Available online at www.sciencedirect.com
ScienceDirect
Optical Materials 30 (2007) 384–392
www.elsevier.com/locate/optmat

Triplet state spectroscopy of σ-conjugated poly[methyl(phenyl)silylene]

Yu. Skryshevski [a,*], Yu. Piryatinski [a], A. Vakhnin [a], I. Blonsky [a],
A. Kadashchuk [a], S. Nešpůrek [b]

[a] *Institute of Physics, National Academy of Sciences of Ukraine, Prospect Nauki 46, 03028 Kiev, Ukraine*
[b] *Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic*

Received 17 February 2006; accepted 20 November 2006

Abstract

Steady-state and time-resolved photoluminescence of poly[methyl(phenyl)silylene] (PMPSi) in solutions and films, and films doped with acetophenone, biphenyl and naphthalene were studied in the temperature range 5–77 K. It was found that the steady-state, prompt and delayed luminescence spectra of PMPS in solutions and solid films are similar under the same excitation and registration conditions. The delayed luminescence spectrum is represented by broad, unsymmetrical and structureless band with maximum at ca. 450 and 465 nm in PMPSi solution and film, respectively. The decay time of this emission, which was assigned to the intrinsic phosphorescence of PMPSi, was found to be within the microsecond time domain; at 77 K it could be observed with the delay time up to 30 μs with respect to excitation pulse. Quite effective triplet–triplet energy transfer was observed. The results indicate that the energy of the lowest triplet state is considerably lower than the energy of the lowest excited singlet state, which involves a strong correlation of Si–Si σ-electrons of the polymer backbone, and can be described in the concept of Frenkel exciton. It was also demonstrated that the vibronic structure of the long-lived emission reported in literature for PMPSi films is most probably due to the presence of chemical defects and impurities and it does not represent the intrinsic feature of the PMPSi triplet.

Keywords: Poly[methyl(phenyl)silylene]; Polysilane; Photoluminescence; Triplet state

---

1. Introduction

Polysilanes (in literature sometimes called like polysilanes, polyorganosilanes, poly(organylsilanediyl)s, organopolysilanes, or catena-silicon polymers) are of considerable research interest because of their electronic, photoelectrical, and non-linear optical properties, and the effect of σ-electron delocalization along the chain [1,2]. Optical and electrical properties of these polymers have been found to differ significantly from structurally analogous carbon-based σ-bound systems such as polystyrene and polyethylene, resembling rather fully π-conjugated systems, like polyacetylenes. Physical properties are very often influenced by the chemical structure of the polymer side groups. Polysilanes are soluble polymers and are able to form thin films with quite a high thermal stability [1]. Various technologies can be used for the thin films preparation: spin coating, casting, vacuum evaporation, plasma deposition, and the Langmuir–Blodgett (LB) technique [3].

Polysilanes absorb light in near UV region [1,2], show fluorescence [1] or photoconductivity [2–5] and exhibit nonlinear optical properties [4,6,7] and effective charge carrier transport [8–13]. Compatibility of polysilanes with both silicon-based technologies and organic materials deposition methods suggest their potential use in nanolithography [14]. Well known is their use for the fabrication of electroluminescent devices [15–18], in electrophotographic media [19], photorefractive devices [20] and as

---

[*] Corresponding author.
E-mail address: nespurek@imc.cas.cz (S. Nešpůrek).

0925-3467/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.optmat.2006.11.062

binding layers in photovoltaic cells [21]. At present there is an interest to use polysilanes for molecular wires [22] and switches [23], and as materials with metastability of electronic states [24]. There is a lot of information in literature concerning poor stability, and photodegradation of polysilanes. The latest experiments show that the stability can be strongly improved by large π-conjugated side groups and that the photodegradation strongly depends not only on photon energy but also on photon flux; at low illumination doses the metastability prevails and photoprocesses are fully reversible.

Several methods, like single- and two-photon absorptions, third-order optical nonlinearity, electroabsorption, reflectance, fluorescence and site-selective fluorescence spectroscopy, were used to investigate the electronic structure of polysilanes. It was suggested that the unique electronic features of these linear polymers are attributed to the σ-conjugation, which originates from overlap of Si sp^3 orbitals [1–3]. The lowest-energy electronic transitions in the absorption spectra were found to be of the excitonic nature with an exciton binding energy exceeding 1 eV, which is typical value of Frenkel-type excitons in molecular crystals [2]. Some experimental results were explained in terms of either the single-chain band model based on the one-electron Su–Schrieffer–Heeger hamiltonian or the segment model in conjunction with the concept of Frenkel exciton in a disordered system. In the former model [6,7], where the whole σ-conjugated backbone acts as a chromophore, the electronic structure of polysilanes is considered as a quasi-one-dimensional semiconductor with a direct optical gap separating the highest occupied valence band and the σ^*-antibonding lowest unoccupied conduction band [25]. Within the framework of this approach, luminescence was explained as recombination of electron–hole pairs, with the appearance of the Stokes shift between absorption and fluorescence spectra considered as evidence of structural relaxation of the backbone in the vicinity of an exciton [26]. Though the calculations based on the single-chain band model can qualitatively explain the observed features of linear and nonlinear absorption as well as of the electroabsorption spectra of polysilanes [6,7], such approach is in disagreement with the results of spectral hole-burning and site-selective fluorescence measurements, and is, therefore, inappropriate for the description of the origin of the excited states. It was shown by site-selective fluorescence spectroscopy [27–29] that coupling of excitons to phonons and vibrations of the chain in polysilanes is very weak, the absorption spectrum is inhomogeneously broadened and a resonant photoluminescence (PL) emission appears upon scanning of the excitation wavelength into the tail of the lowest absorption band. It shifts linearly with the excitation photon energy.

According to the segment model [1,2,4,28], Si–Si σ-electrons are delocalized within a relatively small well-ordered segment of the σ-conjugated polymer backbone. They play the role of chromophore and also form the transport sites for holes [5]. These segments, which may contain several monomer units (not necessarily the same number) are separated by conformational defects. The increase in the number of monomer units in the segment and, correspondingly, its prolongation length results in the lowering of its excitation energy [1,3]. Hence, the segments are distributed in lengths, which, together with a positional disorder, lead to inhomogeneous broadening of the lowest absorption band and to the apparent Stokes shift between the absorption and fluorescence spectra. The latter effect was interpreted in terms of the transfer of neutral excitations (i.e., Frenkel excitons) among segments, which differ in their excitation energies [2,28].

It was pointed out by Abe [30] that the exciton concept in conjugated polymers is somewhat complicated within the framework of the band model. If polymer chain is considered as quasi-one-dimensional semiconductor, the on-chain exciton (Wannier exciton) is defined as an electron–hole pair weakly bound by Coulomb interaction. Here, the electron and hole are quasiparticles of the many-electron system. On the other hand, the transfer of the electronic excitation between the chains becomes possible due to intermolecular coupling, as it takes place with Frenkel exciton, and, therefore, the view of exciton, as the bound state of electron and hole, is not correct because of strong configurational mixing.

In order to make a correct test of the validity of the segment or single-chain band model, one must describe adequately the electronic structure of the material. In particular, it is necessary to examine the energetic position of the first triplet state T_1 and the optically allowed singlet excited state S_1. As the quantum-size confinement to a segment leads to a very strong Si–Si σ-electron correlation, the energy E_T of the triplet T_1 is lower than the energy E_S of the singlet S_1 similarly to small organic molecules [31,32] and oligomers of silanes [4,33]. However, interaction among delocalized σ-electrons is beyond the scope of the simple band theory based on the one-electron tight-binding Su–Schrieffer–Heeger hamiltonian [34]. Abe and co-workers [35] supplemented this hamiltonian by electron–electron interaction terms; in this approximation the singlet-triplet ordering is then determined by the U/V ratio, where U is the Coulomb repulsion energy between two electrons in the overlapping sp^3 orbitals of adjacent Si atoms and V is the Coulomb repulsion energy between two electrons in the nearest-neighbor sp^3 orbitals along the chain. When $U/V \approx 1$, the triplet state is positioned higher than the singlet state. The opposite is true for $U/V > 1.4$, even if we consider a single chain where the lowest allowed electronic state is of the Frenkel exciton type.

Generally, in the case when the S_1 state is higher than the T_1 state, the energy E_T can be determined from phosphorescence spectra. However, the information concerning phosphorescence of polysilanes is poor and sometimes controversial [36–38]. Poly[methyl(phenyl)silylene] (PMPSi) is one of the most-studied polysilanes. To determine the intrinsic phosphorescence spectrum of this polymer, we investigated both the steady-state and time-resolved lumi-