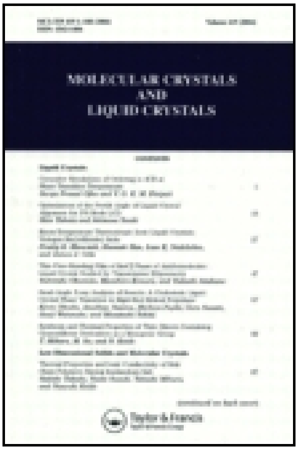

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Photoinduced Metastability and Degradation of Poly[Methyl (Phenyl)Silylene] as seen by Thermoluminescence

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Photoinduced Metastability and Degradation of Poly[Methyl (Phenyl)Silylene] as seen by Thermoluminescence

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Abstract Photodegradation of poly[methyl(phenyl)silylene] (PMPSi) was studied by low-temperature thermoluminescence and photoluminescence. It has been found that this process is nearly reversible at moderate UV exposure; the reverse reaction could be accelerated thermally. The activation energy of the annealing process was determined as 0.65 eV. Different character of the photodegradation was found under the excitation with 366 nm and 250–280 nm light at room temperature (i.e., within σ-σ^* and π-π^* transitions, respectively). σ-σ^* excitation leads to the formation of deep charge carrier traps (E_t= 0.45 eV) of photodestructive origin which are associated with photoscission of Si bonds in the backbone. The presence of electron acceptor dopants strongly inhibits the trapping ability of these traps.

Keywords: photodegradation; poly[methyl(phenyl)silylene]; thermally stimulated luminescence; photoluminescence; Si bonds scission; charge carrier traps

INTRODUCTION

Processes inducing changes in polymer properties are sometimes associated with polymer degradation. Chemical stability of organic polymers can be influenced by temperature, mechanical forces, chemical catalysis and solar and high-energy radiations. Polymer degradation results mainly in chemical bond scission,

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crosslinking and oxidation of both the main chain and side groups. The chemical bond scission of the main chain is mostly an irreversible process; the broken chemical bond cannot be simply recovered. It is evident that reversibility in the process of chemical bond scission-reformation (similarly to some photochromic and thermochromic materials) [1] and, therefore, reversibility in the electronic state [2, 3] formation could lead to a new group of polymers, very interesting for many applications, including electronic ones. Polysilylenes are known as polymers possessing such a property.

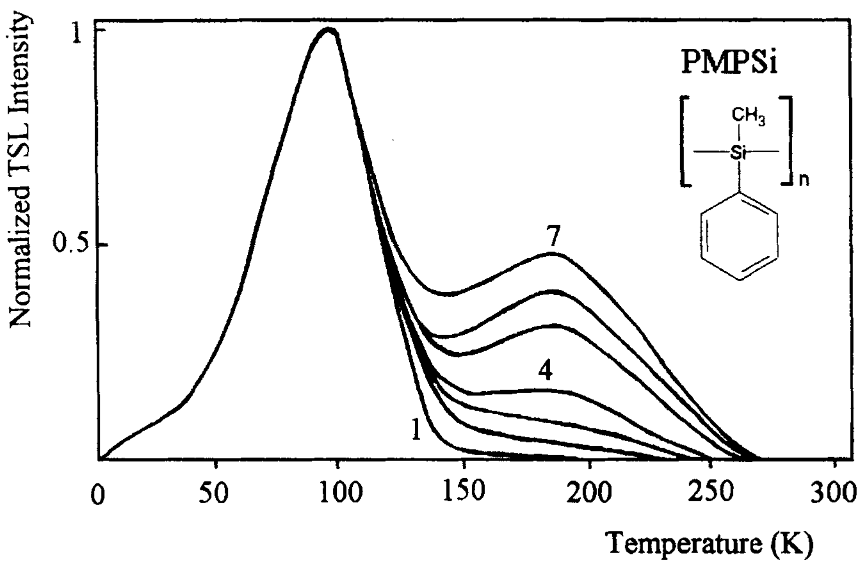


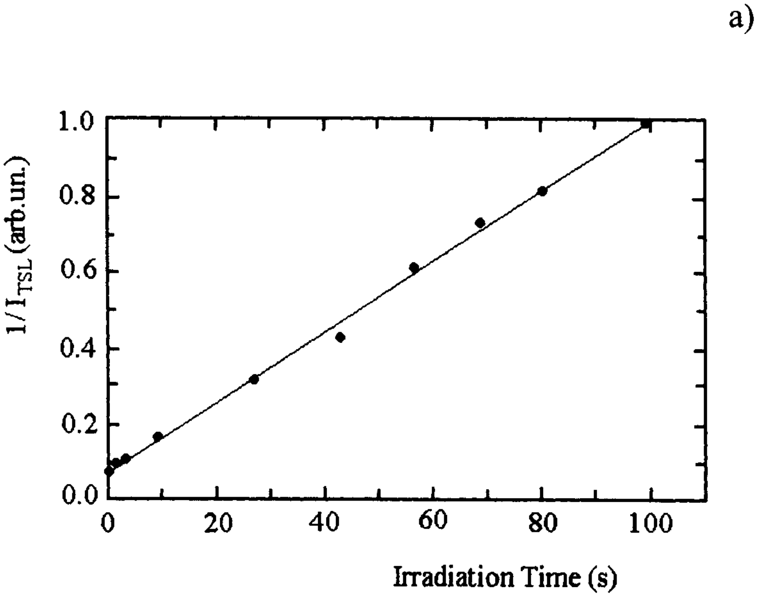
FIGURE 1 Normalized TSL glow curves of PMPSi before (curve 1) and after UV exposure with unfiltered light at room temperature for 3, 10, 30, 100, 160, and 240 s (curves 2, 3, 4, 5, 6 and 7, respectively)

Polysilylenes with their uninterrupted runs of silicon atoms, are a new class of photosensitive polymers with significant delocalization of electrons along the polymer chain. Electronic properties of these linear polymers differ from structurally analogous carbon-based σ -conjugated systems such as poly(ethylene) or poly(styrene), resembling rather fully π-conjugated systems such as poly(acetylene). Physical properties are, among others, strongly influenced by chemical structure of polymer side groups; various polymers with photoconductive, ionic, thermochromic, piezochromic, photorefractive, electrooptical, nonlinear-optical, and liquid-crystalline properties can be synthesized [4]. The high quantum efficiency of charge photogeneration and the high charge carrier drift mobility (of the order 10^{-8} $m^2V^{-1}s^{-1}$), unusually high for polymeric photoconductors [5–7], as well as potential applications as photoresists [8], optical waveguides [9], non-linear optical media [10], etc., stimulated interest in studies of photostability and electronic structure of these polymers.

Upon strong UV irradiation at room temperature, polysilylenes undergo a complex photodegradation process. Starting from photochemical cleavage of Si-Si bonds, oxidation to polysiloxanes, crosslinking and photoablation take place changing the solubility of the polymers, their optical properties and film thickness. Photo-induced changes in polysilylenes have been studied by several techniques, among others by optical absorption [11, 12], thermal and NMR techniques [13], electron spin resonance [14], transient photoconductivity [15–18], post-transit current spectroscopy [2] and flash photolysis [19, 20]. Recently, thermally stimulated luminescence (TSL) has been detected and studied in poly[methyl(phenyl)silylene (PMPSi) [3] and some other polysilylene [21] films. In this paper we report some results concerning photodegradation of PMPSi obtained by TSL and photoluminescence (PL). The TSL technique is known as one of the most sensitive tools for the investigation of destruction of polymers [22], as well as a reliable method for the study of trapping and recombination phenomena in amorphous systems [3, 21, 23]. Among others, the studies were aimed of the formation of deep localized states during the photodegradation process. These states can play an important role in electronic properties of solids. It was found that optical excitations of polysilylenes at room temperature with energy near to the band gap lead to the Si-Si bond scission [24, 25], followed by appearance of deep trapping centers for charge carriers. Recently, a reduction in the charge carrier life-time due to deep trapping on photocreated dangling Si bonds was reported [2, 16]. A decrease in the steady-state photocurrent under UV irradiation has also been reported [26]. It was demonstrated that these effects are reversible after subsequent annealing.

EXPERIMENTAL

TSL measurements were carried out with an automatic equipment for optical thermoactivated spectroscopy over a wide temperature range from 4.2 to 350 K with the accuracy better than 0.1 K. PMPSi samples were mounted in a holder of an optical helium cryostat and, after cooling, irradiated with UV light. For excitation, the light from a high-pressure 500 W mercury lamp was used with some optical filters for light selection. TSL measurements were performed in two different regimes; under the uniform heating with the rate $\beta = 0.15$ K/s and in the fractional heating regime which allows to determine trap depths. Details of the



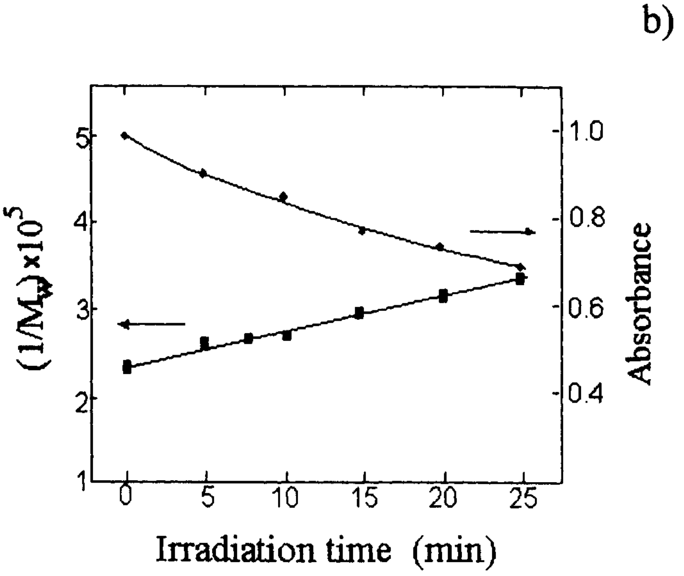


FIGURE 2 a) Reciprocal value of the TSL intensity vs. UV exposure with unfiltered light at room temperature. b) Reciprocal value of the molecular weight (M_W) vs. irradiation time ($\lambda = 350$ nm). Dependence of the absorbance at $\lambda = 347$ nm (σ-σ^* transitions) vs. irradiation time fractional TSL technique and the procedure of data processing were described elsewhere [23, 27]. Photoluminescence (PL) spectra were investigated using an SDL-1 spectrometer combined with an optical helium cryostat. Excitation was performed by light from a 250 W xenon lamp using appropriate glass filters. PL spectrum was corrected for wavelength dependence of the equipment and light distribution of the lamp.

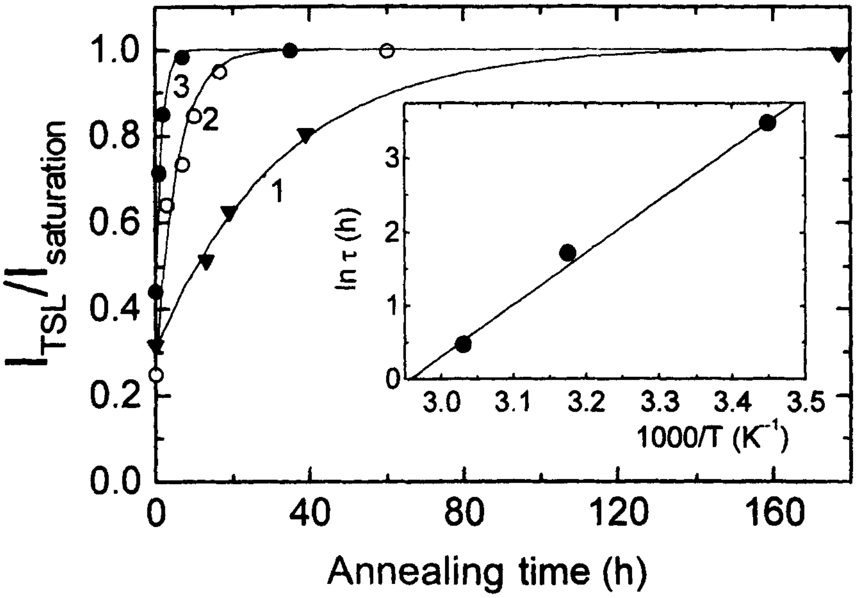


FIGURE 3 Reversibility of the total TSL intensity by annealing at 290, 315, and 330 K (curves 1, 2, and 3, respectively). Solid lines represent fits of the experimental data by the expression of the type $I \sim (1\text{-exp}(\text{-}t/\tau))$ (see the text for explanation). Inset: Arrhenius plot of τ vs. the annealing temperature; the activation energy, 0.65 eV, was determined from the slope

Poly[methyl(phenyl)silylene], (Fig. 1) was prepared by Wurtz coupling polymerization, as described by Zhang and West [28]. Low-molecular-weight fractions were extracted with boiling diethyl ether. The residual polymer, obtained in ca. 17% yield, possessed a unimodal but broad molecular weight distribution, $M_w = 4 \times 10^4$ g mol^{-1}. Thin films for TSL and PL measurements (thickness 3 ÷ 100 μm) were prepared from a toluene solution by both spin-coating and casting on stainless steel substrates. Before deposition, the polymers were three times reprecipitated from toluene solution with methanol and centrifuged (12 000 rpm, 15 min). After deposition, the films were dried at 10^{-3} Pa at 330 K for at least 4 h.

RESULTS

It is known that absorption spectrum of PMPSi film consists of two main long-wavelength peaks at about 338 and 276 nm [12]. It has been shown [29] that the first longest wavelength electronic transition has mainly arisen from delocalized (σ-σ^*) transitions. The peak at the shorter wavelength is associated with pure (π-π^*) transitions in the benzene ring. The fluorescence quantum efficiency is quite high, about 0.15 at 360 nm. Charge carriers can be photogenerated by both types of the excitations. At room temperature, the quantum generation efficiency is about 4 times higher for the 254 nm excitation than for the 355 nm one [30].

It was found that PMPSi films have shown a relatively strong thermoluminescence induced by UV radiation. Figure 1 presents a typical TSL glow curve of PMPSi film (curve 1) under excitation at 4.2 K with unfiltered light for 30 s. As one can see, the TSL glow curve shows a broad peak with a maximum at $T_m \approx 90$ K. The existence of a quasi-continuous trap distribution in PMPSi samples has been found [3]. The mean activation energies, <E>, measured by the fractional TSL, linearly increases with temperature, T. The most appropriate extrapolation could be made by the following empirical formula (in eV) $\langle E \rangle (T) = 0.0028\ T - 0.05$. The activation energy and frequency factor in the maximum of the TSL glow curve is $\langle E_m \rangle = 0.19$ eV and $S \cong 10^{10}\ s^{-1}$, respectively.

Another interesting feature of the TSL is associated with a "high-temperature" peak after UV irradiation at room temperature. Figure 1 presents normalized TSL glow curves of PMPSi after UV exposition at room temperature for 3, 10, 30, 100, 160, and 240 s (curves 2, 3, 4, 5, 6 and 7, respectively). One can see that, in addition to the TSL peak with maximum at ~ 90 K mentioned above, a new additional high-temperature peak with maximum at ~180–190 K and the mean activation energy of about 0.45 eV appeared. It should be pointed out that total TSL intensity is drastically reduced on UV radiation exposition. Figure 2a shows a dependence of the reciprocal value of the TSL intensity (taken as an area under the TSL glow curve) vs. exposition of the preliminary UV irradiation at room temperature. This process is followed by a decrease in the molecular weight of polymer, as it follows from Fig. 2b (determined by gel permeation chromatography). At the same time, absorbance at $\lambda = 347$ nm (σ-σ^* transitions) decreases(Fig. 2b) [31, 32].

The most interesting feature of the "high-temperature" peak is its reversibility. The effect of annealing is shown in Fig. 3 for temperatures 290, 315, and 330 K (curve 1, 2, and 3, respectively). Solid lines represent fits of the experimental data by the expression of the type $I \sim (1 - \exp(-t/t))$, where I is the total TSL intensity (determined as the area under the TSL glow curve), t is the annealing time, and t is the time constant of the annealing process. The time constants comprise 32.5, 5.6 and 1.6 h for the annealing temperatures 290, 315 and 330 K, respectively. Figure 3 was constructed as follows: The sample was irradiated with UV light at room temperature in a dose which gave a decrease in the total TSL (excited at 4.2. K) on the 10% level. Then the sample was annealed at a given temperature to reach the saturation level of the TSL and the sample was degraded again under the same conditions at room temperature (to the 10% level). The temperature of the sample at which the new annealing process was performed was changed and the procedure was repeated. The Arrhenius plot of t vs. the annealing temperature is given in inset of Fig. 3; the slope of this plot yields the activation energy of the annealing process equal to ~ 0.65 eV. It should be emphasized that in the case of strong photodegradation of PMPSi with UV light at room temperature, when the total TSL intensity is about tenfold lower, the annealing does not lead to a complete recovery of the initial TSL; the intensity recovers up to ~ 30% level only. On the other hand, in the case of moderate photodegradation of the polymer, when the total TSL intensity decreased only to the 50% level, thermal annealing manifests a complete reversibility of the observed photocreated changes in PMPSi and a full recovery of the TSL intensity. It should be pointed out that no photodegradation was observed during the UV exposure at liquid helium temperatures.

The above-mentioned results were obtained using an unfiltered UV light of Hg lamp. In order to clarify the role of the photoexcited σ-σ^* and π-π^* transitions in PMPSi in the photodegradation phenomena, the measurements with UV irradiation at 366 and 250–280 nm, respectively, were performed. The 366 nm light was selected with a set of appropriate glass filters; the 250 – 280 nm light was obtained using a chlorine-bromine gas filter (cuvete of $L = 10$ cm). We found that a decrease in the TSL intensity occurs after preliminary irradiation with both 366 nm and 250–280 nm light at room temperature. However, the 366 nm light was more efficient (Fig. 4a) in the photodegradation process (the photon flux was nearly the same for both illumination wavelengths). It should be emphasised, that the above high-temperature TSL peak located at 150–180 K appeared only under 366 nm irradiation, but it was not observed at 250–280 nm exposure. Both 366 and 250 – 280 nm light caused strong polymer photodegradation at high exposure and resulted in incomplete reversibility of the TSL intensity during the annealing process. However, at a moderate polymer photodegradation, a full recovery of the initial TSL intensity independently of the light wavelength was observed (cf. Fig. 4b).

Figure 5a presents the PL spectra of PMPSi without (curve 1) and with preliminary "photodegradation exposure" (366 nm at room temperature during 5 min (curve 2) and 200 min (curve 3)). The spectra were registered at 4.2 K with 313

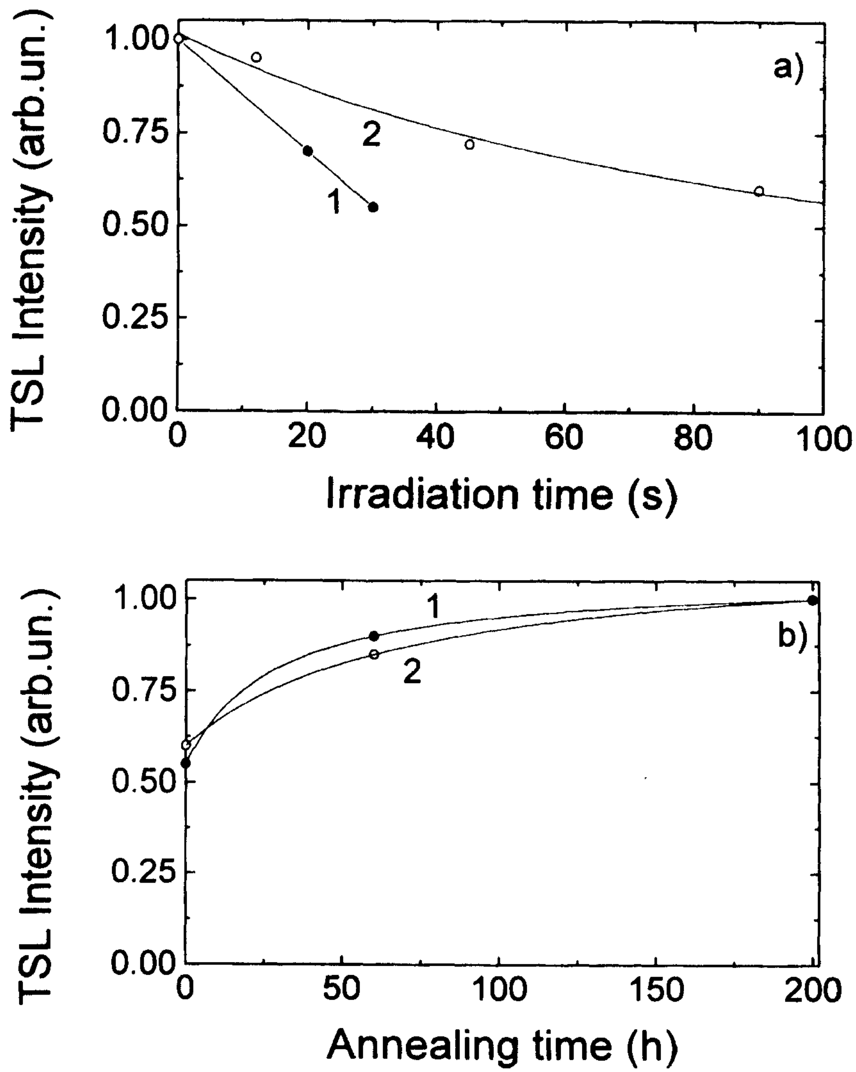


FIGURE 4 a) Decrease in the TSL intensity with UV irradiation ($\lambda = 366$ nm and 250 ÷ 280 nm, curve 1 and 2, respectively). b) Recovery of the TSL intensity of PMPSi samples after annealing at room temperature subjected to moderate photodegradation (showed in (a)) with 366 nm and 250 ÷ 280 nm light (curve 1 and 2, respectively)

nm excitation. One can see that the prolonged exposure to the 366 nm light leads to the short-wavelength shift of the exciton band from $\lambda_{max} \cong 354$ nm (curve 1) to $\lambda_{max} \cong 344$ nm (curve 3). This suggests the backbone scission and formation of shorter polymer segments. It should be noted that although the total PL intensity decreases in the course of photodegradation with the 366 nm light, some increase in the PL signal at about 520 nm was observed indicating the appearance of an additional emissive band most likely associated with photocreated defects in PMPSi. The "defect" PL emission was effectively observed using the excitation with the 365 nm light (see inset in Fig. 5a) or even with $\lambda = 405$ nm. This suggests that the photocreated defects are absorbing at wavelengths longer than 370 nm (basic PMPSi absorption threshold). Thus, visually, the effect of the luminescence color shift from blue (for the non-degraded PMPSi sample) to light-green (for sample after photodegradation) as detected at 4.2 K (the 365 nm excitation light). It should be noted that this PL band at 520 nm also manifested good reversibility in the case of moderate photodegradation of the polymer; it nearly disappeared during the annealing procedure described above and the light-green color of the PL at 4.2 K changed back to blue one.

The photodegradation at room temperature with 250 – 280 nm light for 5 min (Fig. 5b, curve 2) and 200 min (curve 3) caused a decrease in the total luminescence intensity in both the exciton ($\lambda = 354$ nm) and the broad visible band similarly to the previous case of the 366 nm light photodegradation. However, the exciton band did not show any notable shift towards shorter wavelengths (Fig. 5b) and we hardly observed the appearance of the "defect" PL band at $\lambda \sim 520$ nm. Interestingly, when the sample was photodegraded by the 366 nm light at room temperature and then an additional irradiation by the 250–280 nm light was performed, a notable recovery of both the TSL and PL intensities was found. This indicates that the 250–280 nm light notably accelerated recovery of the luminescence in the photodegraded (366 nm light) PMPSi sample.

It should be noted that the photodestruction effect on PL intensity is considerably less pronounced than in the case of TSL. For instance, the TSL intensity fell down about 3 times after a UV exposure for ~ 1 min (unfiltered light, room temperature), the PL intensity fell down 3 times after ~ 200 min exposure using the same light intensities.

Finally, the peculiarities of the photodegradation of PMPSi containing electron acceptor molecules in its bulk should be mentioned. It was found that the presence of acceptor molecules suppressed the deep charge carrier trap (0.45 eV) formed during the photodegradation process. In contrast to the neat PMPSi, the chloranil-doped (2%) polymer shows only a very weak relative increase in the TSL signal in the high-temperature region (~130–200 K) after photodegradation (Fig. 6a). No pronounced new high-temperature TSL peak was observed in addition to the main peak at ≈ 90 K. At the same time, the total TSL intensity of chloranil-doped (2%) PMPSi considerably decreased similarly to the case of photodegradation of the neat PMPSi, although this reduction was less pro-

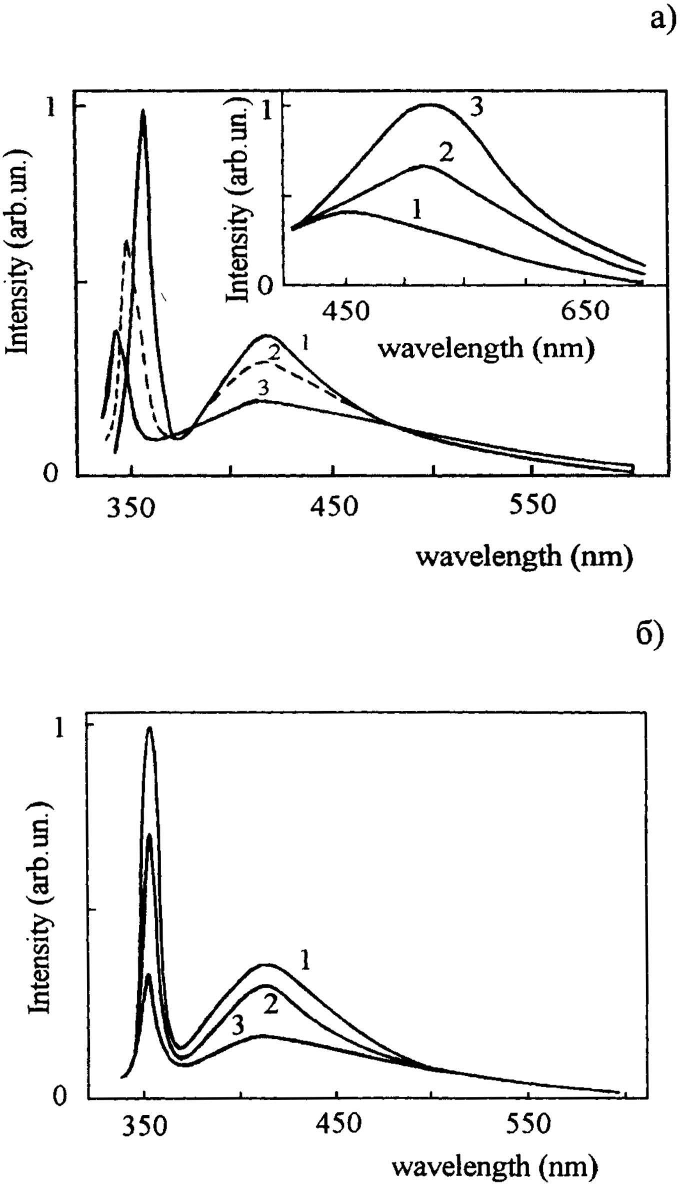


FIGURE 5 a) PL spectra of PMPSi without (curve 1) and with preliminary photodegradation by exposure to 366 nm light at room temperature for 5 and 200 min (curves 2 and 3, respectively). The spectra were registered at 4.2 K with 313 nm excitation. Inset: Spectra recorded with 365 nm excitation. b) PL spectra of PMPSi without (curve 1) and with preliminary photodegradation exposure to 250 ÷ 280 nm light at room temperature for 5 and 200 min (curve 2 and 3, respectively). Spectra were recorded at 4.2 K with 313 nm excitation nounced and the kinetics of the TSL intensity decrease with irradiation time differed from that observed for the neat PMPSi presented in Fig. 2a.

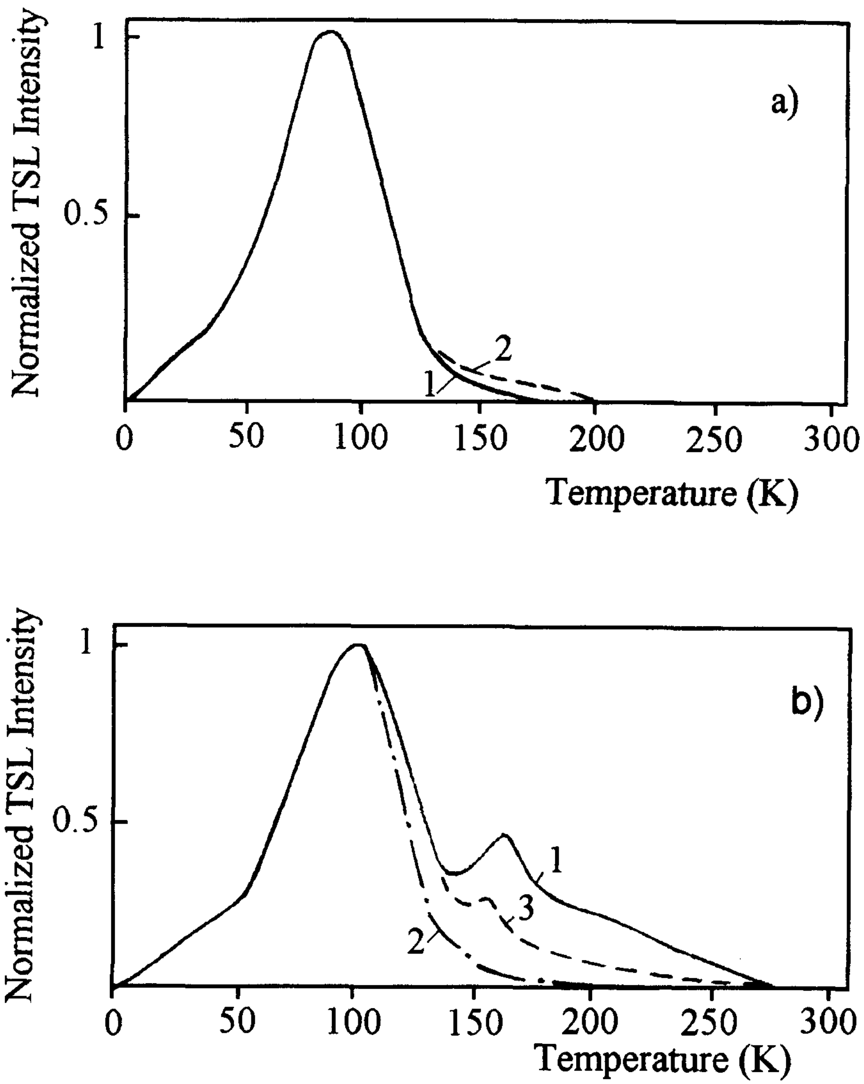


FIGURE 6 a) TSL glow curves of chloranil-doped (2%) PMPSi without (curve 1) and after UV photodegradation at room temperature for 40 s (curve 2). b) TSL glow curves of PMPSi film treated as follows: after preliminary photodegradation of the sample in He atmosphere at room temperature for 40 s (curve 1); subsequent exposure to air at room temperature for 15 min and rapid cooling in He cryostat (curve 2); subsequently annealed in He atmosphere at room temperature for 15 min (curve 3)

A similar and even more pronounced effect was observed in thick (~100 μm) cast oxygen-soaked PMPSi films (exposed to air and then rapidly cooled down to $T < 150$ K in He cryostat), most probably due to good electron-acceptor properties of oxygen molecules. The influence of oxygen on the TSL behaviour could be readily eliminated by annealing the oxygen-soaked samples in helium atmosphere at room temperature for several minutes. We attribute this behaviour to removal of oxygen from the sample at sufficiently high temperature. The oxygen effect on the photodegradation of PMPSi can be characterized as follows: (i) UV photodegradation of polymer in air and subsequent rapid cooling of oxygen-soaked sample in He cryostat does not lead to appearance of any notable high-temperature peak, (ii) the high-temperature TSL peak in photodegraded PMPSi films in helium atmosphere (Fig. 6b, curve 1) completely disappears after oxygen (acceptor) soaking the polymer at room temperature (curve 2). The high-temperature peak can be recovered again as a result of subsequent annealing in helium atmosphere at room temperature (Fig. 6b, curve 3).

DISCUSSION

It is known that photodegradation of PMPSi proceeds via intermediates such as silyl radical and silylene biradical [33, 34]. Three possible reactions for initial photodegradation process were proposed [33]: (i) the first should produce both silylene insertion products and silyl radical-derived products, (ii) the second should give only silyl radical derived products, and (iii) the third should yield only a silylene insertion product with simultaneous formation of the Si-Si bond. It should be noted that a remarkable wavelength dependence of the intermediate during photodegradation was observed for PMPSi which was investigated by flash photolysis and a quenching experiment [34]. The long wavelength excitation (σ-σ^* transition) results in the formation of mainly silyl radicals, while the short-wavelength excitation (π-π^* transition) additionally produces silylene biradicals.

The origin of the main low-temperature TSL peak with maximum at about 90 K (Fig.1, curve 1) was studied in our previous work [3] and was interpreted as associated with charge carrier thermal release from intrinsic tail states of the DOS distribution. Such approach based on the Gaussian disorder model [35] provided reasonable understanding of all observed trends in TSL. Accordingly, the shape of the high-temperature wing of the TSL peak and the energetic position of its maximum could be consistently explained by incorporation of the concept of the energy transport. Analysis of the TSL peak yields for the half-width of the density of states profile for localized charge carriers the value of about 0.0985 eV

[3] which reasonably agrees with the transport energetic parameter, assigning the entire temperature dependence of the charge carrier mobility to disorder. It was shown that the position of the TSL peak maximum is in accord with the predictions of the theory of non-activated energetic relaxation of photogenerated charge carriers within a Gaussian-shaped manifold of localized states, and, therefore, no further feature of the DOS in the gap is necessary for the existence of the low-temperature TSL peak. The absence of TSL signal in the high-temperature region evidences the absence of deep charge carrier trapping in PMPSi before UV irradiation at room temperature.

The appearance of a new high-temperature TSL peak after preliminary UV irradiation (Fig. 1) of the PMPSi sample indicates the formation of deep extrinsic traps (having $< E > = 0.45$ eV), most probably of photodestructive origin, and associated with dangling Si bonds created by photoscission of the Si backbone. Photoinduced deep traps of similar origin in PMPSi have been earlier invoked [15, 16] for the explanation of the reduction in the hole lifetime during charge transport measurements. It should be noted that the low-temperature TSL peak is not notably shifted by the photodestructive process in PMPSi. This agrees with the conclusion that the distribution of hopping states does not change during UV irradiation of PMPSi. Similarly, the hole mobility as well as its temperature and electric field dependences have not been influenced by UV exposure [15, 16].

The decrease in the total TSL intensity as the result of preliminary UV irradiation (Fig. 2a) is quite typical behaviour of polymers which underwent destruction. As it was shown for different polymer systems [22], there is a qualitative correlation between kinetics of the decreasing in the TSL intensity and the decrease in molecular weight of the polymer which underwent the destruction. It seems that such correlation exists also in the case of PMPSi since the functional dependence of kinetics presented in Fig. 2a at least qualitatively coincides with the obtained dependence of the reciprocal value of molecular weight (Fig. 2b) on the irradiation time. Thus an interesting possibility arises to use the TSL technique for the study of destruction processes in Si- backbone polymers.

The annealing effect presented in Fig. 3 correlates well with the earlier observed recovery effect of collected charges in PMPSi (as determined by photocurrent transients) [16] and with the evidence of formation of metastable electronic states. The time constant of the recovery of the TSL intensity during annealing at room temperature is estimated as 37 h, close to the value of 51 h reported in Ref. [16]. It is interesting that after strong photodestruction of PMPSi, the recovery of the TSL intensity by annealing saturates at about the $I/I_0 = 0.3$ level (here $I_0$is the TSL intensity before the UV exposure). Very similar behavior was observed also by photocurrent transients measurements [14, 16]. However, in the present work we have found that the time constant strongly decreases with increasing annealing temperature (T_{ann}) (see inset of Fig. 3); thus, the TSL intensity recovery is a thermally activated process with the activation energy ~ 0.65 eV. Such value is a typical activation energy for unfreezing of the molecular motion as well as for molecular diffusion in organic solids [36]. It should be mentioned that so far no change in the time constant with increasing T_{ann} has been reported; only a relative increase in the collected charge (Q/Q_0) (Q_0 is the collected charge before UV exposure) from the value of about 0.3 in room temperature annealing up to about 0.9 after annealing at T_{ann} = 335 K was observed.

In our TSL measurements, during the photodestruction of PMPSi with long UV exposures (which probably results also in some irreversible photochemical modifications of the polymer), we did not observe such considerable increase in the I/I_0 ratio with increasing annealing temperature, only the time constant appeared to be strongly temperature-dependent. A possible reason could be found in a much higher light power in our experiment, about three orders of magnitude in comparison with that used in Ref. [14–16]. Therefore, a comparison of the relative changes in I/I_0 and Q/Q_0 should be made with certain caution. On the other hand, the moderate level of the photodestruction allowed to reach the complete reversibility of the TSL intensity after subsequent annealing (Fig. 4b), i.e., the formation of metastable states was dominant.

The investigations of PL spectra of PMPSi registered at 4.2 K after preliminary photodestruction at room temperature with the 366 and 250 ÷ 280 nm light (Fig. 5a and 5b, respectively) have revealed that photodestructive processes have somewhat different character. The photodegradation of PMPSi with the 366 nm light leads (i) to a decrease in both the PL and TSL intensity, and (ii) to a short-wavelength shift of about 10 nm of the exciton PL band at 354 nm (Fig. 5a), which seems to be a consequence of a decrease in the molecular weight of the polymer in the photodestructive process. This agrees well with earlier results [34] that mainly silyl radical products are formed at such kind of excitation. The appearance of new "green" PL at ~520 nm (as well as of the high-temperature TSL peak) could be associated with photodestructive products (most probably with bond scission) in PMPSi. Thus, the photoinduced metastable electronic states can also act as deep exciton traps.

On the other hand, the photodegradation with the 250 – 280 nm light does not lead to a shift of the exciton PL at 354 nm (Fig. 5b), while the total luminescence intensity (as well as TSL intensity) tends to decrease. We also could not see a new PL band at 520 nm and did not observe the appearance of the high-temperature TSL peak. Thus, the photodegradation during short-wavelength excitation proceeds in a different way, without significant chain scission, apparently via silylene biradical products formed at polymer chain ends. This supports the third mentioned reaction route (product of silylene insertion with simultaneous formation of the Si-Si bond). An interesting and unusual fact, which evidently merits further investigation, is that the 250 ÷ 280 nm irradiation of samples photodegraded earlier by the 366 nm light leads to a notable recovery of both the TSL and PL intensity. Thus, the 250 ÷ 280 nm light excitation accelerates the recovery process of PMPSi samples after their photodestruction with the 366 nm light.

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