase over the initial value, as the structure might be even improved via scission and recombination of chains in more energetically favourable conformations thus improving the delocalization length of PSi's segments.

4. CONCLUSION

The results of the spectroscopic characterization of films of PMPSi and copolymer P[DMSi-MPSi] shows that there are a fundamental differences between the structure of the material in thin (tens of nm) and thick (submicrometer) films. It has been shown that in thick films the length of conjugated polymer chain segment is significantly longer than that of the thin films which is explained by formation of mesoscale confined polymer phase which has higher degree of polymer chain alignment favouring all-trans conformation and thus more dense polymer packing and towards degradation less susceptible structure than in case of thin films. Hence, the mesoscale layer formation seems to be the structural factor underlying metastability observed in PSIs.

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LITERATURE