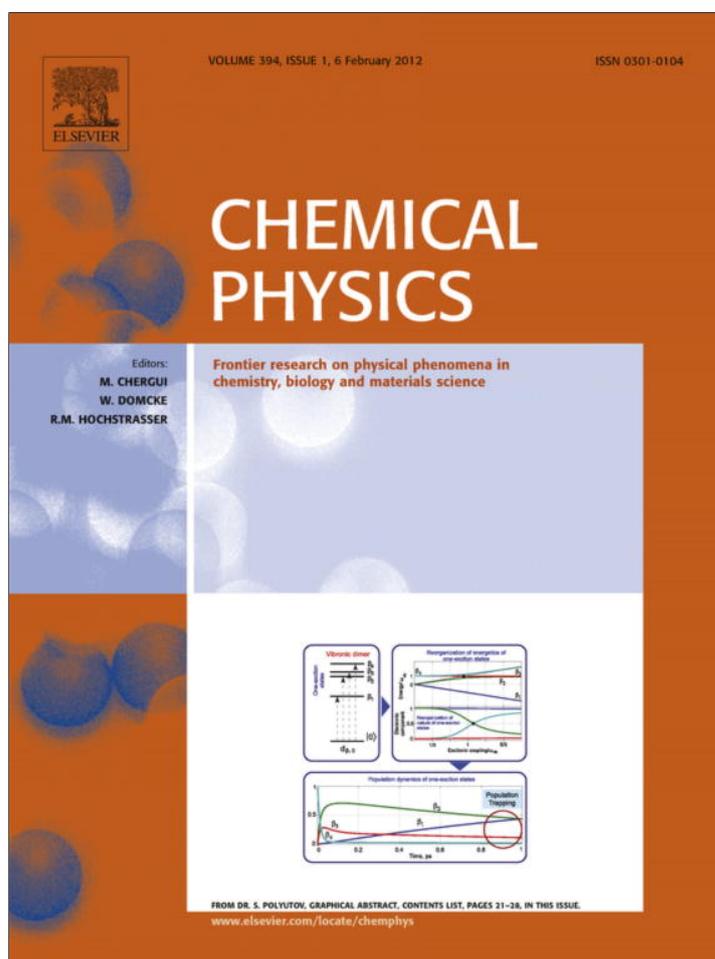


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## Unusual features of charge carrier traps energy spectra in silicon organic polymers revealed by advanced TSL

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### ABSTRACT

The peculiarities of charge carrier traps' energy spectra in poly (di-n-hexylsilane) films have been studied by the enhanced fractional thermally stimulated luminescence (TSL) in the temperature range of 5–200 K. For the first time, we have shown that the majority of fractional energy values (>80%) is distributed between a set of horizontal energy levels suggesting a discontinuity of the traps' energy spectrum. These data distinctly differ from the results of earlier studies where a quasilinear dependence of the activation energy on temperature was found. It is shown that the significant width of TSL bands originates from the dispersion of the frequency factor. It is also established that the values obtained for the activation energy correlate well with the frequencies of the symmetric Raman active Ag modes at 268 and 373 cm<sup>-1</sup> of the silicon chain, which confirms the suggestion about the hole location on the segments of the silicon organic polymers backbone.

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### 1. Introduction

Polysilanes belong to silicon organic polymers and consist of  $\sigma$ -conjugated Si backbone and organic side groups. The best characterized systems are poly (di-n-hexylsilane) (PDHS) and poly (methylphenylsilane) (PMPS). It is commonly accepted that the charge carrier transport in these polymers is controlled by the charge carrier hopping through intrinsic states derived from domain-like segments of the silicon chains [1,2]. In the present work we study the energy spectra of photogenerated charge carriers in PDHS using fractional thermally stimulated luminescence (TSL). TSL is a recombination luminescence at a linearly elevating temperature. TSL is directly related to the detrapping processes and is not influenced by the transport processes [3]. So, low-temperature TSL is an efficient method for studying localized states' activation energy and their energy distribution in disordered polymers [3–6].

The earlier study of the distribution of trapped charge carriers in PMPS by the fractional TSL method showed the existence of a quasi-continuous trap distribution [5]. General description of PDHS does not give an unambiguous answer whether the energy spectrum of the traps is discrete or quasi-continuous. On the one hand, a change of the lengths of polymeric segments between the conformational defects induces the appropriate shift of electronic energy [7]. This suggests a quasi-continuous spectrum of the traps, which was evidenced experimentally by the fact that the TSL curves of

PDHS films were too broad as for a monoenergetic trap (as calculated by Eq. (1)). On the other hand, there are experimental evidences in favor of a substantial ordering in this polymer. The PDHS films are of a substantial crystallinity [8]. The degree of the crystallinity of PDHS polymer reaches 65–80% [9]. The existence of a specific ordering in this material is also confirmed by the spectroscopic and X-ray data. Indeed, X-ray reflections in the PDHS are fairly distinct resembling crystalline phase [10–12]. IR [9] and Raman [10,13,14] spectra of PDHS are composed of narrow bands like the crystalline spectra. Furthermore, an order–disorder thermochromic transition is observed in this polymer [10]. The TSL method allows one to determine the thermal activation energy of the traps, which is directly related to the vibrational processes, because the thermal energy is supplied to the traps by quanta of ambient vibrations – phonons. To solve the problem about the character of the energy spectrum of the traps in PDHS, the peculiarities of charge carrier traps energy spectra in this polymer are studied by the enhanced low-temperature fractional TSL. As will be shown below, in the PDHS films a discrete distribution of the traps activation energy is observed. This observation distinctly differs from the earlier reported results obtained by traditional fractional technique [5].

### 2. Experimental technique

The TSL measurements were carried out with automatic equipment for optical thermoactivated spectroscopy over a wide temperature range from 4.2 to 200 K with the heating rate of  $\beta = 0.25$  K/s.

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The PDHS films were fabricated by direct casting from toluene solution on stainless steel substrates. Such substrates were used to improve the thermal contact. We used several PDHS films with a thickness of 5  $\mu\text{m}$ : freshly prepared polymer films (samples 1, 2), as well as the films irradiated with unfiltered light of Hg band lamp at room temperature before the TSL study (samples 3, 4). Such irradiation leads to an increase in the traps number due to the polymer chains photodestruction [15].

The charge carriers in the PDHS were photogenerated by the sample excitation by unfiltered light of Hg lamp for 2 min at 4.2 K. Due to strong TSL intensity of the polymer films, the TSL signal was detected with a photomultiplier operated in a stable current mode.

The TSL intensity  $I$  in the absence of charge carriers re-capture is given by

$$I \propto -\frac{dn}{dt} = sn \exp\left(-\frac{E}{kT}\right). \quad (1)$$

The TSL intensity relates to the rate of thermal release of charge carriers from the traps. Thus, it is proportional to the number of filled traps ( $n$ ) and the probability that the carrier energy ( $E$ ) is sufficient for release. This probability is expressed by the Boltzmann factor as for a quasi-stationary process, which the TSL is. The other features are included in the proportionality factor ( $s$ ) (frequency factor). As temperature increases the concentration of the filled traps decreases, whereas the carriers release becomes more intensive. Thus the temperature dependence of the TSL intensity is nonmonotonous curve (glow curve).

The fractional TSL technique is used to determine the activation energy of the trapped charge, i.e. to get a number of initial portions of TSL curves during each temperature oscillation of excited sample (partial heating-cooling). The estimation of the activation energy of the traps is based on the assumption that the filled traps concentration is practically unchanged during a current heating process (1–5% of the total filled traps). So, TSL intensity is determined only by the Boltzmann factor.

$$I = I_0 \exp(-E/kT), \quad (2)$$

where  $I_0 = sn_0$  and  $n_0$  is initial concentration of the filled traps for the current cycle,  $T$  – temperature. The activation energy  $E$  of carrier charge for each temperature oscillation determine as

$$E = -k \frac{d(\ln I)}{d(1/T)}. \quad (3)$$

The advantage of the fractional method is a possibility of getting a sequence of the fractional energy values, which significantly increases their reliability independently of the kinetics process. Usually, a saw-type heating is used due to simplicity [16]. In this case, short-term temperature oscillations are superimposed on the slow uniform heating, so that every next heating cycle begins at a higher temperature. Another mode of this method involves fractional step-like heating [4]. Each next cycle starts with the intensity, higher than the initial intensity of the previous cycle. Therefore, the total number of cycles is limited by the dynamic range of registration. This restricts the number of cycles obtained (no more than 20–30 in the temperature range of 5–100 K), which reduces the resolution of the fractional method. We used another regime of the temperature cycling where after each partial heating with simultaneous TSL detection the sample is quickly cooled down to the temperature, at which the emitted light intensity ceases to decrease. Thus, every new cycle in our advanced method starts with the lowest level of intensity. Heating is applied in a controllable manner programmatically. The number of curves is restricted only by the amplification of the registration system rather than its gain range. TSL intensity of investigated polymers is quite

high. This makes it possible to increase the registration system sensitivity by 2–3 orders of magnitude as compared with that one needs for the registration of integrated TSL curves. This allows one to register more than 150 cycles in the temperature range of 5–100 K, which improves the method resolution substantially.

Another advantage of the advanced method is the possibility to determine a zero signal level at the beginning and at the end of each cycle. This gives an opportunity to eliminate zero drift for each cycle by linear interpolation of the dark signal. This possibility is very important since a significant amplification is used for registration of the fractional curves and therefore zero drift value may take a significant part of the gain range.

Measurement of dark signal for each cycle reveals a kind of background emission accompanying the low temperature cycles. This background emission is likely of tunnel nature that is not directly associated with thermal emptying of the traps. The background intensity decreases slowly from cycle to cycle with the temperature increase. To get a detailed mathematical treatment of the cycle curves, a special program was developed that allows one to subtract background under the assumption that it remains constant within a single cycle. The results of the background subtraction are shown in Fig. 1. The curve (a) represents the plot of the cycle without the background correction. This dependence is significantly differs from the linear one. The curve (b) was obtained for the same cycle after the background correction to the value that corresponds to the minimum of standard deviation (MSQ) of experimental points from the linear dependence of  $\ln I = \ln I_0 - E/kT$ . The plot of  $\ln I$  on  $1/T$  (Fig. 1(b)) is linear only after the background correction. Despite of the fact that the background value takes only 4% of the maximum fraction intensity ( $I_{\max} = 65000$ ), the activation energy values increase by 30% after the background correction, and MSQ decreases by the order of magnitude.

Fig. 2 presents the background intensity as a function of the relative number of the emptying traps expressed as  $[(n_0 - n_i)/n_0] \times 100$  ratio, where  $n_0$  is the number of filled traps after termination of excitation,  $n_i$  is the number of the remaining charges left after the completion of the  $i$ th cycle. The background value is reduced to the maximum intensity  $I_{\max}$  of the cycle.

### 3. Results and discussion

TSL was investigated on freshly prepared PDHS films, as well as preliminary irradiated films by unfiltered light of Hg band lamp at room temperature. The TSL curves of PDHS films are shown in Fig. 3. Curve 1 is characteristic for freshly prepared films (sample 1), and looks like a broad structureless band. Curve 2 is typical of

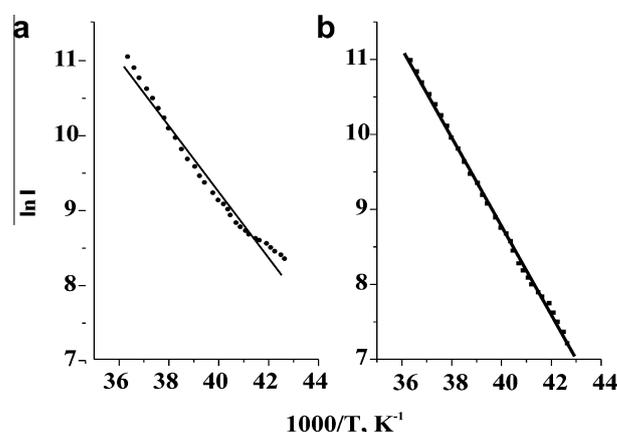


Fig. 1. Plot of the  $\ln I$  TSL on  $1/T$  without (a) and with (b) the background subtraction. Experimental points (b) were fitted using equation:  $\ln I = \ln I_0 - E/kT$ .

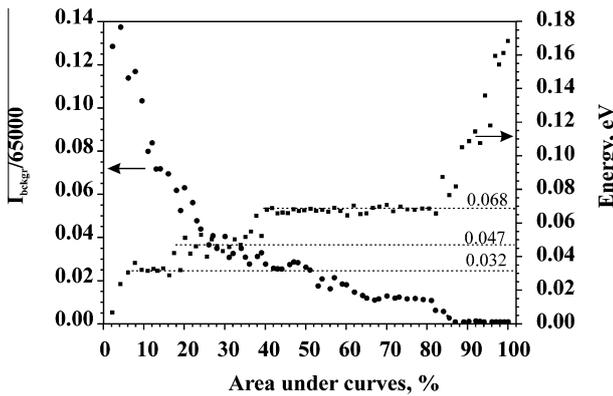


Fig. 2. Background intensity as a function of the relative number of the emptying traps and temperature dependence of the activation energy of the traps for film previously exposed to UV radiation at room temperature (sample 4).

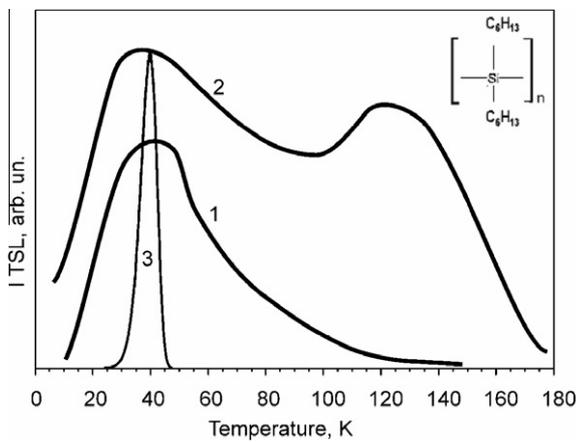


Fig. 3. TSL curves of PDHS films: 1 – as-prepared film (sample 1), 2 – film previously exposed to UV radiation at room temperature (sample 3). Calculated TSL peak obtained according the discrete trap model using  $E = 0.046$  eV and  $T_{\text{max}} = 40$  K (curve 3). The inset shows the structural formula of PDHS.

the films previously irradiated by UV light at room temperature (sample 3). This curve contains the additional broad band with a maximum at  $\sim 125$  K which corresponds to new deeper traps resulted from the photodestruction of polymer chains [15].

The activation energy dependence versus the effective temperature is shown in Fig. 4 for the sample 1. The effective temperature  $T_{\text{eff}}$  is defined as the temperature for the maximum of cycle intensity ( $I_{\text{max}} = 65000$ ). It is calculated from Eq. (2):

$$T_{\text{eff}} = \frac{E}{k \ln(I_{\text{max}}/I_0)},$$

where  $E$  is energy calculated for the cycle,  $I_0$  defined as the average value of  $N$  experimental points for  $i$ th cycle is calculated as

$$I_0 = \frac{\sum_{i=1}^N I_i \exp(E_i/kT_i)}{N}.$$

It is seen that the values of the activation energy of the traps are distributed by three plateaus at 0.034, 0.046 and 0.115 eV. The uncertainty of the measurements does not exceed 0.001 eV. The same result was received for other freshly prepared samples. Note, that the activation energies of these two lowest traps of 0.033 and 0.046 eV practically coincide with the positions of the lines in PDHS Raman spectrum with energies  $\hbar\omega_1 = 268 \text{ cm}^{-1}$  (0.0322 eV) and  $\hbar\omega_2 = 373 \text{ cm}^{-1}$  (0.0463 eV) corresponding to  $A_g$  vibrational modes of the silicon backbone [10,13,14].

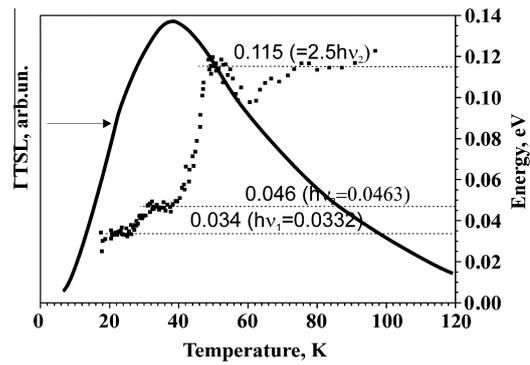


Fig. 4. TSL curves and temperature dependence of the activation energy of the traps for the as-prepared PDHS film (sample 1). The effective temperature for the activation energy was determined according to Eq. (2).

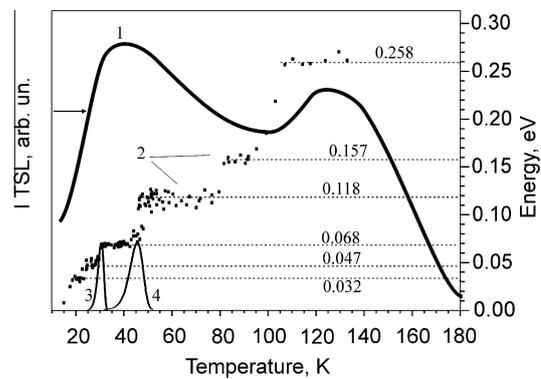


Fig. 5. TSL curves (1) and the temperature dependence of the activation energy (2) for the sample 3. Calculated TSL peaks were obtained according to the discrete trap model using  $E = 0.0462$  eV; position of the maximum at 31 K and  $s = 1.9 \times 10^{10} \text{ s}^{-1}$  (curve 3) and position of the maximum at 47 K and  $s = 1.4 \times 10^6 \text{ s}^{-1}$  (curve 4).

Fig. 5 shows the TSL curve and the activation energy dependence versus the  $T_{\text{eff}}$  for the sample 3. In this case the activation energy values form plateaus at 0.032, 0.047, 0.068, 0.118, 0.157 and 0.258 eV (which is consistent also with the data obtained on the other samples, Fig. 2). Eventually, the activation energy within the range of the plateaus remains the same. On the other hand, this discreteness contradicts, from the first glance, to the following points: (i) integrated curve is structureless; (ii) the plateaus with the same energy have essential widths. For instance, plateau of 0.068 eV energy extends from 31 K up to 47 K (Fig. 5), which cannot be fitted, unless the frequency factor varies. Thus, to interpret this contradictory behavior we suggest the dispersion of the frequency factor. Then the fractional curve can be fitted as a superposition of components which are elementary curves with the same energy  $I(T) = \sum_i s_i n_i \exp(-E/kT) = I_0 \exp(-E/kT)$  and various frequency factors. Their values for different points of the fractional curve can be calculated from:

$$s = \frac{E\beta}{kT_m^2} \exp\left(\frac{E}{kT_m}\right), \quad (4)$$

where  $\beta = dT/dt$  is the heating rate, and  $T_m$  is the temperature of the maximum of the elementary curve. For example, the frequency factors corresponding to the initial (31 K) and final (47 K) points for the 0.068 eV plateau were found to be  $S_1 = 1.9 \times 10^{10} \text{ s}^{-1}$ , and  $S_2 = 1.4 \times 10^6 \text{ s}^{-1}$ , respectively. These values were used to derive the elementary curves 3 and 4 (Fig. 5) calculated according to Eq. (1) for the activation energy of 0.068 eV. The widths of elementary curves are much smaller than the width of the respective plateau,

which, in turn, is less than the width of the entire TSL curve. Thus, the total width of TSL curves is suggested to be due to the frequency factor dispersion rather than to the dispersion of the trap energies as it was considered earlier.

We now need to focus upon the mechanism of the charge release in the PDHS polymer. It is known the charge transport in PDHS is of the polaron type. The segments of the silicon chain can be considered as the traps for positive charges [1,2]. The conformational defects at the ends of the segments create barriers for the positive polarons. Thus, a positive polaron is delocalized within the segment, while an electron is localized on the conformational defect. The polaron polarizes the nearest surrounding, which induces a local potential well. At low temperatures the polaron tunnels through the potential barrier only from the lowest vibrational level  $n = 0$  whereas the temperature increase enhances the probability for the polaron to reach an electron and recombine with it, which contributes to the TSL signal. Obviously, the probability of this process increases significantly if the polaron is in an excited vibrational state. The polaron transition to the excited vibrational state occurs as a result of its interaction with symmetric  $A_g$  vibrational modes of the silicon chain. Thus, heat energy is absorbed by the polaron via the  $A_g$  silicon chain vibrations, which allows us to relate activation energies of two traps at 0.033 and 0.047 eV to  $A_g$  vibrational modes in Raman spectrum of the silicon chain with energies of  $\hbar\omega_1 = 268 \text{ cm}^{-1}$  (0.0332 eV) and  $\hbar\omega_2 = 373 \text{ cm}^{-1}$  (0.0463 eV) respectively. Similar approach was proposed for the interpretation of the thermal activation of the charge carrier detrapping, so called “wet dog” effect [17]. The authors related this phenomenon to the macromolecular relaxation.

Regarding the detrapping mechanism from high-energy traps, we restrict ourselves by the finding of the fact that their energies appear to be multiples of the semi-integral value of a quantum of the vibrational energy: 0.068 ( $1.5\hbar\omega_2$ ), 0.118 ( $2.5\hbar\omega_2$ ), 0.157 ( $3.5\hbar\omega_2$ ) and 0.258 ( $5.5\hbar\omega_2$ ) eV where the corresponding multiplicity values are specified in brackets. More detailed analysis of the energy spectrum of the traps in silicon organic polymers will be published elsewhere after carrying out additional experiments.

The existence of TSL background could be explained in terms of the proposed model. We suggest that the source of this background luminescence is the polaron tunneling through a conformational barrier from the ground vibrational level of  $n = 0$ . At low temperatures, the population of excited levels of traps is by many orders of magnitude smaller than that of the ground state; therefore the background intensity is mainly determined by the total concentration of traps. During the process of the fractional luminescence the traps are gradually detrapped, that causes corresponding decreases in the background intensity (Fig. 2).

Another fact which must be taken into account is the difference between the mechanisms of the carriers release in crystals and polymers. In crystals, with their long-range ordering, the transparency of potential barriers is the same for all traps of the same sort. A released charge carrier is shared overall by the entire crystal; therefore, the frequency factor is included in Eq. (1) as a constant.

In the case of disordered media, such as polymers, the traps are the polymer segments of different length. Since the energy of the corresponding electronic states depends on the segment length [7], the transparencies of the potential barrier differ for the traps even with the same energy. Accordingly, the frequency factor depends on the segment length. In other words, the frequency factor for the traps with similar activation energy can vary in a wide range.

#### 4. Summary

The improved technique of the low-temperature fractional TSL registration has been elaborated. The technique enables to increase the spectral resolution and to eliminate the background emission of a tunneling nature which decreases gradually with the temperature increase.

It is experimentally observed a discrete energy of the charge carrier traps for the PDHS films. This observation distinctly differs from the results of earlier studies where the quasi-continuity dependence of the activation energy on temperature was found. Thus, the total width of TSL curves is suggested to be due to the dispersion of the frequency factor (determined by the transparency of the potential barriers) rather than the traps' energy dispersion. Hence the frequency factor of some trap can vary by the several orders of magnitude. The TSL activation energies correlate well with the frequencies of the symmetric Raman  $A_g$  modes (0.0334 and 0.0463 eV) of the silicon chain.

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