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Influence of Carbazol-9-yl Substitution in Polysilanes on Charge Carrier Trapping and Recombination

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Summary: A series of poly{[3-(carbazol-9-yl)propyl]silane-*co*-methylphenylsilane}s were investigated by optical absorption, photoluminescence and thermoluminescence measurements. It was found that the optical absorption bands of the carbazolyl side groups superimpose on those of the Si backbones in the ultraviolet range. This feature reduces photodegradability of Si-Si bonds during UV irradiation. The TL spectra recorded in the 15 – 325 K temperature range after photoexcitation at 15 K show that the carbazolyl side groups act as trapping sites in polysilanes. Increasing density of carbazolyl groups results in increasing population of deeper (*ca.* 150 meV) traps. Spectral analyses of the thermoluminescence at different temperatures are discussed and compared with analogous results for poly(9-vinylcarbazole) (PVK). It is concluded that the monomeric mechanism of luminescence dominates at low temperatures while the excimeric mechanism prevails at higher temperatures, similarly to PVK.

Keywords: carbazol-9-yl; luminescence; polysilanes; radiative recombination; thermoluminescence; trapping

Introduction

Silicon-backbone linear oligomers and polymers – polysilanes (also named polysilylenes) are functional polymer materials showing interesting photophysical properties.[1,2] The unique photoelectric properties of polysilanes, high-hole drift mobility (of the order of 10^{-4} cm^2/V s) and strong ultraviolet optical absorption and photoluminescence (PL) are associated with σ conjugation along the Si backbone.[3,4] The carbazol-9-yl-substituted polysilanes are systems of special interest (in spite of their low degree of polymerization), because these materials possess both charge generation and charge transport sites.[5-7]

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Experimental

The copolymers and homopolymers of the carbazol-9-yl-substituted silane were prepared and purified according to the methods described by Tabei *et al.*[8] The polymer compositions, molecular weight distributions and glass transitions temperatures (T_g) are listed in Table 1.

The films of carbazol-9-yl-substituted polymers were obtained by casting from dichloromethane/dichloroethane (1:1) solution on quartz glass substrates for optical absorption and PL measurements (thickness > than 1 μm) and on steel plates for thermoluminescence (TL) measurements (7 – 10 μm). The poly(methylphenylsilane) (PMPSi) films were cast from tetrahydrofuran solution. For TL experiments, the polymer films were placed between a thermostatted stage and sapphire plate and squeezed together with a brazen frame anchored thermally to the stage in vacuum chamber (closed-cycle cryogenic system APD Cryogenics, type Displex); the heating rate was 7 K/min. The measurements were carried out in the 15 K - 325 K range after photoexcitation at 15 K using nitrogen pulsed laser. The luminescence was monitored with a photomultiplier Thorn EMI 9789 QB. Spectral analyses of the thermoluminescence were carried out using a grating monochromator with sweeping time 40-60 s in the range from 350 nm to 600 nm.

Table 1. Characteristics of investigated polymers.

Polymer	Monomers		Copolymer composition [1]	T_g	Molecular weight [2]	
	MPSi	CzSi		[K]	M_n	M_w
PMPSi	10	0	–	298	5220	8890
PSiK (10:1)	10	1	10:0.5	299	3380	5830
PSiK (10:3)	10	3	10:2.8	300	8460	16400
PSiK (10:5)	10	5	10:3.3	297	5020	8150
PSiK (10:10)	10	10	10:6.0	295	850	1940
PSiK	0	10	–	296	1580	2440

MPSi – methylphenyldichlorosilane, CzSi – [3-(carbazol-9-yl)propyl] dichloro(methyl)silane

[1] By ^{29}Si NMR

[2] By GPC in dichloromethane, polystyrene calibration

Results and discussion

Two characteristic bands at 275 and 335 nm are seen in the absorption spectrum of PMPSi. Introduction of the carbazole groups causes an appearance of three new maxima at 264, 295 and 345 nm (see Fig. 1). The presence of two isosbestic points (at 270 and 300 nm) in the absorption spectra of solutions (not shown here) for all substituted polysilanes proves the existence of two independent chromophoric groups.

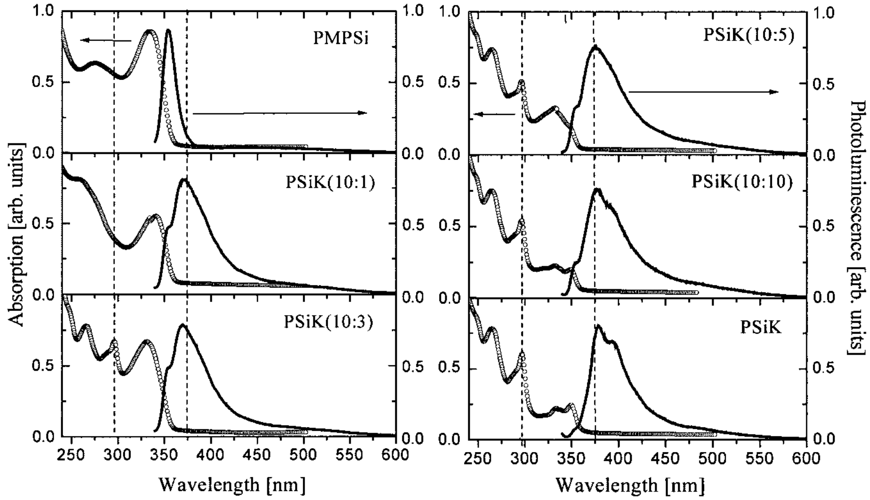

Figure 1. Optical absorption spectra (circles) and photoluminescence spectra under 337 nm excitation (solid lines) of polysilane films. The dashed lines indicate the position of the most characteristic absorption and PL maxima of carbazol-9-yl group.

The photoluminescence spectra of PMPSi, obtained after excitation with 337 nm wavelength, show a single emission band at about 360 nm. In the long-wavelength range (over 400 nm), one can observe also another, very weak broad band reported also by others.[4] The intensity of the 360 nm band associated with the σ^*-σ transition of silane chains, decreases upon increasing the carbazole group concentration due to the screening effect. We cannot exclude that for the systems with low carbazole contents also monomeric emission of carbazole groups may appear in this wavelength range (355 nm). At the same time the excimer emission of the carbazole groups (at ca. 370 and 420 nm) increases gradually. Similar photoluminescence spectra for such systems were reported earlier.[4,6] In the case of PSiK (10:5), PSiK (10:10) and PSiK, one can see the long-wavelength shoulder probably associated with the aggregates or extended excimer of carbazole rings, which may be formed in the systems with higher concentration of carbazol-9-yl groups. The TL spectra for different polysilane samples photoexcited at 15 K are presented in Fig. 2a. The TL spectrum of PMPSi

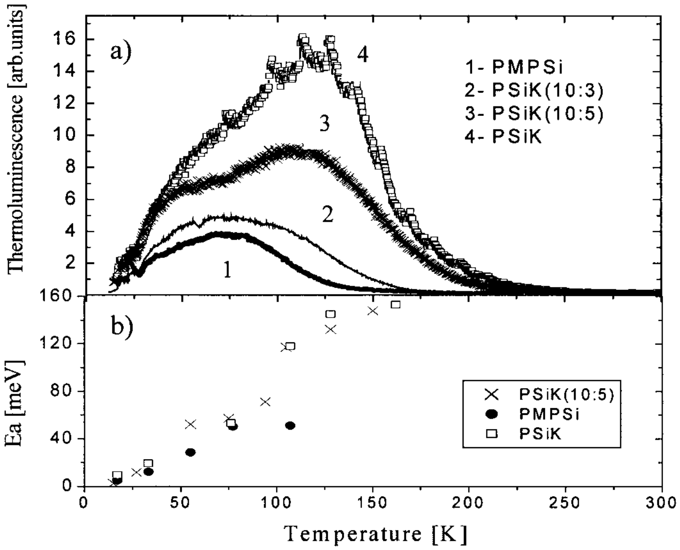

Figure 2. Thermoluminescence of silane homo- and copolymers (a), activation energy diagram (b), estimated from the partial heating experiments.

is the weakest, with a maximum at *ca.* 75 K and with a low-temperature (35-45 K) shoulder. This indicates that only shallow traps for charge carriers are present in PMPSi, which remains in good accordance with the former results obtained by Kadashchuk *et al.*[9] From the partial heating experiments, one can estimate that the traps with depth about 50 meV play a dominant role (see Fig. 2b). Introduction of carbazol-9-yl side groups results in a progressive increase in the thermoluminescence intensity and in the change of the TL spectra shape. In the TL spectrum for PSiK (10:5), one can clearly distinguish two maxima: the high-temperature maximum at around 120 K and the low-temperature one at around 45 K. This spectrum is similar to that previously obtained for poly(vinylcarbazole) (PVK), but in the latter the two maxima are better separated.[10] The occurrence of two TL maxima indicates that upon heating, the charge carriers are subsequently liberated from two different trapping levels. From the partial heating experiments, the depths of these two levels can be estimated as 40 meV and 120-130 meV, respectively. The TL spectrum of PSiK has the main maximum around 140 K and a shoulder on the low-temperature side, indicating the presence of another maximum. Partial heating results show that traps with depth 150 meV predominate in the PSiK (see Fig. 2b).

To identify the origin of radiative recombination processes giving rise to the TL maxima, the spectral analyses of the light emitted during the TL runs (at temperatures close to the TL maxima) have been performed (see Fig. 3a, b). For PMPSi, one band in the range 440 - 540 nm is observed, corresponding to the weak, long-wavelength band in the photoluminescence spectra. Spectral analysis of the TL for all copolymers with carbazol-9-yl groups (with the exception of PSiK (10:1)) showed two bands. For the PSiK (10:5), the spectral analysis was performed at the first TL maximum at *ca.* 45 K and at the second, stronger TL maximum at *ca.* 120 K – in the same TL run. In both cases the spectra show two distinct bands at *ca.* 470 nm and *ca.* 520 nm (Fig. 3b). The spectrum of isothermal phosphorescence at 15 K, although very weak (not shown here), also reveals these two bands. These bands are associated with triplet states of carbazole groups: monomeric at about 470

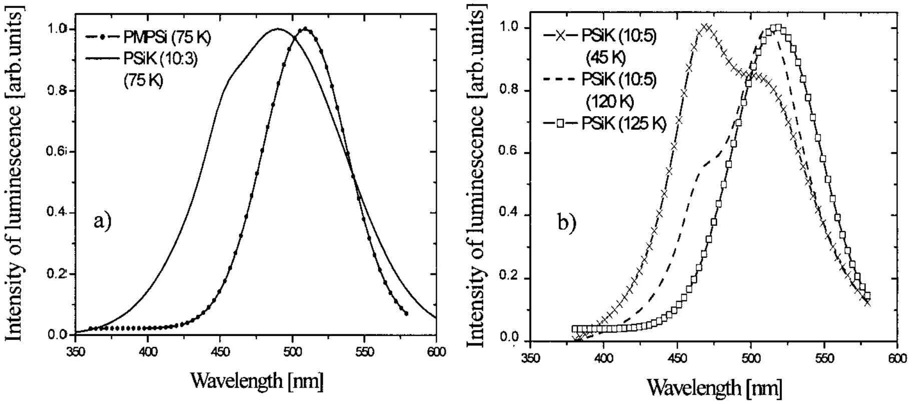

Figure 3. The normalized spectra of the light emitted in the course of the TL at temperatures close to the TL maxima for the investigated polysilanes.

nm and excimeric at about 520 nm. The ratio of the excimeric to monomeric emission intensity is higher for the high-temperature TL maximum. For PSiK, the TL emission is dominated by excimer sites (see Fig. 3b). Similar spectral evolution of the light emitted in the course of TL with increasing temperature was found for PVK.[9] Comparing the spectra of the PSiK (10:5) and PSiK samples shown in Figs. 2 and 3, one can conclude that full substitution of polysilane with carbazol-9-yl groups causes an increase in the population of deeper traps and of excimeric states contributing to thermoluminescence.

Conclusion

Introduction of carbazol-9-yl side-groups into polysilanes chain influences absorption, photoluminescence and thermoluminescence spectra. The carbazol-9-yl groups in polysilanes are chromophores separated from the main chain, protecting the Si-Si bonds from photodegradation by UV light. Photoluminescence spectra indicate the presence of aggregates (or other extended excimer structures) at high carbazole group concentrations. Spectral analysis of the emitted light indicates that the triplet monomeric mechanism of luminescence dominates at low temperatures and the triplet excimeric mechanism prevails at higher temperatures. These results are similar to those found for PVK. The carbazol-9-yl side-groups introduced to polysilanes form new photogeneration/recombination centres and act also as trapping sites. Increasing density of carbazol-9-yl groups results in increasing population of deep traps.

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