

POLYSILANES THIN FILMS DOPED BY COUMARIN

Pavel URBÁNEK, Ivo KURŤITKA, Petr KRČMÁŘ, Jan MASLIK, Jiří BARTOŠ

Tomas Bata University in Zlin, Zlin, Czech Republic, EU, urbanek_pavel@centrum.cz

Abstract

In our work, we present a study of the influence of dopant on optoelectrical properties of polysilane and especially its photoluminescence. Poly[(dimethylsilane)-(methylphenylsilane)] – P(DMSi-MPSi) was used as the p-type conductive polymer and coumarine 440 as the dopant. Thin films with thickness in hundreds nanometers were prepared both from neat polymer and from blend P(DMSi-MPSi)/Coumarine 440. Absorption characteristics of films were measured by UV/VIS spectrometry. The photoluminescence (PL) of thin films was investigated by fluorimetry.

Keywords: Polysilane, dye dopant, photoluminescence, optoelectrical properties

1. INTRODUCTION

Linear polysilanes called polysilylenes (PSis) are a group of σ -conjugated polymers with the backbone consisting entirely of silicon atoms. PSis are considered as a polymer material applicable in many electrical, optical and optoelectrical applications because of the effect of σ -electron delocalization along the main single bonded chain, which is responsible for their unique electronic and photoelectrical properties [1, 2].

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 macroinitiators 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 to prolong the durability of the active layer. Stable luminescence of PSi is one of the main challenges with respect to their prospective applications such as photosensing material or in electric devices [3] and Coumarine as an organic n-type dopant appears as a suitable agent for enhancing of the optoelectric properties of PSis [4] because in the host–dopant system, the probability per unit time of energy transfer from excited-energy donor to energy acceptor depends on the overlap of the emission spectrum of donor and absorption spectrum of acceptor [5].

In presented work, coumarin 440 was used as the dopant of P(DMSi-MPSi) and the optoelectronic properties of thin films from doped polysilane and their UV stability were investigated and evaluated..

2. EXPERIMENTAL

Copolymer poly[dimethylsilane-methylphenylsilane] P[DMSi-MPSi] was obtained from Flourchem Ltd., UK (Batch 060032-1). Coumarin was delivered by Exciton, OH, USA. Polystyrene was used as reference polymer matrix, virtually inactive in studied effects. Films from neat copolymer and polystyrene for PL measurements were prepared from solutions in toluene using spin coating method with spin rate 2500 rpm and drop casting as well. The thin films from blend P[DMSi-MPSi]/Coumarin were prepared from solution in toluen, whereas the concentrations of Coumarin in the mixture was 25 %(w/w). The achieved thickness of films was about one hundred nanometers in case of spin coating and 1 micrometer in case of drop casting respectively. Quartz glass and undoped single crystal silicon wafers were used as substrates. Absorption spectra of thin films were measured by UV-Visible Spectrophotometer Cary 300 Conc. Fluorimeter FSL 920 from Edinburgh Instruments was used for the measuring of PL spectra. The thickness was measured by

profilometer (Talystep). 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

Figure 1 shows both absorption and excitation spectra of Coumarin measured in inactive polystyrene matrix and excitation and emission spectra of neat and doped P[DMSi-MPSi]. It indicates that emission spectra of neat P[DMSi-MPSi] and absorption and excitation spectra of Coumarin are overlapped. This is required assumption for energy transfer between energy donor and acceptor. The excitation spectra show that the excitation in mixture P[DMSi-MPSi]/Coumarine proceeds like in the neat polymer. P[DMSi-MPSi] emission peak was observed at the wavelength of 353 nm and its corresponding excitation edge was located at 340 ± 5 nm. It means the energy band gap of P[DMSi-MPSi] is 3.5 eV. The highest occupied molecular orbital (HOMO) level of P[DMSi-MPSi] is 5.3 eV [6]. According to the HOMO level and excitation spectrum data, the lowest unoccupied molecular orbital (LUMO) level is determined to be 1.6 eV. The energy levels of HOMO (5.37 eV) and LUMO (2.5 eV) of Coumarine 440 [7] are located inside the energy band of P[DMSi-MPSi]. Thus, excitation energy of P[DMSi-MPSi] can be efficiently transferred from P[DMSi-MPSi] to Coumarin. Moreover based on these facts, we suggest that the green emission (in Figure 2, left graph, curve 1) is caused by energy transfer from polymer to dye dopant Coumarin. Such explanation can be supported by the fact that the blue emission of Coumarin is suppressed and only sharp emission of P[DMSi-MPSi] dominates in the region at about 350 nm

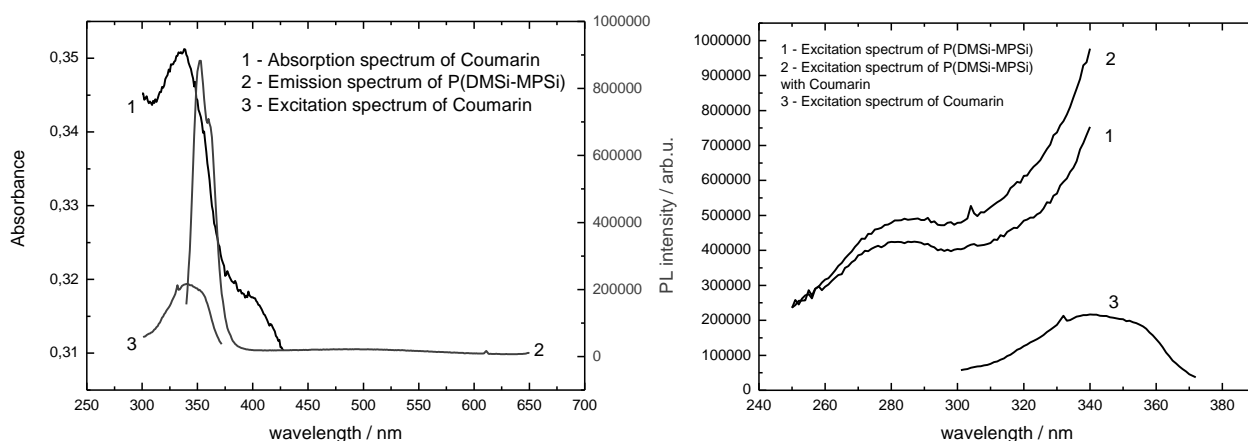


Fig. 1 The overlap of absorption and excitation spectra ($\lambda_{em}=350$ nm) of Coumarin and emission spectrum of P(DMSi-MPSi) ($\lambda_{ex}=330$ nm) – left side. Excitation spectra of Coumarin, neat and doped P(DMSi-MPSi) ($\lambda_{em}=350$ nm) – right side.

The influence of the dopant on the stability of the copolymer was investigated in a PL decays study, which results are shown in Figure 2, right graph. In case of degradation at 330 nm, observed patterns resemble more annealing than degradation as PL intensity is recovered to 100 % in case of neat copolymer. Development of 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. These two microstructural effects could be considered as the underlying mechanism of PL increase back at the initial value in neat P[DMSi-MPSi] [3]. Film cast from toluene solution of the mixture P[DMSi-MPSi]/Coumarine undergoes slow degradation, at the time 140 seconds the degradation is slowed-down and small PL recovery is observed. After time 500 seconds the degradation continues with slow PL decreasing again to the 45 % of initial PL

value. These phenomena can be explained by fact that molecules of dopant change the degradation and relaxation mechanisms of the copolymer and the PL recovery cannot occur.

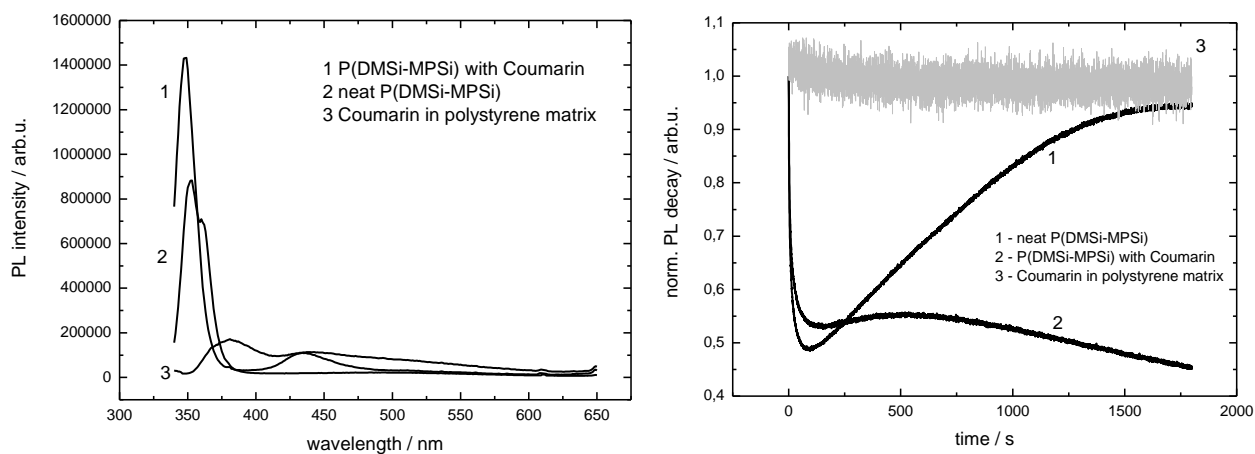


Fig. 2 Emission spectra of Coumarin in polystyrene, neat and doped P(DMSi-MPSi) ($\lambda_{\text{ex}}=330$ nm) – left side. PL decay curves of Coumarin in polystyrene, neat and doped P(DMSi-MPSi) ($\lambda_{\text{ex}}=330$ nm, $\lambda_{\text{em}}=350$ nm) – right side.

Such state, where the dopant hinders the polymer matrix recovery is undesired and can be correlated with the effect of the dopant on the photoluminescence as can be seen in Fig. 2, left graph. It is evident, that there is a 5 nm blue shift of the main UV polysilane luminescence peak caused by the emission from short delocalized segments of the PSis chain in case of P[DMSi-MPSi]/Coumarin 440 mixture, while the luminescence from energetically more favourable states, i.e. segments with longer conjugation length, is hindered, probably due to the energy transfer to the guest molecule. However according to our previous observations [3], the active role of long delocalized segments is a necessary condition for the polymer self-recovery during the PL decay, as it stabilizes the weak bond creation and their subsequent relaxation while the degradation scission of short chain segments in lower energetically favourable conformations leads to the opposite effect..

4. CONCLUSION

Poly[(dimethylsilane)-(methylphenylsilane)] - P(DMSi-MPSi) was used as a luminescent polymer matrix and Coumarin 440 as an energy acceptor in the structure of host-dopant system to investigate the intermolecular energy transfer between P(DMSi-MPSi) and Coumarin and to investigate the influence of the dopant on photoluminescence of the polymer. The addition of the dopant in the copolymer caused the blue shift of the emission and moreover, the green emission of the blend material was observed. It indicates the excitation energy transferred from P(DMSi-MPSi) to Coumarin. Next observed effect of the dopant was enhancing of PL intensity when polymer and dopant were mixed. The adverse influence of the dopant on the PL stability of P(DMSi-MPSi) was proven because the PL decay curves of neat polymer manifested self-recovering and metastability phenomena while P(DMSi-MPSi) with Coumarin exhibited only retardation effects but not self-recovering, probably due to the blockation of the role of long conjugated segments in polysilane macromolecules. To conclude, Coumarin 440 seems to be a suitable dye dopant for controlling photoluminescence properties of P(DMSi-MPSi) but the further research in this field is necessary to improve the stability of the copolymer dye blend and thus, to improve its application potential as a material for luminescent devices.

ACKNOWLEDGEMENT

This article was written with support of Operational Program Research and Development for Innovations co-funded by the European Regional Development Fund (ERDF) and national budget of Czech Republic, within the framework of project Centre of Polymer Systems (reg. number: CZ.1.05/2.1.00/03.0111).

This work was supported by the Internal Grant Agency of Tomas Bata University in Zlin (grant No. IGA/FT/2012/025).

This contribution/article was written with support of Operational Program Education for Competitiveness co-funded by the European Social Fund (ESF) and national budget of Czech Republic, within the framework of project Advanced Theoretical and Experimental Studies of Polymer Systems (reg. number: CZ.1.07/2.3.00/20.0104).

LITERATURE

- [1] JONES, Richard G.; Silicon-Containing Polymers; Michl West Chapter 18. ISBN: 0412831104.
- [2] NEŠPŮREK Stanislav et al.; Journal of Optoelectronics and Advanced Materials Vol. 7, No. 1, February 2005, p. 223 – 230.
- [3] URBÁNEK Pavel et al.; The Influence of Thickness and Used Solvent on Luminescence and Photodegradation of Polysilane Thin Films; Nanocon 2011; Conference proceedings: 2011. p.94-100, ISBN 978-80-87294-23-9.
- [4] FONG H. H. et al.; Organic light-emitting diodes based on a cohost electron transporting composite, APPLIED PHYSICS LETTERS, 88, 113510, 2006.
- [5] PARK J., SEOUL C., KIM T. Efficient inter-molecular energy transfer via dye-dopants in poly(methylphenylsilane) based electroluminescent devices. Current Applied Physics 5 (2005) 293–296.
- [6] NEŠPŮREK S., ECKHARDT A.; Poly(silylene)s: Charge Carrier Photogeneration and Transport; Polym. Adv. Technol. 12, 427-440 (2001).
- [7] PSCHENITZKA F. and STURM J. C., Excitation mechanisms in dye-doped organic light-emitting devices; Appl. Phys. Lett., vol. 79, pp. 4354-4356, Dec. 2001.