PHYSICAL REVIEW B, VOLUME 65, 165218

Polaron effects on thermally stimulated photoluminescence in disordered organic systems

V. I. Arkhipov
IMEC, Kapeldreef 75, B-3001 Heverlee-Leuven, Belgium

E. V. Emelianova
Semiconductor Physics Laboratory, University of Leuven, Celestijnenlaan 200D, B-3001 Heverlee-Leuven, Belgium

A. Kadashchuk and I. Blonsky
Institute of Physics, National Academy of Sciences of Ukraine, Prospect Nauki 46, 03028 Kiev, Ukraine

S. Nešpůrek
Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovský Sq. 2, 162 06 Prague 6, Czech Republic

D. S. Weiss
Heidelberg Digital L.L.C., 1999 Lake Ave., Rochester, New York 14650-2108

H. Bässler
Institute of Physical, Nuclear and Macromolecular Chemistry and Material Science Center, Philipps-Universität Marburg,
Hans-Meerwein-Strasse, D-35032 Marburg, Germany

(Received 9 August 2001; revised manuscript received 4 February 2002; published 16 April 2002)

Thermally stimulated photoluminescence (TSPL) in disordered organic materials subjected to the polaron formation was studied both theoretically and experimentally. Since TSPL measurements were performed after some dwell time on samples, which have been photoexcited at helium temperature, the initial energy distribution of polarons was formed in the course of low-temperature energy relaxation. In order to calculate this distribution, an analytic model of low-temperature energy relaxation of polarons in a disordered hopping system was formulated. This model proves that energy relaxation of polarons is much slower than that of charge carriers in a similarly disordered but rigid hopping system. At moderate values of the polaron binding energy the suppressed rate of low-temperature relaxation leads to a shift of TSPL curves to lower temperatures as compared to what could be expected in the absence of the polaronic effects. This shift is both obtained from analytic calculations and observed experimentally in some polysilylene derivatives.

DOI: 10.1103/PhysRevB.65.165218 PACS number(s): 78.55.Kz, 78.40.Me, 73.61.Ph

I. INTRODUCTION

In the last decade, the hopping concept was successfully applied to the analysis of a broad variety of charge-carrier transport and relaxation phenomena in various disordered organic materials.[1–5] Recently this formalism was extended to include intersite energy correlation and/or long-range potential flactuations.[6] In parallel with the development of the hopping formalism polaron effects on charge transport in organic solids were extensively discussed in the literature during last two decades.[2,7–14] The small polaron model[7–9] was often exploited implying that a localized carrier is strongly coupled to vibrations of the molecule at which it resides. The strong electron-phonon coupling causes carrier self-trapping and creates a quasiparticle, a polaron, which can move to an adjacent molecule only by carrying along the associated molecular deformation. The adiabatic zero-field activation energy of the polaron mobility is $E_p/2$, where E_p is polaron binding energy. Typical values of the apparent activation energy E_a range from 0.3 to 0.6 eV in organic materials that would imply the polaron binding energy of $0.6\cdots1.2$ eV. Such large values of E_p is hardly justifiable for small organic molecules especially if one bears in mind that their crystalline counterparts usually reveal the value of 0.15 eV as the upper limit of the polaron binding energy.[15]

The essential difference between the polaron and disorder models is that the latter, at variance with the former, implies a sufficiently weak electron-phonon coupling and, concomitantly, the activation energy of charge transport reflects the static energy disorder of the hopping sites. In contrast, the polaron model suggests a strong electron-phonon coupling and negligible contribution of energy disorder to the activation energy of carrier mobility. Since the structural distortion is an intramolecular process, E_p is not subjected to meaningful variation. Concomitantly, the polaronic charge transport must obey the Gaussian statistics and the photocurrent transients should neither feature a long tail nor become dispersive at any temperature. However, neither of these predictions was confirmed experimentally in disordered organic materials. In addition, the small polaron model fails to account for the observed Poole-Frenkel-type field and non-Arrhenius temperature dependences of the thermally equilibrium carrier mobility.

Nevertheless, the importance of polaron effects for charge transport is still under debate since the deformation energy might be comparable to the disorder effects in some organic systems. In principle, upon adding or removing an electron from a molecule the molecular skeleton must change because of the readjustment of the individual bond lengths. It was demonstrated[12–14] that the interplay between the polaronic and disorder effects may be responsible for the specific temperature dependence observed in such materials. Bässler *et al.*[12] suggested that the effective zero-field activation energy of the mobility, $E_a^{(\mathrm{eff})}$, can be approximated by a sum of the disorder and polaron contributions as

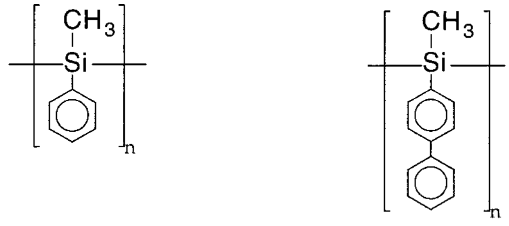
$$E_a^{(\mathrm{eff})}=E_a^{(p)}+E_a^{(d)}=\frac{E_p}{2}+\frac{4}{9}\frac{\sigma^2}{kT}, \tag{1}$$

where $E_a^{(p)}$ and $E_a^{(d)}$ are the polaronic and disorder contributions, respectively, σ is the width of the density of states (DOS) distribution, T the temperature, and k the Boltzmann constant. E_p is mostly determined by intramolecular distortions and therefore it is not affected by the spatial and energy distributions of hopping sites. Equation (1) provides the basis for determination of both σ and E_p from a plot of $E_a^{(\mathrm{eff})}$ vs $1/T$. Concomitantly, the deviation from linearity of both $\ln\mu$ vs T^{-1} and $\ln\mu$ vs T^{-2} dependences was the only experimentally accessible indication for the importance of the polaron effects.[4,12–14]

So far, the study of the carrier mobility activation energy seems to remain the only possibility of estimating the polaron binding energy in disordered organic solids. This is rather a complicated and dubious procedure because it requires precise measurements of field and temperature dependencies of the mobility as well as extrapolating $E_a^{(\mathrm{eff})}$ to the infinite temperature. Therefore new experimental approaches are essential in order to obtain more certain evidences of possible polaron formation and provide a deeper insight into the role of this effect in charge carrier kinetics in disordered organic materials. In the present work we make an attempt to elucidate a possible effect of polaron formation on thermally stimulated photoluminescence (TSPL) in organic systems.

Prior to TSPL measurements the sample is photoexcited at helium temperature and therefore the initial energy distribution of localized carriers is formed in the course of the low-temperature energetic relaxation.[16–18] The polaron effects must lead to considerably *slower* low-temperature energy relaxation as compared to the polaron-free systems. The polaron binding energy will also affect the rate of thermally assisted carrier jumps during the heating run and both these effects must be revealed in TSPL curves. Therefore the evaluation of E_p from TSPL experimental data requires modeling both low-temperature energy relaxation and thermally assisted hopping in disordered materials with the polaronic effect. These models are formulated in Sec. II and III of the present paper.

Several polysilylene derivatives were chosen as model systems for the experimental study of TSPL. Polysilylenes being σ-conjugated main chain polymers have attracted much attention as a new class of advanced material on account of their unique photophysical properties, most of which arise from the σ-electron delocalization along the silicon backbone, and their potential utility.[19–21] The high quantum photogeneration efficiency[22,23] and the large charge-carrier drift mobility[24,25] of the order 10^{-4} cm^2 V^{-1} s^{-1} stimulated their research. The charge-carrier transport has been believed to be controlled by charge hopping through intrinsic states derived from domainlike segments of the silicon chain.[26,27] Recently, it was well established that charge-carrier mobility in polysilylenes is influenced by side-group substituents:[28–30] the temperature dependences of mobility in polysilylenes containing only nonaromatic alkyl substituents were smaller than those including aromatic groups. One hypothesis explaining this fact is that polaron binding energy increases for polysilylenes containing highly polarizable aromatic substituents.[30]


Poly[methyl(phenyl)silylene] Poly[biphenyl(methyl)silylene]

(PMPSi) (PBMSi)

FIG. 1. Chemical structures of the studied polymers.

The polaron binding energy in these materials has been earlier estimated from the charge transport measurements.[12,31] The electric field has a strong influence on the polaron dynamics and polaronic effects may play a different role in the carrier transport at strong fields than in TSPL experiments in which the field is absent. Therefore the polaron binding energy estimated from transport and TSPL measurements might be somewhat different.

In the present study we concentrate mainly on poly(biphenyl-methylsilylene) (PBPMSi) for which the polaron binding energy of $E_p=0.22$ eV was recently reported.[31] This value is the largest one so far found in disordered organic materials. A strong coupling of the excess elementary charge to a torsional mode of the biphenyl unit[32] as well as a large polarizability of this substituent[31] are presumably responsible for the strong polaronic effect in this material. The characteristics of TSPL observed in PBPMSi are remarkably different from those measured earlier in many disordered organic systems and we attribute this difference to a strong polaron effect in this polymer. For comparison, TSPL peaks were also measured in poly(methylphenylsilylene) (PMPSi) in which the polaron binding energy is known to be smaller. Chemical structures of the two polymers are shown in Fig. 1.

II. LOW-TEMPERATURE ENERGY RELAXATION OF POLARONS IN A DISORDERED HOPPING SYSTEM

Low-temperature relaxation of charge carriers in a disordered hopping system can occur only via energetically downward hopping. The rate of carrier jumps ν from a starting site of the energy E_s to a target site of the energy $E_t > E_s$ is determined by the rate of tunneling over the distance r separating these two sites:

$$\nu=\nu_0\exp(-2\gamma r), \tag{2}$$

where ν_0 is the attempt-to-jump rate and γ the inverse localization radius. Once a carrier jumped into a target site its energy must decrease due to the polaronic relaxation down to $E=E_t-E_p$ where E_p is the polaron binding energy. Although one might expect that E_p is also subjected to variation in a disordered material the present consideration will be restricted to the case of a constant polaron binding energy.

If a carrier has jumped into a state of the energy E_t and undergone the polaronic relaxation only states of energies lower than $E=E_t-E_p$ are accessible for further jumps at low temperatures. The average number of such states, $n(r,E)$ within a sphere of the radius r centered at an occupied starting site of the energy E is given by the following expression:

$$n(E,r)=\frac{4\pi r^3}{3}\int_{-\infty}^{E}dE'g(E'), \tag{3}$$

where $g(E)$ is the density-of-states (DOS) distribution function. The probability density W to find the nearest deeper neighbor at the distance r is determined by the Poisson probability distribution as

$$W(E,r)=\exp[-n(E,r)]\frac{\partial n(E,r)}{\partial r}. \tag{4}$$

The probability w that, at the time t, the carrier still occupies a starting site, which is separated from the nearest deeper neighbor by the distance r, is also given by the Poisson distribution:

$$w(r,t)=\exp[-\nu_0 t\exp(-2\gamma r)]. \tag{5}$$

Combining Eqs. (4) and (5) and integrating over r yields the occupational probability $f(E,t)$ for a localized state with the energy E at the time t,

$$f(E,t)=\int_0^{\infty}dr\frac{dn(E,r)}{dr}\exp[-n(E,r)]\times\exp[-\nu_0 t\exp(-2\gamma r)]. \tag{6}$$

The last exponential in the integrand of Eq. (6) is a steep function of the variable r around $r=r_j$ that can be approximated as

$$\begin{array}{l}\exp[-\nu_0 t\exp(-2\gamma r)]\cong 0,\ \ r<r_j(t)\\ \exp[-\nu_0 t\exp(-2\gamma r)]\cong 1,\ \ r>r_j(t)\end{array},\ \ r_j(t)=(1/2\gamma)\ln(\nu_0 t). \tag{7}$$

Concomitantly, Eq. (6) reduces to[33,34]

$$f(E,t)=\exp\left[-n\left(E,\ \frac{1}{2\gamma}\ln(\nu_0 t)\right)\right]=\exp\left(-\frac{\pi}{6\gamma^3}[\ln(\nu_0 t)]^3\int_{-\infty}^{E}dE'g(E')\right). \tag{8}$$

The normalized occupational density of states $\rho(E,t)$ can be calculated as a product of the occupational probability and the DOS function. The result reads

$$\rho(E,t)=\frac{f(E,t)g(E+E_p)}{\int_{-\infty}^{\infty}dEf(E,t)g(E+E_p)}=\frac{g(E+E_p)\exp\left(-\frac{\pi}{6\gamma^3}[\ln(\nu_0 t)]^3\int_{-\infty}^{E}dE'g(E')\right)}{\int_{-\infty}^{\infty}dEg(E+E_p)\exp\left(-\frac{\pi}{6\gamma^3}[\ln(\nu_0 t)]^3\int_{-\infty}^{E}dE'g(E')\right)}. \tag{9}$$

Temporal evolution of the function $\rho(E,t)$ is shown in Fig. 2(a) for a Gaussian DOS distribution of unoccupied target sites:

$$g(E_t)=\frac{N_t}{\sqrt{2\pi}\sigma}\exp\left(-\frac{E_t^2}{2\sigma^2}\right), \tag{10}$$

with σ being the width of the distribution. Figure 2(b) illustrates the low-temperature energy relaxation in a similar disordered hopping system but with $E_p=0$. Although the polaronic effect does cause an immediate downward shift of the carrier energy distribution further energy relaxation is strongly impeded by the activation energy comparable to E_p. This implies a very weak dependence of the carrier energy distribution upon the dwell time between the sample photoexcitation and the onset of the heating run.

III. THERMALLY STIMULATED HOPPING OF POLARONS IN A DISORDERED MATERIAL

At a finite temperature T the rate of carrier jumps over the distance r between hopping sites of the energies E_s and E_t is described by the Miller-Abrahams expression[35] that can be written in terms of a universal hopping parameter u defined as

$$\nu=\nu_0\exp(-u),\ \ u=2\gamma r+\begin{cases}0, & \Delta E<0,\\ \dfrac{\Delta E}{kT}, & \Delta E>0,\end{cases} \tag{11}$$

where ΔE is the energy difference between starting and target sites and k the Boltzmann constant. In the adiabatic case, the transfer energy ΔE which is required for an upward polaron jump from a starting site of the energy E_s-E_p to a

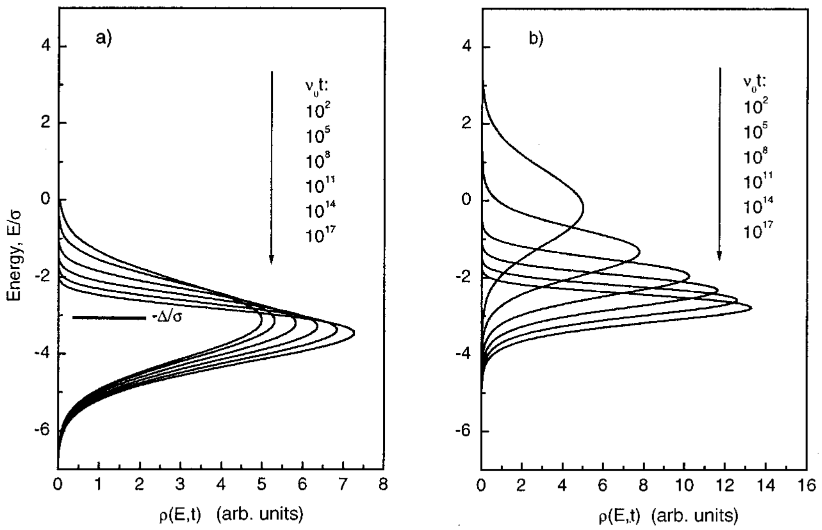


FIG. 2. Energy relaxation of charge carriers in a positionally and energetically disordered hopping system (a) with and (b) without the polaronic effect.

target site of the energy E_t is $\Delta E = E_t - E_s + E_p/2$. Almost all previously studied disordered organic materials revealed double-peak DOS distributions in TSPL experiments.[16,17] In materials with such DOS functions most carriers are localized within the lower peak while carrier jumps occur via the upper one. Therefore charge-carrier relaxation is controlled by jumps with $\Delta E > E_p/2$.

The average number of target sites $n(u,T,E)$, whose hopping parameters are less than u with respect to a starting site of the energy $E = E_s - E_p$, may be evaluated as

$$\begin{aligned} n(u,T,E) &= 4\pi \int_0^{u/2\gamma} dr\, r^2 \int_{-\infty}^{E+(E_p/2)+kT(u-2\gamma r)} dE_t\, g(E_t) \\ &= \frac{\pi u^3}{6\gamma^3}\Bigg[\int_{-\infty}^{E+(E_p/2)} dE_t\, g(E_t) \\ &\quad + \int_{E+(E_p/2)}^{E+(E_p/2)+kTu} dE_t\, g(E_t) \\ &\quad \times \left(1 - \frac{E_t - E - (E_p/2)}{kTu}\right)^3\Bigg]. \end{aligned} \tag{12}$$

Since, according to Eq. (11), the jump rate strongly decreases with increasing hopping parameter, most carriers jump into target sites characterized by the minimum hopping parameter $u_{\min}$ available for a given starting site. This parameter is determined by the condition that the average number of hopping neighbors with $u \leqslant u_{\min}$ must be equal to 1:

$$n(u_{\min}, T, E) = 1. \tag{13}$$

In TSPL experiments, the initial energy distribution of localized carriers is formed in the course of rather a long low-temperature energy relaxation. Increasing temperature accelerates the carrier random walk and therefore first jumps of carriers from localized states, which they have occupied before the heating started, must be rate limiting steps that determine the TSPL kinetics.

In the following, we consider a linear heating regime,

$$T(t) = T_0 + \beta t, \tag{14}$$

where T_0 is the initial temperature at which carriers were generated and β the heating rate. The probability $w(T,E)$ for a carrier to remain in a localized state of energy E_s when the temperature reaches a given value T is determined by the Poisson distribution of probabilities as

$$w(T,E) = \exp\left\{-\frac{\nu_0}{\beta}\int_{T_0}^{T} dT' \exp[-u_{\min}(T',E)]\right\}. \tag{15}$$

The total density of carriers which remain localized at the temperature T, $p(T)$, can be found by integrating over energy the product of the initial energy distribution of localized carriers, $\rho_0(E)$, and the probability for a carrier to avoid thermally activated jump from a localized state of energy E up to the temperature T. The result reads

$$\begin{aligned} p(T) = \int_{-\infty}^{\infty} dE\, \rho_0(E) \exp\Bigg\{-\frac{\nu_0}{\beta}\int_{T_0}^{T} dT' \\ \times \exp[-u_{\min}(T',E)]\Bigg\}. \end{aligned} \tag{16}$$

The TSPL intensity $I(T)$ is proportional to the radiative recombination rate which is, in turn, controlled by the rate of first carrier jumps from initially occupied deep states, $|\beta dp(T)/dT|$. Differentiating Eq. (16) then yields

$$\begin{aligned} I(T) \propto \nu_0 \int_{-\infty}^{\infty} dE\, \rho_0(E) \exp[-u_{\min}(T,E)] \\ \times \exp\left\{-\frac{\nu_0}{\beta}\int_{T_0}^{T} dT' \exp[-u_{\min}(T',E)]\right\}. \end{aligned} \tag{17}$$

Equations (12), (15), and (17) determine the temperature dependence of the TSPL intensity for given functions $g(E)$ and $\rho_0(E)$. These equations can be further simplified under the specific conditions of TSPL measurements. The energy relaxation of photoexcited carriers towards deeper states occurs during rather a long dwell time before heating. Concomitantly, carriers have no hopping neighbors for further downward jumps on the time scale shorter than the dwell

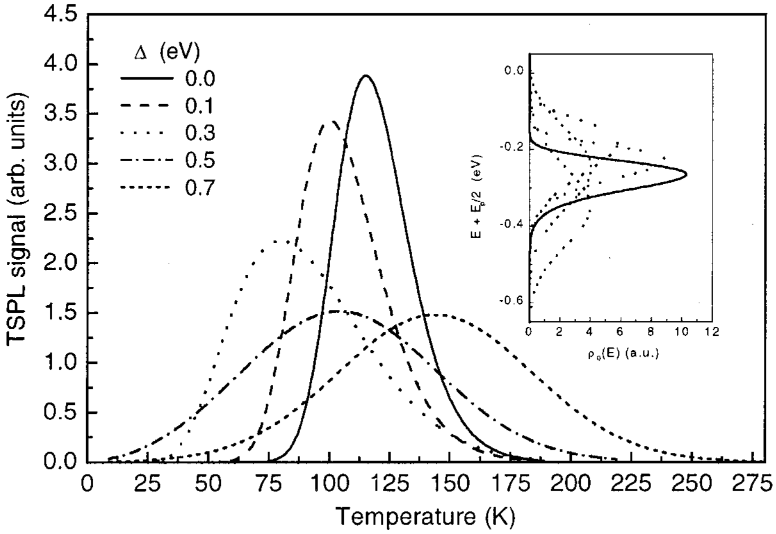


FIG. 3. Temperature dependence of TSPL intensity in a disordered material with different polaron binding energies. The inset shows the initial distribution of localized carriers over the effective activation energy $E+(E_p/2)$. The following set of parameters was used for the calculation: $\sigma=0.1$ eV, $N_l/\gamma^3=0.01$, $\beta=0.15$ K/s, $v_0=10^{13}\ \mathrm{s}^{-1}$, $t_{\mathrm{rel}}=100$ s.

time. In addition, increasing temperature makes easier carrier jumps to hopping sites with higher energies. Under these circumstances, one may disregard the possibility of downward carrier jumps as rate-limiting steps during the heating run. This corresponds to neglecting the first term in the right-hand side of Eq. (12). The result is

$$n(u,T,E)=\frac{\pi}{6(\gamma kT)^3}\int_{E+(E_p/2)}^{E+(E_p/2)+kTu} dE_t g(E_t) \times\left(E+\frac{E_p}{2}+kTu-E_t\right)^3. \tag{18}$$

After replacement of variables,

$$E_{\mathrm{tr}}=E+\frac{E_p}{2}+kTu_{\mathrm{min}}, \tag{19}$$

this equation becomes

$$\int_{E+(E_p/2)}^{E_{\mathrm{tr}}} dE_t g(E_t)(E_{\mathrm{tr}}-E_t)^3=\frac{6}{\pi}(\gamma kT)^3. \tag{20}$$

Bearing in mind that the minimum hopping parameter determines the carrier hopping rate as $\nu\propto\exp(-u_{\mathrm{min}})$ and that, according to Eq. (19), this rate can be written as $\nu\propto\exp\{-[E_{\mathrm{tr}}-E-(E_p/2)]/kT\}$, the energy E_{tr} can be identified as the effective transport energy. Since realistic DOS functions strongly decrease with increasing energy the main contribution to the integral in the right-hand side of Eq. (20) comes from energies close to the upper bound of integration. Therefore, for sufficiently deep initially occupied states and for temperatures well above T_0, Eq. (20) can be written as

$$\int_{-\infty}^{E_{\mathrm{tr}}} dE_t g(E_t)(E_{\mathrm{tr}}-E_t)^3=\frac{6}{\pi}(\gamma kT)^3. \tag{21}$$

Equation (21) indicates that most carriers, localized on states deeper than E_{tr}, make thermally assisted jumps to hopping sites of energies around E_{tr} and that the energy E_{tr} does not depend upon the energy of a starting site E.

In terms of the effective transport energy[16,17,36,37] the TSPL intensity can be written as

$$I(T)\propto\nu_0\int_{-\infty}^{\infty} dE\rho_0(E)\exp\left[-\frac{E_{\mathrm{tr}}(E,T)-E-(E_p/2)}{kT}\right] \times\exp\left\{-\frac{\nu_0}{\beta}\int_{T_0}^{T} dT' \times\exp\left[-\frac{E_{\mathrm{tr}}(E,T')-E-(E_p/2)}{kT'}\right]\right\}. \tag{22}$$

Equations (20)–(22) have the same forms as the equations describing the TSPL intensity in the absence of the polaronic effect[16,17] with E replaced by $E+(E_p/2)$. This implies that the major effect of polaron formation is a significantly slower low-temperature energy relaxation as compared to that in materials with $E_p=0$.

It is worth noting that nongeminate recombination of charge carriers into excitons can also contribute to TSPL signal. However, the kinetics of both geminate and nongeminate recombination is controlled by carrier release from localized states. Therefore the interpretation of TSPL data requires specific assumptions regarding mechanisms of neither photogeneration nor recombination of charge carriers.

TSPL glow curves, calculated from Eqs. (20) and (22), for a double-peak Gaussian DOS distribution parametric in the polaron binding energy E_p are shown in Fig. 3. The effect of polaron formation on TSPL curves is remarkably nonmonotonous. Increasing polaron binding energy from $E_p=0$ to $E_p=0.3$ eV shifts the TSPL peak to lower temperatures while further increase of E_p breaks this trend and moves TSPL curves back to higher temperatures. This evolution of the maximum peak position is accompanied by monotonic increase of the peak width. One should expect that the polaron binding energy, which causes the strongest low-temperature shift of the TSPL peak, must depend upon other material parameters, notably upon the DOS width. Therefore the above-mentioned characteristic value of E_p is bound to the specific set of parameters used for calculating the curves in Fig. 3.

The nonmonotonous dependence of the TSPL peak position upon the polaron binding energy can be explained by the quantitatively different effects of the polaron formation on thermally stimulated hopping and low-temperature energy relaxation. The polaron contribution to the activation energy of thermally activated upward carrier jumps is only a half of the polaron binding energy. Therefore the polaronic effect suppresses thermally activated jump much weaker than the low-temperature energy relaxation. If the polaron binding energy is not too large the energy distribution of polarons before the onset of the heating run can be effectively shallower for upward jumps than the energy distribution of charge carriers in the same hopping system devoid of the polaron formation. However, at larger values of E_p the polaronic contribution to the activation energy of carrier jumps becomes dominant and, concomitantly, TSPL peaks shift to higher temperatures with increasing polaronic binding energies. In general, a broad TSPL peak, whose maximum is located at a temperature lower than one could expect at this peak width, can be considered as an indication of an important contribution of the polaronic effect to the carrier kinetics in a disordered hopping system.

IV. EXPERIMENTAL AND RESULTS

Polysilylene films were prepared from a toluene solution by casting on stainless-steel substrates. After deposition, the films were dried at 10^{-3} Pa at 330 K for at least 4 h. TSPL measurements were carried out with a laboratory-made apparatus for optical thermoactivated spectroscopy, covering the temperature range from 5 through 350 K. After cooling down to 5 K, the samples were illuminated for 30 s with a high-pressure 500 W mercury discharge lamp and then heated at the rate of 0.15 K/s. Following photoexcitation, TSPL signal was detected with a cooled photomultiplier operated in the photon-counting mode, which was positioned immediately next to the cryostat window. The measurements were performed both at the constant heating rate $\beta = 0.15$ K/s and under the fractional heating regime (additional details of the TSPL technique are described elsewhere[32,38,39]).

Normalized TSPL glow curves of PMPSi and PBPMSi measured after UV excitation at 4.2 K are shown in Figs. 4(a) and (b) by curves 1 and 5, respectively. Additional infrared (IR) irradiation through a filter with the transparency band ranging from 900 to 4500 nm affects the TSPL glow curves of the studied polysilylenes. During the IR irradiation, the sample was immersed in liquid helium and no sample heating was detected. However, the IR irradiation shifts the TSPL peaks to higher temperatures and decreases the TSPL intensity. Curves 2–4 and 6–8 in Figs. 4(a) and (b) show normalized TSPL glow curves of PMPSi and PBPMSi, obtained after the exposure of the samples to IR irradiation at 4.2 K for 5–30 min following the conventional UV excitation. It is worth noting that the IR irradiation only slightly shifts the TSPL peak of PMPSi while the shift is really huge for PBPMSi.

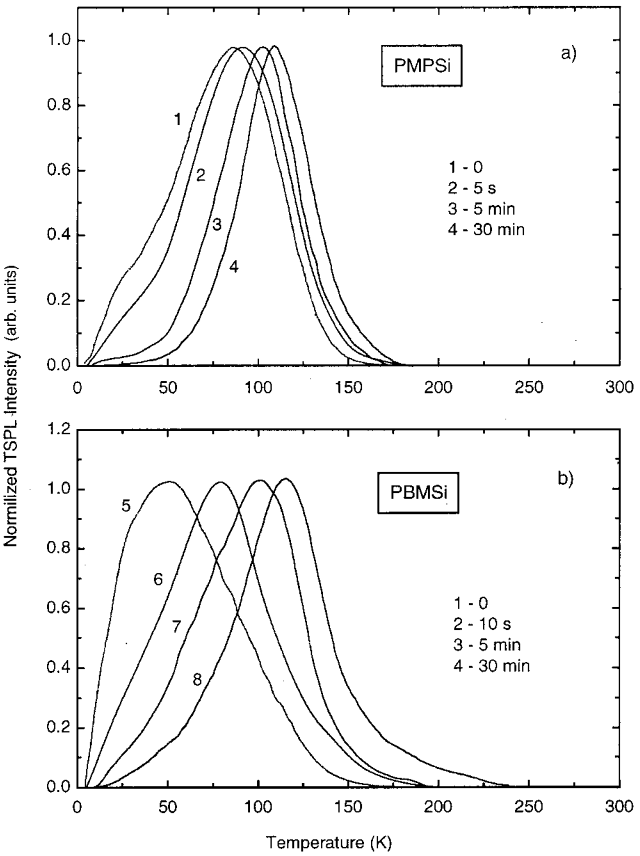


FIG. 4. Normalized TSPL glow curves of (a) PMPSi and (b) PBPMSi measured after UV excitation at 4.2 K (curves 1 and 5) and after additional IR irradiation (curves 2–4 and 6–8).

V. DISCUSSION

The apparent activation energy of the charge carrier mobility, $E_a^{(\mathrm{eff})}$, increases from 0.3 eV in PMPSi (Ref. 25) to 0.36 eV in PBPMSi.[31] It is believed that $E_a^{(\mathrm{eff})}$ consists of two components, one of which is caused by the energy disorder and a further activated component is related to the polaron binding energy. Dohmaru *et al.*[30] suggested that the latter component is determined by the nature of the substituents; highly polarizable aromatic substituents will make this component bigger than nonaromatic ones. In addition, one might expect that the polaron binding energy in PBPMSi should be higher because of the stronger charge coupling to the torsional mode of the biphenyl unit. A similar effect has been reported for molecularly doped polymers in which the presence of a biphenyl substituent in some charge transporting molecules was responsible for small polaron formation.[13] The polaron binding energy was indeed found to be $E_p = 0.22$ eV in PBPMSi (Ref. 31) and 0.16 eV in PMPSi.[12] Recently, Pan *et al.*[40] reported an even somewhat smaller value of the native polaron binding energy $E_p = 0.08$ eV in PMPSi.

TSPL characteristics of PMPSi are rather similar to those measured in many other disordered organic systems.[16,17,32,38,39] A more detailed description of TSPL in PMPSi can be found elsewhere.[38] The polaron binding energy in PMPSi was estimated as $E_p = 0.16$ eV.[12] With the

Gaussian DOS width σ estimated as either 0.07 eV (Ref. 12) or 0.078 eV (Ref. 38) the polaronic contribution may account for about 25% of the total $E_a^{(\mathrm{eff})}$ in this polymer.[12] One arrives at the same conclusion, of course, if the reasoning is based on a smaller value of $E_p = 0.08$ eV in PMPSi obtained by Pan *et al.*[40]

The TSPL measurements in PBPMSi revealed the behavior which is very different from what was observed in PMPSi as well as in all other so far studied disordered organic systems. The following major distinctions should be mentioned.

(i) Charge transport measurements in PBPMSi yielded $E_a^{(\mathrm{eff})} = 0.36$ eV, which is the largest value among studied polysilylenes, and the DOS width in this polymer was estimated as large as $\sigma = 0.09$ eV.[31] However, the TSPL peak maximum of PBPMSi is located at a very low temperature around 50 K well below TSPL maximum of PMPSi [cf. curves 1 and 5 in Figs. 4(a) and (b)]. This is in striking difference with the commonly observed correlation between the activation energy of the charge-carrier mobility and the temperature of the TSPL peak maximum.[32,38,39] This indicates *much slower* low-temperature charge-carrier energy relaxation in PBPMSi than in PMPSi.

(ii) The TSPL peak of PBPMSi is very asymmetric and its maximum gradually shifts towards higher temperatures upon IR irradiation. This asymmetry can hardly be explained by the presence of additional extrinsic traps since no indication of them was found in the results of transport measurements and the observed gradual IR induced shift of the peak maximum did not indicate the occurrence of traps. Therefore this behavior seems to be an inherent property of PBPMSi. It is also worth noting that the observed shift of the peak maximum from 50 to ~120 K is huge and that nothing comparable was observed in other polymers.

The observed characteristic features of TSPL in PBPMSi can be readily explained in terms of polaron formation in this material. As it was shown in Sec. II of the present paper polaron relaxation leads to a much slower (hampered) energy relaxation of photoexcited carriers than predicted by theories formulated for a rigid disordered matrix. The energy distribution of relaxed polarons is therefore much closer to the maximum of the DOS distribution as illustrated by the curves in Fig. 2(a). The suppressed low-temperature energy relaxation, in its turn, leads to an anomalously low temperature of the TSPL peak maximum.

A very profound effect of IR irradiation on TSPL curves can also be explained by the polaronic relaxation. IR irradiation causes local heating in the surrounding of charged molecules that, at low temperatures, efficiently stimulate energy relaxation towards the deeper tail states of polarons which are otherwise stuck in rather shallow localized states. Concomitantly, charge carriers get a possibility to occupy those tail states which would be accessible for them if there were no polaron effects. Therefore the TSPL glow curves measured in PBPMSi after additional IR irradiation are in a good agreement with the charge transport data. Particularly, curve 8 in Fig. 4(b) is shifted towards higher temperatures as compared to curve 4 in Fig. 4(a) just as one would expect on the basis of the charge-carrier-mobility activation energy in those polymers.

VI. CONCLUSIONS

Polaron formation strongly affects both low-temperature energy relaxation and thermally assisted hopping of charge carriers in disordered organic materials. If the polaron binding energy is comparable with or larger than the DOS width the energetically downward hopping is strongly suppressed by the lack of deeper vacant sites which are only accessible for further jumps at low-temperatures. Therefore after a fast initial polaronic relaxation the energy distribution of polarons remains almost ‘‘frozen in’’ over the entire dwell time between low-temperature photoexcitation of the sample and the onset of TSPL heating run. With increasing temperature, energetically upward polaron jumps become the dominant hopping mode and these jumps control the TSPL kinetics. The polaronic contribution to the activation energy of every individual upward jump is equal to *half* of the polaron binding energy, $E_p/2$, while the low-temperature energy relaxation of polarons within the DOS distribution is slowed down because the polaron energy distribution is shifted down by E_p. This leads to a stronger polaronic effect on the low-temperature relaxation than on the thermally stimulated hopping. Therefore, at moderate values of E_p, the polaronic effect shifts TSPL peak to lower temperatures as compared to its position for material with a similar DOS width and with $E_p = 0$. This explains an apparent contradiction between a high activation energy of the drift mobility in a low temperature of the TSPL peak in organic materials subjected to the polaron formation.

ACKNOWLEDGMENTS

A.K. and S.N. are grateful to NATO for the financial support under the grant PST.CLG 975222. V.I.A. and H.B. acknowledge financial support from the Volkswagen Foundation. E.V.E. is grateful to KU Leuven for financial support. The financial support from Heidelberg Digital L.L.C. (USA) and from the Grant Agency of the Academy of Sciences of the Czech Republic (Project No. 1050901) are also acknowledged.

---

[1] M. Pope and C. E. Swenberg, *Electronic Processes in Organic Crystals and Polymers*, 2nd Edition (Oxford University Press, Oxford, 1999).

[2] P. M. Borsenberger and D. S. Weiss, *Organic Photoreceptors for Imaging Systems* (Dekker, New York, 1993); *Organic Photoreceptors for Xerography* (Dekker, New York, 1998), and references therein.

[3] H. Bässler, in *Semiconducting Polymers: Chemistry, Physics and Engineering*, edited by G. Hadziioannou and P. F. van Hutten (Wiley-VCH, Weinheim, 2000), p. 365.

[4] H. Bässler, Phys. Status Solidi B **175**, 15 (1993), and references therein.

[5] H. Bässler, in *Disordered Effect on Relaxational Processes*, edited by R. Richter and A. Blumen (Springer-Verlag, Berlin, Heidelberg, 1994), p. 585.

[6] S. V. Novikov, D. H. Dunlap, V. M. Kenkre, P. E. Parris, and A. V. Vannikov, Phys. Rev. Lett. **81**, 4472 (1998).

[7] D. Emin, Phys. Rev. B **46**, 9419 (1992).

[8] L. B. Schein, D. Glatz, and J. C. Scott, Phys. Rev. Lett. **65**, 472 (1990).

[9] L. B. Schein, Philos. Mag. B **65**, 795 (1992), and references therein.

[10] P. M. Borsenberger and L. B. Schein, J. Phys. Chem. **98**, 233 (1994).

[11] P. E. Parris, V. M. Kenkre, and D. H. Dunlap, Phys. Rev. Lett. **87**, 126601 (2001).

[12] H. Bässler, P. M. Borsenberger, and R. J. Perry, J. Polym. Sci., Part B: Polym. Phys. **32**, 1677 (1994).

[13] B. Hartenstein, H. Bässler, S. Heun, P. Borsenberger, M. Van der Auweraer, and F. C. De Schryver, Chem. Phys. **191**, 321 (1995).

[14] E. H. Magin and P. M. Borsenberger, J. Appl. Phys. **73**, 787 (1993).

[15] E. A. Silinsh and V. Capek, *Organic Molecular Crystals: Interaction, Localization, and Transport Phenomena* (AIP Press, New York, 1994).

[16] V. I. Arkhipov, E. V. Emelianova, H. Bässler, and A. Kadashchuk, Chem. Phys. **266**, 97 (2001).

[17] A. Kadashchuk, Yu. Skryshevski, A. Vaknin, N. Ostapenko, E. V. Emelianova, V. I. Arkhipov, and H. Bässler, Phys. Rev. B **63**, 115205 (2001).

[18] B. Movaghar, B. Ries, and M. Grunewald, Phys. Rev. B **34**, 5574 (1986).

[19] A. Fujii, K. Yoshimoto, M. Yoshida, H. Yoshino, H. Ueno, M. Kakimoto, and H. Kojima, Jpn. J. Appl. Phys., Part 1 **35**, 3914 (1996).

[20] S. M. Silence, J. C. Scott, F. Hache, E. J. Ginsturg, P. K. Jenker, R. D. Miller, R. J. Twieg, and W. E. Moerner, J. Opt. Soc. Am. B **10**, 2306 (1993).

[21] R. D. Miller and J. Michl, Chem. Rev. **89**, 1359 (1989).

[22] S. Nešpùrek, V. Cimrová, J. Pfleger, and I. Kmínek, Polym. Adv. Technol. **7**, 459 (1996).

[23] I. Kmínek, S. Nešpùrek, E. Brynda, J. Pfleger, V. Cimrová, and W. Schnabel, Collect. Czech. Chem. Commun. **58**, 2337 (1993).

[24] R. G. Kepler, J. M. Zeigler, L. A. Harrah, and J. R. Kurtz, Phys. Rev. B **35**, 2818 (1987).

[25] S. Nešpùrek, Macromol. Symp. **104**, 285 (1996).

[26] M. A. Abkowitz and M. Stolka, Philos. Mag. Lett. **58**, 239 (1988).

[27] K. Yokoyama and M. Yokoyama, Philos. Mag. B **61**, 59 (1990).

[28] M. A. Abkowitz, Philos. Mag. B **65**, 817 (1992).

[29] M. A. Abkowitz and M. Stolka, Solid State Commun. **78**, 269 (1991).

[30] T. Dohmaru, K. Oka, T. Yajima, M. Miyamoto, Y. Nakayama, T. Kawamura, and R. West, Philos. Mag. B **71**, 1069 (1995).

[31] S. Nešpůrek, H. Valerian, A. Eckhardt, V. Herden, and W. Schnabel, Polym. Adv. Technol. **12**, 306 (2001).

[32] A. Kadashchuk, D. S. Weiss, P. M. Borsenberger, S. Nešpůrek, N. Ostapenko, and V. Zaika, Chem. Phys. **247**, 307 (1999).

[33] M. Grünewald and B. Movaghar, J. Phys.: Condens. Matter **1**, 2521 (1989).

[34] V. I. Arkhipov and G. J. Adriaenssens, J. Phys.: Condens. Matter **8**, 7909 (1996).

[35] A. Miller and E. Abrahams, Phys. Rev. **120**, 745 (1960).

[36] M. Grünewald and P. Thomas, Phys. Status Solidi B **94**, 125 (1979).

[37] D. Monroe, Phys. Rev. Lett. **54**, 146 (1985).

[38] A. Kadashchuk, N. Ostapenko, V. Zaika, and S. Nešpůrek, Chem. Phys. **234**, 285 (1998).

[39] A. Kadashchuk, V. Zaika, and P. M. Borsenberger, J. Imaging Sci. Technol. **43**, 213 (1999).

[40] L. Pan, M. Zhang, and Y. Nakayama, J. Chem. Phys. **110**, 10 509 (1999).