THE EFFECT OF THE EXALITE DOPANT ON PHOTOLUMINESCENCE OF POLYMETHYLPhENYLSILANE IN THIN FILMS

Petr KRČMÁŘ, Pavel URBÁNEK, Ivo KUŘITKA, Jan MAŠLÍK, Jiří BARTOŠ
Tomas Bata University in Zlín, Zlín, Czech Republic, EU, ivo@kuritka.net

Abstract
Polysilanes are known as representatives of σ-conjugated polymers which exhibit unique characteristic properties such as absorption and photoluminescence in UV region with a small Stoke’s shift, which is closely related to their electronic structure and exciton formation on the main silicon chain. This group of materials is considered for optoelectronic applications, for instance in nanolithography, in OLED devices or in photovoltaics as an active layer. In this work, we used poly(methylphenylsilane) as a p-type semiconductive material and Exalite 351 as an electron acceptor in the structure of host-dopant system for active layer in electronic devices in order to investigate the influence of dopant on photoluminescence of PMPSi. Polymer and polymer/dopant thin films were deposited on silicon substrate, with thickness in range of hundreds nanometers. The properties of thin films were characterized by UV/VIS absorption spectrometry and by fluorimetry.

Keywords:
Polysilanes, dopants, optoelectrical properties, thin films

1. INTRODUCTION
Polysilanes (PSis) are photoconductive polymers with the backbone consisting entirely of silicon atoms. This group of materials is an example of a rare group of polymers that have σ-conjugated bonding orbitals along the main chain, which is responsible for their unique properties such as non-linear optical properties, UV degradability, metastability and self-recovering [1, 2]. PSis chains, with two organic substituents on each silicon atom, behave as one-dimensional system with weak intermolecular interaction, whereas side groups influence the physical and electrical properties of polysilanes. The electron excitation plays an important role because it can be accompanied by photoluminescence (PL) as a consequence of excitonic deactivation [3, 4]. On the other hand, the UV absorption can lead to the degradation of the main chain and this is ineligible effect which causes the PL decay [5]. To modify the polymer optoelectrical properties and thus improve its stability, polysilanes can be doped by molecular doping agents, where the agents play a role of energy acceptors. 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 [6].

In this work, we used poly(methylphenylsilane) as the energy donor and Exalite 351 as the energy acceptor in the structure of host–dopant system in order to investigate the inter-molecular energy transfer between the polysilane and the dye dopants.

2. EXPERIMENTAL
Polymethylphenylsilane (PMPSi) was delivered from FluoroChem (Batch 060033-1), UK. Exalite 351 was obtained from Exciton Dayton, OH, USA. Thin films from neat polymer were prepared by spin coating method from the solution in toluene. The thin films from host-dopant material were cast from solution in toluene as well, but the process was divided into two steps. Firstly Exalite 351 was dissolved in toluene and secondly, the appropriate amount of PMPSi was added to this solution. The ratios between the polymer and
dopant were 3:0.5; 3:1 and 3:2 respectively. Prepared materials were spin cast onto Si and quartz glass substrates for UV/VIS absorption and fluorimetry measurements carried out on UV-Visible Spectrophotometer Cary 300 Conc. and fluorimeter FSL 920 (Edinburgh Instruments) respectively. PL spectra were taken at the pressure 1 Pa and the temperature 25 °C. Measurement of layer thickness was carried out on mechanical profilometer Taylor Hobson – Talystep.

3. RESULTS AND DISCUSSION

Figure 1 shows the absorption and PL excitation spectra of PMPSi thin film and absorption and PL excitation spectra of PMPSi doped with Exalite 351 with concentration of polymer to dopant in ratio 3:0.5, 3:1 and 3:2.

![Graph showing absorption spectra and PL excitation spectra of PMPSi and doped PMPSi](image)

**Fig. 1** The absorption spectra and PL excitation spectra (emission at 360 nm) of thin films from neat and doped PMPSi.

The absorption peaks of PMPSi are located at typical wavelengths, but with increasing concentration of Exalite the absorption peak at 330 nm is decreasing. Fig. 2 shows the PL emission spectra of PMPSi thin film and the emission spectrum of PMPSi doped with Exalite and PL decay curves of neat and doped PMPSi. From Figure 2, it is obvious that emission maxima of the doped material are red-shifted about 5 nm and the PL intensity increases. This phenomenon can be explained as transfer energy from dopant excited states to the polymer chain and then exciton deactivation with increasing intensity. The excitation spectra show that the excitation arises like for PMPSi and the excitation of Exalit is not apparent. This can be explained so that there almost total energy overlap exists and the excited energy from Exalite is transferred to the longest conjugated polymer segments. In other words, the inter-molecular energy transfer occurred, however its virtual hidden due to the proximity of absorption and emission lines for host polymer and the dopant. Other observed phenomena is that Exalite addition causes the retardation of the UV degradability of PMPSi, which is described by slope of PL decay curves in logarithmic scale, shown in Table 1. The degradation of PMPSi after addition of Exalite is slower in one order than the degradation of neat PMPSi.
**Fig. 2** Emission PL spectra (excitation at 330 nm) and logarithmic PL decay (excitation at 330 nm, emission at 360 nm) of thin film from neat and doped PMPSi.

**Tab. 1** Slope of logarithmic PL decay curves of neat and doped PMPSi.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Slope of decay curve</th>
</tr>
</thead>
<tbody>
<tr>
<td>neat PMPSi</td>
<td>-0.348</td>
</tr>
<tr>
<td>PMPSi + Exalite 3:0.5</td>
<td>-0.175</td>
</tr>
<tr>
<td>PMPSi + Exalite 3:1</td>
<td>-0.175</td>
</tr>
<tr>
<td>PMPSi + Exalite 3:2</td>
<td>-0.193</td>
</tr>
</tbody>
</table>

**4. CONCLUSION**

Poly(methylphenylsilane) (PMPSi) was used as a luminescent polymer matrix and Exalite 351 as dopant in the structure of host–dopant system to investigate the intermolecular energy transfer between PMPSi and Exalite. As the doping concentration of Exalite 351 increased, the doped PMPSi emission peak increased, while neat PMPSi emission was lower. It indicates the excitation energy transferred from Exalite to PMPSi (inter-molecular energy transfer). A red-shifted luminescent peak was observed at wavelength about 355 nm, whereas the emission maximum of neat PMPSi was at 355 nm and emission maxima of doped PMPSi were at 360 nm. Next observed effect of the dopant was the retardation of the UV degradability of PMPSi. To improve the efficiency of devices, the dopant concentration plays an important role in the EL device and inter-molecular energy transfer mechanism between PMPSi as host materials and dye dopants have to be further investigated.

**ACKNOWLEDGMENT**

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

LITERATURE


