Monatshefte für Chemie 132, 159–168 (2001)

Monatshefte für Chemie
Chemical Monthly

Visible Photoluminescence in Polysilanes

Stanislav Nešpůrek[1,2,*], **František Schauer**[2], and **Andrey Kadashchuk**[3]

[1] Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, CZ-16206 Prague 6, Czech Republic
[2] Faculty of Chemistry, Technical University of Brno, CZ-61200 Brno, Czech Republic
[3] Institute of Physics, National Academy of Sciences of the Ukraine, UR-252650 Kiev 22, Ukraine

Summary. The photoluminescence spectrum of poly-(methyl-(phenyl)-silanediyl) shows a strong narrow peak in the UV region which is of excitonic nature and related to σ^*-σ transitions. The broad emission peak in the visible region is related to polymer branching, charge transfer transitions, and defect electronic states (backbone scission). Chemical substitution of the Si backbone with π-conjugated side groups allows to generate photoluminescence also in the visible region.

Keywords. Polysilane; Poly-(methyl-(phenyl)-silanediyl); Photoluminescence; Electron transfer; Exciton.

Introduction

The electronic properties of polysilanes have been found to differ significantly from those of structurally analogous carbon-based σ-bond systems resembling rather fully π-conjugated systems like polyacetylenes. Some polysilanes, *e.g.* poly-(methyl-(phenyl)-silanediyl) (**1**), show, in addition to a strong excitonic UV photoluminescence, a broad emission peak in the visible region whose origin has been claimed to be controversial and unclarified [1]. *Kishida et al.* [2] have shown that the introduction of branching points (one silicon atom is chemically bonded to three other Si atoms instead of two as usual in linear chains) enhances the visible photoluminescence, whereas the sharp UV luminescence band is suppressed. In ^{29}Si NMR studies [3] it was found that even a small quantity (about 1%) of Si-based branching defects, which resulted in weak Si–Si bonding states, had a significant effect on the visible photoluminescence. *Toyoda* and *Fujiki* [4] have compared the luminescent properties of **1** and poly-(pentyl-(phenyl)-silanediyl), *i.e.* of two materials with different branching levels. The data suggested that branching might be responsible for the presence of the visible photoluminescence. However, a detailed study of the temperature dependence of photoluminescence of **1** (cf. Fig. 1) suggested that the visible photoluminescence band is composed of several luminescent centres whose efficiencies are temperature dependent. Therefore, we studied the origin of the visible luminescence of **1** in detail. The possibility of a chemical extension of the photoluminescence to the visible spectral region by

---

[*] Corresponding author

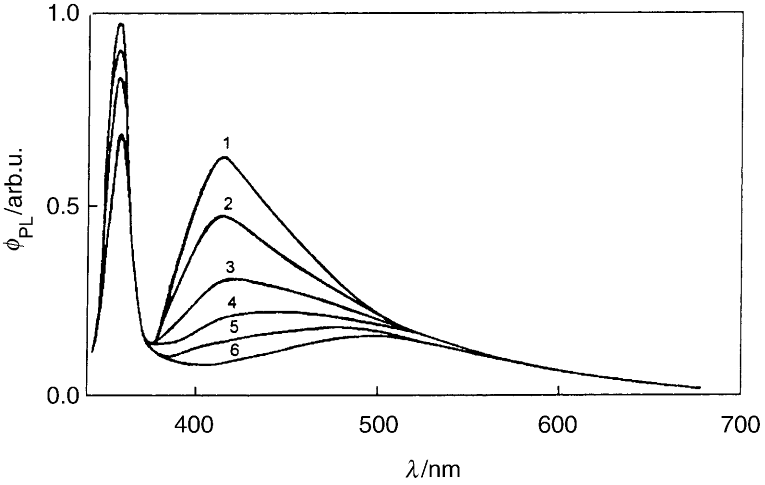


Fig. 1. Temperature dependences of the photoluminescence spectra of 3 μm thick spin-coated films of polymer **1**; $T_{ex} = 5\,K$ (curve 1), 20 K (2), 30 K (3), 50 K (4), 100 K (5), and 150 K (6); $\lambda_{ex} = 313\,nm$

substitution of the Si backbone with π-conjugated side group chromophores is discussed as well.

Results and Discussion

Optical absorption, photoluminescence, and excitation spectra of polymer **1**

The absorption spectrum of a solid film of **1** consists of three main peaks with maxima at 332, 270, and 194 nm [5]. It has been shown [6] that the first long-wavelength electronic transition arises mainly from delocalized σ-σ^* transitions. The peak at $\lambda = 270\,nm$ is associated with π-π^* transitions in the benzene ring. In addition to the mentioned σ-σ^* and π-π^* absorption bands, a very weak tail in the visible region was observed [7].

Photoluminescence spectra (see Fig. 1) of thin (~3 μm) spin-coated films measured at different temperatures under excitation with $\lambda_{ex} = 313\,nm$ consists of two main emission bands, a relatively sharp band in the short-wavelength region with the maximum at $\lambda_{max} = 356 \pm 3\,nm$ and a broad band in the visible part of the spectrum. The temperature dependence of the broad visible band (the emission intensity decreases with increasing temperature) is much stronger than that of the sharp UV band. A remarkable feature of the visible photoluminescence is that at 5 K its maximum is situated at about 410 nm (Fig. 1, curve 1), whereas at $T > 100\,K$ the maximum is shifted to about 500 nm (Fig. 1, curves 5 and 6). From the energy diagram of **1** (Fig. 2) it is evident that at least four energy levels are present in the energy gap: the polaron level E_p, the defect trap hole level (0.45 eV deep [8]) E_t^h, the level of the charge transfer exciton $^1(\sigma,\pi^*)^{CT}$, and the level of luminescent branching points E_{BP}. An important property of the visible photoluminescence is that it is stronger when the excitation is carried out *via* π-π^* transitions of the phenyl substituent than *via* the σ-σ^* excitations of the silicon skeleton. This could

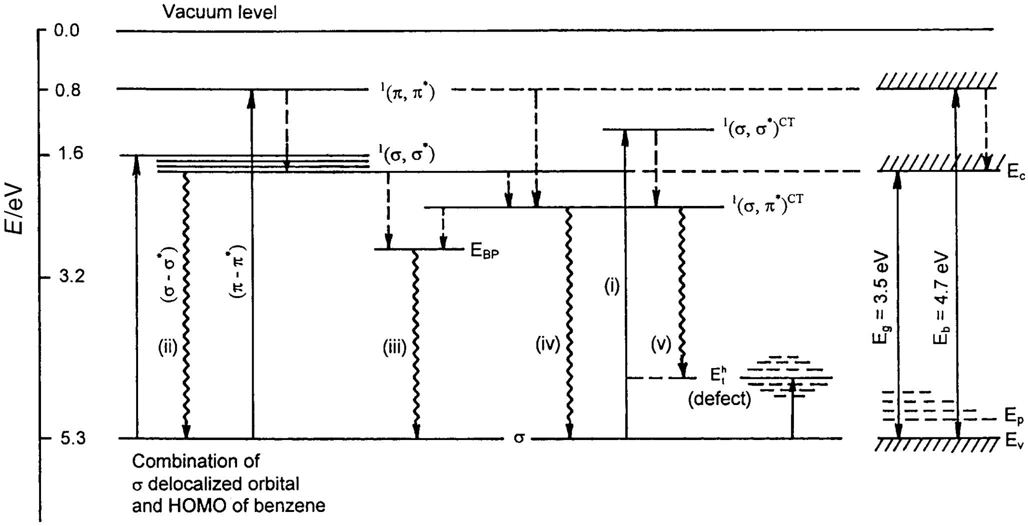


Fig. 2. Schematic energy diagram of poly-(methyl-(phenyl)-silanediyl); E_{BP}: energy of branching points, $E_{\mathrm{t}}^{\mathrm{h}}$: defect (Si–Si bond scission) levels, E_{p}: polaron level, E_{v}, E_{c}: energies of the edge of the valence and conduction band, E_{g}: energy gap, E_{b}: second energy gap, $^{1}(\sigma,\pi^{*})^{\mathrm{CT}}$, $^{1}(\sigma,\sigma^{*})^{\mathrm{CT}}$: energies of intramolecular and intermolecular charge transfer states, σ-σ^{*}, π-π^{*}: electronic transitions due to the light excitations; transition from the σ to $^{1}(\sigma,\sigma^{*})^{\mathrm{CT}}$ state (*i*) was observed in electroabsorption and photoluminescence excitation spectra, photoluminescence from the $^{1}(\sigma,\sigma^{*})$ state (*ii*) and from branching points E_{BP} (*iii*) was observed even at room temperature, photoluminescence from the $^{1}(\sigma,\pi^{*})^{\mathrm{CT}}$ charge transfer state (*iv*) and (*v*) at low temperatures

be associated with the fast initial geminate recombination of charges generated during the σ-σ^{*} excitation [9]. The subsequent photoinduced electron transfer to the phenyl group forms the charge transfer state [10] $^{1}(\sigma,\pi^{*})^{\mathrm{CT}}$. Thus, we assume that the short-wavelength part of the visible luminescence with the maximum at about 410 nm is associated with the emission from the $^{1}(\sigma,\pi^{*})^{\mathrm{CT}}$ charge transfer state, whereas the luminescence with the maximum at about 500 nm is due to branching of the Si skeleton. This is in agreement with the excitation spectra of the photoluminescence monitored at 5 K for the sharp ($\lambda = 356$ nm) and broad ($\lambda = 410$ nm) emissions. In both cases the optical transitions σ-σ^{*} ($\lambda \sim 345$ nm) and π-π^{*} ($\lambda \sim 265$ nm) are visible. In addition, another optical transition at 302 nm was detected in the excitation spectrum of the visible luminescence. The position of this new band almost coincides with the reported band in the electroabsorbance spectrum [11] which suggests the formation of a polar charge transfer state.

Thermostimulated and isothermal recombination luminescence

A thermostimulated luminescence glow curve of polymer **1** after excitation with unfiltered UV light of Hg discharge lamps for 30 s at 5 K is presented in Fig. 3a. No signal was detected for $T > 170$ K. This indicated that in fresh unphotodegraded samples only shallow localized states were present. Figure 3b shows the spectral distribution of thermostimulated emission measured in the thermostimulated luminescence peak maximum (curve 1). A photoluminescence spectrum monitored

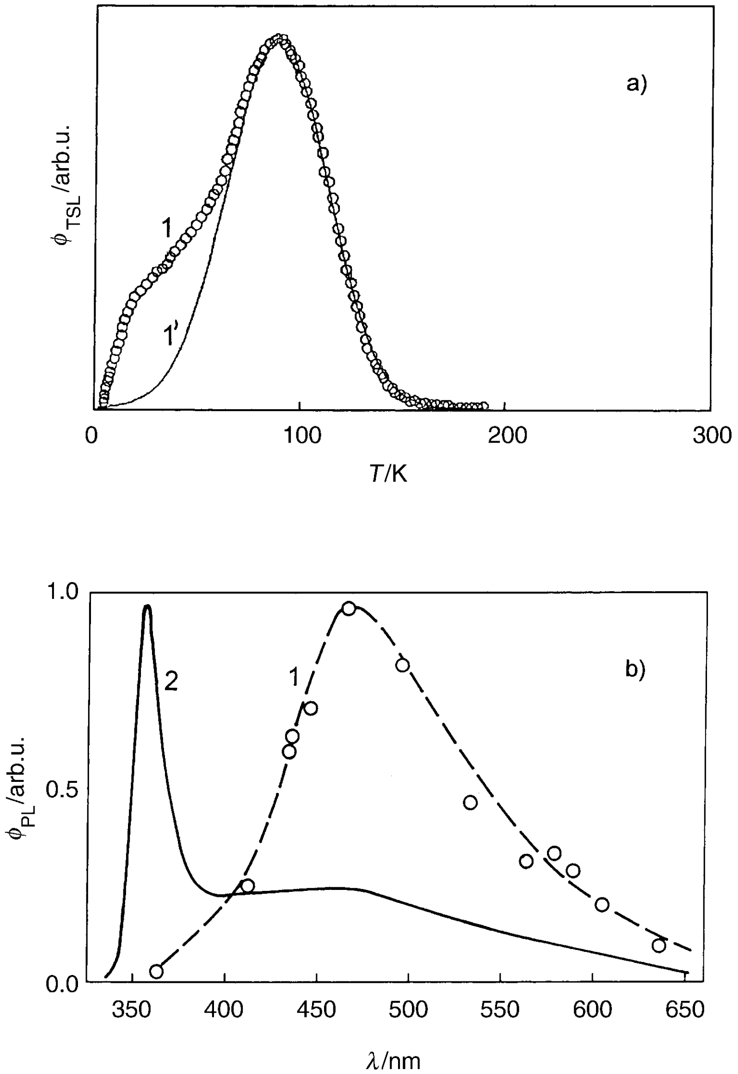


Fig. 3. a) Thermostimulated luminescence glow curve of poly-(methyl-(phenyl)-silanediyl) (curve 1) after excitation with unfiltered light of Hg discharge lamp at 5 K; curve 1′ is the extrapolation using a *Gauss*ian shape of the thermostimulated luminescence peak; b) spectral distribution of thermostimulated luminescence monitored at $T = 100$ K (curve 1); the spectrum of photoluminescence monitored at 100 K under 313 nm excitation (curve 2) is given for comparison

at 100 K (curve 2) under 313 nm excitation is given for comparison. It seems that only the broad visible luminescence band is responsible for the thermostimulated emission. Thus, the visible luminescence is, at least partly, related to the luminescent recombination of localized charge carriers.

Light-induced photoluminescence and thermostimulated luminescence quenching were found. With prolongated irradiation times the photoluminescence intensity decreased, but the photoluminescence spectrum profile remained unchanged. This effect showed reversibility when the sample was heated to room temperature and subsequently cooled again for another run. The process of recovery of the photoluminescence intensity showed clearly a thermoactivated character; the temperature at which the full recombination could be achieved was the same as that at which the thermostimulated luminesence signal disappeared. Similarly, the thermostimulated luminescence intensity reached a maximum value after about 30 s of irradiation and decreased for longer doses. The reversibility of this effect was the same as with photoluminescence, evidencing the same feature of both phenomena, most likely associated with decreasing quantum yield of radiative transitions due to deeply trapped charges or localized photogenerated ion pairs.

Photodegradation effect on photoluminescence intensity

In contrast to the preceding paragraph, where only trapped charged species were responsible for the fluorescence tuning, our attention here will be aimed at the influence of photodegraded species. It was mentioned by *Fujiki* [3] that photodegradation of **1** by UV light occurs predominantly at room temperature.

Figure 4 presents the photoluminescence spectra of a film before (curve 1) and after 5 min (curve 2) and 200 min (curve 3) photodegradation with light of $\lambda = 365$ nm. It can be seen that an increase in the photodegradation dose leads to a short-wavelength shift of the exciton band from $\lambda_{max} = 354$ nm (curve 1) to $\lambda_{max} \cong 344$ nm (curve 3) and to a decrease in the total photoluminescence intensity. At the same time, a weak increase in photoluminescence in the spectral region of 520–540 nm was observed. This photoluminescence band was more pronounced using excitation at $\lambda_{ex} = 366$ nm (see inset in Fig. 4) or even $\lambda_{ex} = 405$ nm. This suggests the existence of an additional emissive band, most likely associated with

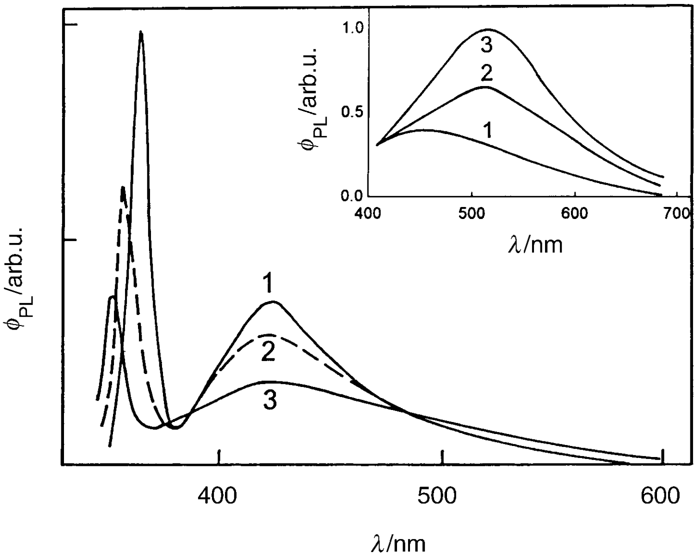
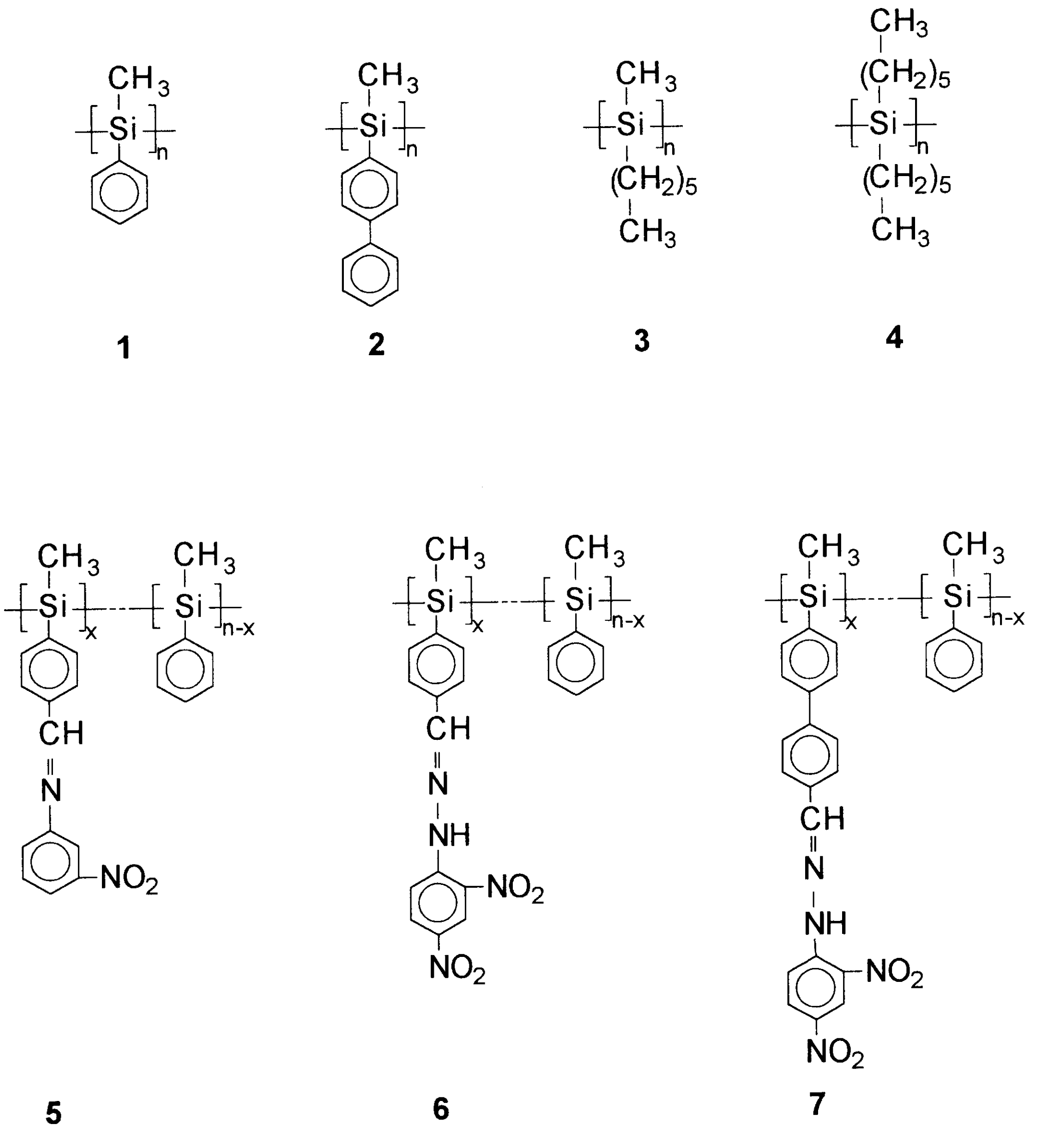


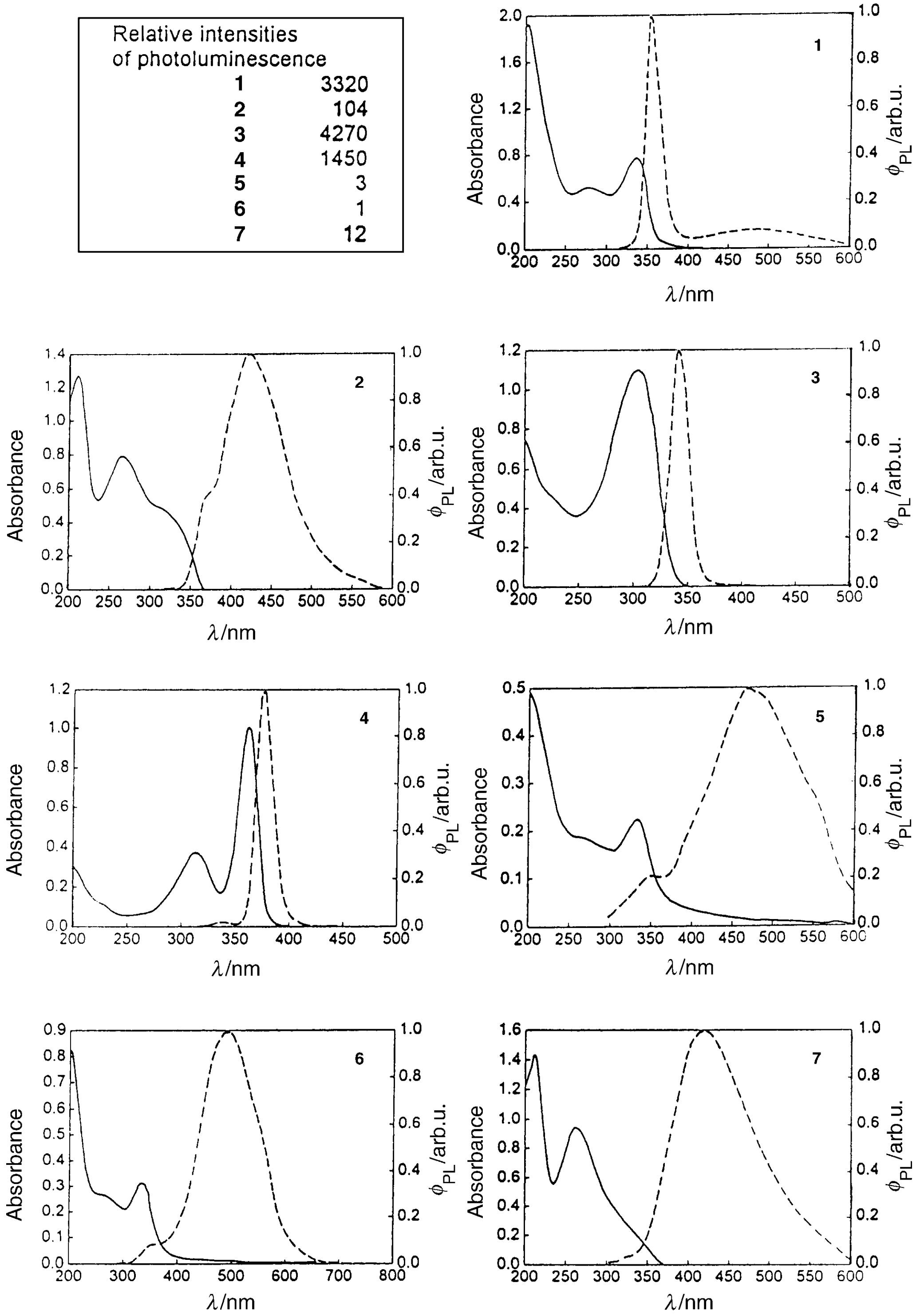
Fig. 4. Dependences of photoluminescence spectra of spin-coated film of polymer **1** on the photodegradation time ($\lambda_{irr} = 365$ nm, room temperature; cf. text); spectra were detected at $T = 5$ K with $\lambda_{ex} = 313$ nm; inset: spectral distributions of the luminescence intensity with respect to irradiation time ($\lambda_{ex} = 366$ nm)

photocreated defects. Visually, the colour of the photoluminescence changed from blue for a virgin sample to green for the photodegradated sample.

UV irradiation at wavelengths shorter than 360 nm at room temperature leads to Si–Si bond scission; the molar mass of the polymer decreases. At the same time, the position of the absorption band associated with σ-σ^* transitions is shifted to short wavelengths, and its intensity decreases. Simultaneously, new traps for holes 0.45 eV deep are formed [8] as follows from thermoluminescence measurements. The shift of the blue photoluminescence for virgin film to light-green after photodegradation of the sample could be associated with the interaction of intramolecular charge transfer excitons with trapped holes. The recombination luminescence is then expected at about 500 nm as follows from a rough estimation of the energetics



Scheme 1



Relative intensities of photoluminescence

1	3320
2	104
3	4270
4	1450
5	3
6	1
7	12

Fig. 5. Absorption spectra (full curves) and photoluminescence spectra (dashed curves) of thin films of polymers (Scheme 1) prepared by spin-coating

(cf. Fig. 2). Previous studies [8] indicate that the trapping states are metastable and can be annealed thermally. The transformation of the photoluminescence from green back to blue follows the trap annealing. Thus, the blue photoluminescence can be switched to green by UV irradiation and back to blue by thermal annealing.

Chemically induced visible photoluminescence of polysilanes

It was found that the chemical substitution of the benzene ring in **1** can generate photoluminescence in the visible part of the spectrum. In Fig. 5, the photoluminescence and absorption spectra of solid films of several polymers are presented. Extension of the π-conjugated system of side groups leads to the occurence of visible photoluminescence as can be demonstrated by poly-(biphenyl-4-yl-(methyl)-silanediyl) (**2**). On the other hand, the absence of π-electrons in the side groups leads to σ^*-σ exciton photoluminescence only as follows from measurements on poly-(hexyl-(methyl)-silanediyl) (**3**) (here visible luminescence was not observed even when expected from branching points) and poly-(dihexylsilanediyl) (**4**). The presence of polar groups leads to a shift of photoluminescence to the red region as evidenced from investigations on poly-(methyl-(phenyl)-silanediyl/methyl-(3-(((3-nitrophenyl)-imino)-methyl)-phenyl)-silanediyl) (**5**), poly-(methyl-(phenyl)-silanediyl/(4-((2,4-dinitrophenylhydrazono)-methyl)-phenyl)-methylsilanediyl) (**6**), and poly-(methyl-(phenyl)-silanediyl/(4′-((2,4-dinitrophenylhydrazono)-methyl)-biphenyl-4-yl)-methylsilanediyl) (**7**) (Scheme 1).

Experimental

Materials

Poly-(methyl-(phenyl)-silanediyl) (**1**) was prepared by sodium-mediated *Wurtz* coupling polymerization. The low-molecular-weight fraction was extracted with boiling diethyl ether. The residual polymer, obtained in *ca*. 17% yield, possessed a unimodal but broad molar mass distribution ($M_w = 4 \times 10^4\,g \cdot mol^{-1}$). Before deposition of films, the polymer was three times reprecipitated from a toluene solution with methanol. The final toluene solution was centrifuged (12000 rpm, 15 min). After deposition, the films were dried at 10^{-3} Pa and 330 K for at least 4 h.

Poly-(biphenyl-4-yl-(methyl)-silanediyl) (**2**) was synthesized by sodium-mediated *Wurtz* coupling of biphenyl-4-yl-(dichloro)-methylsilane in boiling toluene. Butyl lithium was added to the system one hour after mixing the components. Then the remaining sodium was reacted with ethanol, and the solution formed was washed with water and dried. Polymer **2** was precipitated by addition of propan-2-ol. The polymer was purified by several reprecipitations from *THF* solution with propan-2-ol. The high-molecular-weight fraction remaining after extraction with diethyl ether corresponds to a monomer conversion of about 40%. Its average molar mass ($M_w = 1.6 \times 10^5\,g \cdot mol^{-1}$) was determined by the light scattering method.

Poly-(hexyl-(methyl)-silanediyl) (**3**) and poly-(dihexylsilanediyl) (**4**) were synthesized by a *Wurtz*-type coupling reaction of dichloro-(hexyl)-methylsilane and dichloro-(dihexyl)-silane, respectively, with sodium in boiling toluene at 387 K. The dichlorosilanes were commercial products from ABCR GmbH. After the coupling reaction, a low-molecular-weight fraction was extracted from the crude polymer with boiling diethyl ether. Subsequently, the polymers were reprecipitated three times from *THF* solution with propan-2-ol. The polymers possess an unimodal molar mass distribution with an average molar mass of $8.2 \times 10^5\,g \cdot mol^{-1}$ (determined by the light scattering method in benzene solution).

Polymers **5**, **6**, and **7** were prepared similarly in the following way (here only the synthesis of **6** is discussed in detail). The parent polymer **1** was chloromethylated with a mixture of chloromethyl methyl ether and $SnCl_4$ in dry $CHCl_3$ using the procedure described in Ref. [12]. The degree of chloromethylation was controlled by the amount of chloromethyl methyl ether, temperature, and reaction time. Quaternization of the resulting product yielding the pyridinium salt was accomplished by heating the chloromethylated polymer in a boiling ethanol/pyridine mixture. Then, most of the solvent was removed on a rotary evaporator, and the product was precipitated by addition of diethyl ether and reprecipitated from ethanol solution with diethyl ether. The conversion in this step was nearly 100%. In the following step the pyridinium salt of **1** underwent a *Kroehnke* reaction with 4-nitroso-N,N-dimethylaniline and sodium methoxide in *THF* or THF/MeOH. Subsequently, the reaction mixture was poured into an excess of water saturated with NaCl. The precipitated polymer was filtered off, washed thoroughly with water, dried, and reprecipitated into an excess of hexane. As a result, a brownish-yellow powder was obtained in 73% yield. This polymer was further acid-hydrolyzed in a THF solution of aqueous HCl. The product was washed with water, dried, and reprecipitated twice from *THF* solution with methanol. The yield was about 87%. The resulting white powder consisting of polymer **1** with some of its benzene rings substituted with $-CH{=}O$ groups was used as a starting polymer for preparation of the copolymer under study.

The final polymer **6**, with degrees of substitution ranging between 0.55 and 15%, was prepared by addition of 2,4-dinitrophenylhydrazine in aqueous $HClO_4$ to a solution of the aldehyde polymer in *THF*. The polymer was filtered off and precipitated twice from *THF* solution with methanol before further physical studies. Using size-exclusion chromatography, the molar mass was determined to be $M_w = 1.9 \times 10^4\,g \cdot mol^{-1}$ (degree of substitution 15%).

Samples

Films for photoluminescence measurements were prepared from a toluene solution by spin coating (2000 rpm, 50 s) on stainless steel substrates. The thickness of the films varied from 500 nm (photoluminescence excitation spectra) to 100 μm (thermostimulated luminescence).

Methods

Photoluminescence spectra were measured using an SDL-1 and Hitachi MPF-4 spectrometer. Excitation was performed by light from a Hg or Xe discharge lamp with appropriate filters or a monochromator for monitoring excitation spectra.

Thermostimulated luminescence measurements were performed with automatic equipment for optical thermoactivated spectroscopy over a temperature range from 4.2 to 350 K. The samples were mounted in the holder of a cryostat and, after cooling, irradiated with UV light. Thermostimulated luminescence measurements were performed both with uniform heating ($\beta = 0.15\,K \cdot s^{-1}$) and in the fractional heating regime [7].

Acknowledgements

The work was sponsored partly by the Grant Agency of the Academy of Sciences of the Czech Republic (grant No. A1050901) and by the Ministry of Education, Youth, and Sports of the Czech Republic (grant OC 518.10/1999 COST), and partly by Award No. UE1-326 of the U. S. Civilian Research & Development Foundation for the independent states of the former Soviet Union (CRDF). The authors would like to acknowledge technical co-operation of Mrs. *D. Dundrová* in the preparation of the manuscript and help of Dr. *I. Kmínek* in the synthesis of polymers.

References

[1] Fujii A, Yoshimoto K, Yoshida M, Ohmori Y, Yoshino H (1995) Jpn J Appl Phys **34**: 1365
[2] Kishida H, Tachibana H, Matsumoto M, Tokura Y (1995) J Appl Phys **78**: 3362
[3] Fujiki M (1992) Chem Phys Lett **198**: 177
[4] Toyoda S, Fujiki M (1998) Chem Phys Lett **293**: 38
[5] Navrátil K, Šik J, Humlíček J, Nešpůrek S (1999) Opt Mater **12**: 105
[6] Harrah LA, Zeigler JM (1987) Macromolecules **20**: 610
[7] Ito O, Terajima M, Azumi T, Matsumoto N, Takeda K, Fujino M (1989) Macromolecules **22**: 1718
[8] Kadashchuk A, Ostapenko N, Zaika V, Nešpůrek S (1998) Chem Phys **234**: 285
[9] Nešpůrek S, Herden V, Kunst M, Schnabel W (2000) Synth Met **109**: 309
[10] Sakurai H, Sugiyama H, Kira M (1990) J Phys Chem **94**: 1837
[11] Kepler RG, Soos ZG (1991) Phys Rev B **43**: 12530
[12] Ayres JT, Mann CK (1965) J Polym Sci, Polym Lett Ed **3**: 505

Received June 23, 2000. Accepted (revised) August 7, 2000