JOURNAL OF IMAGING SCIENCE AND TECHNOLOGY • Volume 43, Number 3, May/June 1999

Thermally Stimulated Luminescence in Molecularly Doped Polymers

A. Kadashchuk,* N. Ostapenko, V. Zaika
Institute of Physics, National Academy of Sciences of Ukraine, Kiev, Ukraine

P. M. Borsenberger
Office Imaging Division, Eastman Kodak Company, Rochester, New York, USA

The low-temperature thermally stimulated luminescence (TSL) technique has been applied for the first time for probing the energetic disorder of localized states in molecularly doped polymers (MDPs) as substituted triphenylamines doped into poly(styrene) (PS). TSL of both the neat MDPs, as tri-*p*-tolylamine (TTA) and tri-*p*-anisylamine (TAA) doped PS, and the doubly doped polymers, as TTA doped PS containing small concentrations of di-*p*-anisyl-*p*-tolylamine (DAT), was studied. The results are described in terms of the Gaussian disorder model and the energetic relaxation of photogenerated charge carriers, that provide reasonable understanding of all observed trends in the TSL. Analysis of both the energetic position of the TSL peak maximum and the shape of its high-energy wing allowed extraction of a parameter characterizing the energetic disorder in MDPs, which agreed well with the width of the density-of-states determined from charge transport measurements. The effect of extrinsic trapping because of DAT on TSL properties can be reasonably interpreted in terms of the effective energetic disorder and the TSL results are in good agreement with those obtained earlier by charge transport studies.

Journal of Imaging Science and Technology 43: 213–219 (1999)

Introduction

In recent years, much attention has been paid to charge carrier transport phenomena in molecularly doped polymers (MDPs) because of their practical importance.[1] Several applications could be mentioned: organic electrophotographic photoreceptors,[1,2] electro-luminescent[3] and electrophotovoltaic[4] devices, and photorefractive media,[5] etc. MDP typically consists of charge-transporting molecules (strong electron donors or acceptors capable of transporting charge carriers) randomly dispersed in an electrically inert polymer host acting as a binder. It is generally accepted that hole or electron transport occurs by thermally activated hopping between adjacent donor or acceptor molecules, respectively.

MDPs represent examples of amorphous systems where charge transport has most often been described within the framework of the Gaussian disorder model[6] of Bässler. This model is based on disorder controlled hopping of charge carriers through a manifold of localized states with a Gaussian density-of-states (DOS) distribution. The distribution of site energies is often caused by energetic disorder and is characterized by the width of the DOS, σ (parameter of the model). Most studies of charge transport in MDP have been based on conventional photocurrent transient measurements and performed on systems where charge trapping could be neglected. Recently, Wolf and co-workers[7] and Borsenberger and co-workers[8] studied the effect of extrinsic traps on the transport properties of charge carriers in doubly doped polymers, and extended the disorder formalism to include the effect of trapping. It was shown that the effect of shallow traps can be accounted for by the replacement of σ with an effective width, σ_{eff}, dependent on both trap depth and concentration, the basic phenomenology of transport remaining unaltered.[7,8]

The aim of the present work is to explore the use of low-temperature thermally stimulated luminescence (TSL) spectroscopy for probing the energetic disorder of localized states in MDPs (both the neat systems and those containing extrinsic shallow traps). Recently, the applicability of the TSL method for evaluation of the energetic disorder parameter in carbazole pendant group polymers[9] and σ-conjugated polysilylenes[10,11] has been demonstrated. It is known[12–14] that the DOS of disordered organic systems is not subject to direct optical probing, therefore, the only methods suitable for such purpose are those that are based on thermally induced transitions among the manifold of carrier states.[9-11,13] Our approach is based on the assumption that the lowest energy portion of an energetically disordered manifold of localized states at very low temperatures may manifest itself in TSL as trapping centers for charge carriers. Actually, at the low temperature limit, $kT \ll \sigma$, the charge carrier hopping occurs toward states of lower and lower energy, until, on reaching the band tail, the concentration of such states is so low that further hops are impossible and, consequently, the charge carriers finally become trapped in the tail sites, which are the local minima of the site energy. Therefore, by analyzing the trap distribution function, one may estimate the shape of the deepest part of the DOS distribution and, consequently, the parameter of the energetic disorder, σ.

This approach is conceptually similar to that employed earlier by Bässler[13,15] using the thermally stimulated

---

Original manuscript received November 2, 1998

* corresponding author; *E-mail:* kadash@iop.kiev.ua

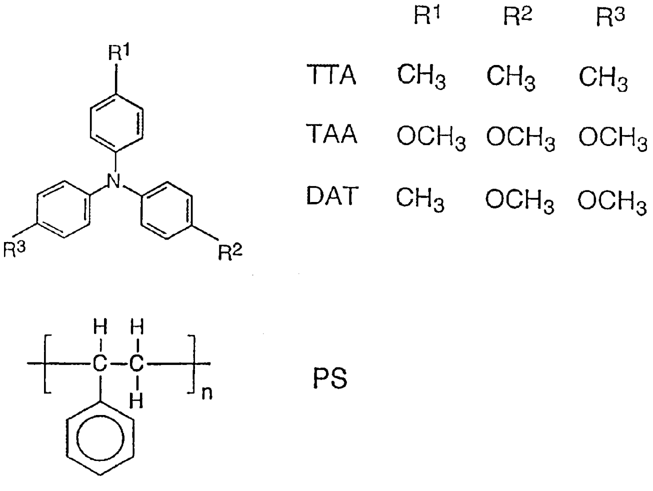
current (TSC) technique for studying the width of the DOS distribution in disordered tetracene layers by analyzing the shape of the high-energy wing of a TSC peak. In this connection it should be mentioned that TSC technique has attracted increasing attention recently in the hope of obtaining important information on the DOS distribution in the bandgap of disordered solids.[16-20] However, as previously shown,[16,17] a basic limitation for the application of the TSC method for DOS probing, in hopping transport systems with very low charge mobility, seemed to be due to that the TSC peak can be irrelevant to direct detrapping. This is because it is influenced by transport process, i.e., it is determined by the increasing mobility of carriers with increasing temperature (so-called "transport peak") and, therefore, its position on a temperature scale is field and thickness dependent.[16]

On the other hand, the main advantage of applying the TSL method for systems with very low charge mobility, in contrast to other techniques, is that TSL, if caused by geminate recombination, is not influenced by the transport processes and is directly related to detrapping.[16–18] The geminate character of the TSL can be proved by quenching the TSL intensity with an applied electric field.[9,16,18] Of special relevance for disordered polymer systems is the employment of the method of TSL with temperature modulation, the so-called fractional TSL,[21–25] which is a useful tool for determining trap depths when different groups of traps are not well separated in energy, or are continuously distributed (which, in our experience, is a very typical situation for amorphous polymers), and it allows the analysis of the trap spectra even when they are complex. The fractional TSL technique (also called the fractional glow technique), that has long been proposed by Gobrecht and Hofmann,[21] is an extension of the initial rise method and is based on cycling the sample with a large number of small temperature oscillations superimposed on a uniform heating. The main reason for applying this method is that the usual quantitative evaluation of the TSL glow curves is very inaccurate, or even impossible if the traps are continuously distributed in depth or if the trap spectrum consists of several types of traps with discrete but very close lying activation energies. In this case, the glow peaks fuse one into another so that many different traps may produce a composite peak and may be scarcely (or even not at all) indicated by *individual* glow maxima. The width and symmetry of such composite glow peaks are no longer suitable for ordinary derivation of trapping parameters.[21] It is recognized[21-23] that the method of fractional TSL avoids the disadvantages of the common glow curve methods, is characterized by greater accuracy and a high resolving power, and it does not require a knowledge of the frequency factors and retrapping probabilities.[21, 22]

In the present work, we report the first TSL study of some substituted triphenylamines doped into poly(styrene) (both the neat trap-free MDPs and trap-containing systems). The TSL behaviors of the MDPs studied are interpreted in terms of the Gaussian disorder model and the energetic relaxation of photogenerated charge carriers within a manifold of states of Gaussian distribution.

Experimental

The molecular structures of the compounds used in this study are illustrated in Fig. 1. Charge transporting molecules (CTM): tri-*p*-tolylamine (TTA) and tri-*p*-anisylamine (TAA), as well as molecules of di-*p*-anisyl-p-tolylamine (DAT) acting as a weak hole trap were supplied by Eastman Kodak Company. Poly(styrene) (PS) was provided by the Institute of Chemistry, Acad. of Sci. of Ukraine. All materials were used as received. Samples were prepared by dissolving the appropriate ratios of CTM and PS in dichloromethane, then the resulting solutions were cast on a metal substrate. The films were dried for 3 h at 40°C in air, then at room temperature for 2 h *in vacuo*. All samples of the neat MDP contained 40% TTA (or TAA) with respect to PS. The CTM concentrations are expressed as the wt.% of the total, which is equivalent to the mass ratio. In the case of doubly doped polymers, the concentration of the DAT ranged from 0.05 to 4 wt.% with respect to TTA. The solids concentration of the coating solution was 10%.



	R^1	R^2	R^3
TTA	CH_3	CH_3	CH_3
TAA	OCH_3	OCH_3	OCH_3
DAT	CH_3	OCH_3	OCH_3

Figure 1. The molecular structures of tri-*p*-tolylamine (TTA), tri-*p*-anisylamine (TAA), di-*p*-anisyl-*p*-tolylamine (DAT), and poly(styrene) (PS).

TSL measurements were carried out with an automatic equipment for optical thermoactivated spectroscopy over a wide temperature range from 4.2 K to 350 K with an accuracy better than 0.1 K. The polymer samples were mounted in a holder of the optical helium cryostat and, after cooling, they were irradiated with UV light. For excitation, the light from a high-pressure 500 W mercury lamp was used. After terminating the excitation the luminescence signal was detected with a cooled photomultiplier operated in photon-counting mode. 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.

Our fractional TSL technique, and the procedure of data processing, were similar to that described in Refs. 22, 25. The main difference was in the temperature range extension from the commonly used liquid-nitrogen temperature down to the liquid-helium temperature. The mean activation energy $<E>$ is determined during each temperature cycle as

$$<E> = -d\,[\ln I\,(T)]/d\,(1/\mathrm{kT}), \qquad (1)$$

where I is the intensity of the thermoluminescence, T is the temperature in the measuring cycle, and k is the Boltzmann constant. A trap distribution function, $H\,(E)$, can be determined in arbitrary units as:[22]

$$H\,(E) \sim I\,(T)/(d < E>/dT). \qquad (2)$$

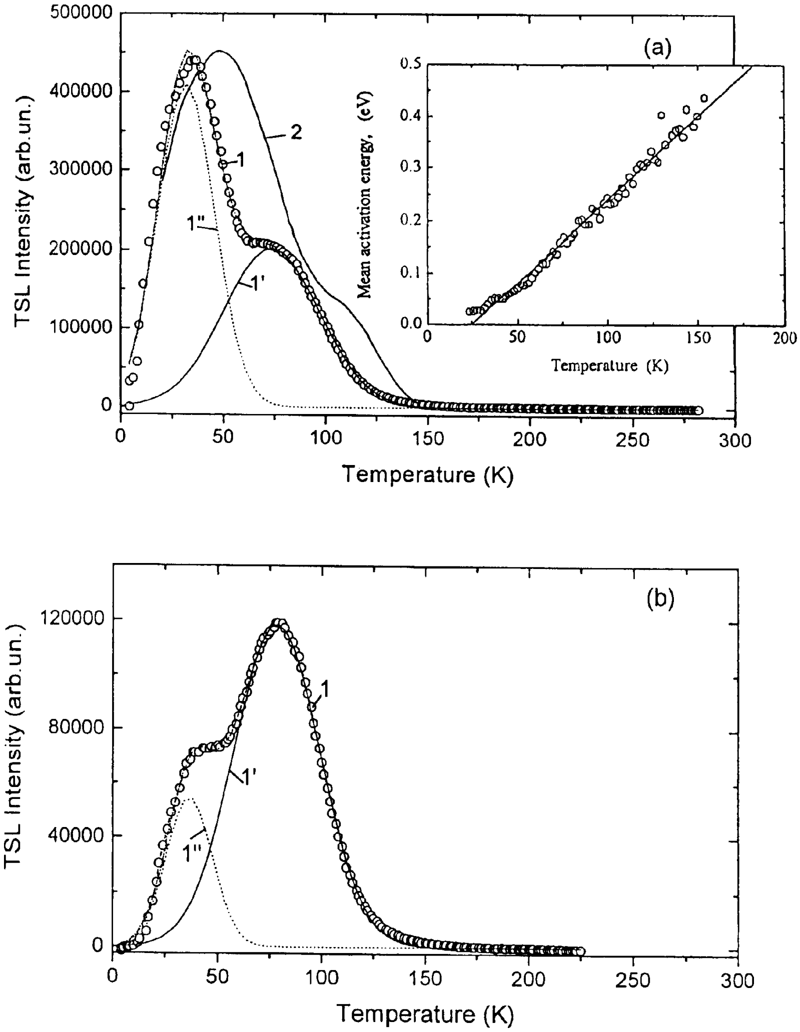


Figure 2. (a) TSL glow curve under excitation with unfiltered light of Hg lamp for 30 s at 4.2 K for TTA:PS (Curve 1) and TAA:PS (Curve 2); Curves 1' and 1" represent deconvolutions using Gaussian functions. The temperature dependence of the mean activation energy <*E*> as obtained by fractional TSL (inset); extrapolation used an empirical expression (4) to give by the solid line in the inset. (b) TSL peak of TTA:PS obtained after 30 min exposure to additional IR irradiation (Curve 1), after standard UV excitation for 30 s. The transparency band of the IR-filter used in experiment was 900-4500 nm.

The frequency factor at the maximum of TSL peak, S is given by the formula:

$$S = \langle E_m \rangle \beta / kT_m^2 \exp(\langle E_m \rangle / kT_m), \qquad (3)$$

where T_m and $\langle E_m \rangle$ are the temperature and the activation energy of the maximum of the TSL peak, respectively. All measurements were done in the helium atmosphere.

Results

Trap-Free Polymer Systems. It was found that the neat TTA-doped PS, as well as systems containing extrinsic traps, showed very strong thermoluminescence induced by UV-radiation at liquid helium temperature. Figure 2(a) presents a typical TSL glow curve for the neat TTA (40%) doped PS film (TTA:PS) (Curve 1). As one can see, the low-temperature TSL under UV-excitation at 4.2 K arises immediately after sample heating has begun to heat up and extends to ~150 K. The existence of a quasi-continuous trap distribution in this system has been found. The mean activation energies, <*E*>, as revealed by the fractional TSL [Fig. 2(a), inset], linearly increase with temperature according to the following empirical formula (in eV)

$$\langle E \rangle(T) = 0.0032 \times T - 0.08 \qquad (4)$$

These results indicate the lack of the charge-carrier deep trapping in studied the MDP and on the presence of a large concentration of shallow localized states capable of charge carrier capturing at 4.2 K.

The TSL glow curve of TTA:PS is evidently composed of two peaks: low-temperature with maximum at $T_m \cong$ 35 K and high-temperature peak at $T_m \cong$ 75–78 K. Curves 1′ and 1″ in Fig. 2(a) present the separation the TSL glow curve into two Gaussians. It should be noted that the Gaussian function used for the approximation of the high-temperature TSL peak [Fig. 2(a), Curve 1′] has a width of about 25 K. In energy terms this is equivalent to 0.08 eV because of Eq. 4, (25 × 0.0032 = 0.08). The activation energy and frequency factor in the maximum of the above-mentioned TSL peaks are $<E_m> = 0.032$ eV and $S = 2 \times 10^3$ s^{-1} (for the peak at 35 K), and $<E_m> = 0.16 \div 0.17$ eV and $S = 3 \times 10^9$ s^{-1} (for the peak at 75 K), respectively.

It should be pointed out that the low- and high-temperature TSL peaks of TTA:PS most likely have somewhat different physical origins as supported by their different frequency factors. Frequency factors of order 3×10^9 s^{-1} for the high-temperature peak is quite typical for amorphous photoconducting polymers: a comparable value was obtained for the main TSL peak of polyvinylcarbazole (PVK)[25] (10^8 s^{-1}) and poly(methylphenylsilylene) (PMPSi)[10] (10^{10} s^{-1}), while the anomalous low value of order 10^3 s^{-1} for the low-temperature peak at 35 K could be a result of recombination of an electron and hole (probably closely situated) by charge tunneling. It is a well-known fact that a low S-value is often associated with under-barrier tunnel transitions. The detailed study of this problem will be presented elsewhere. We note that a similar (but not always so pronounced) low-temperature feature at $T \leq 50$ K is inherent for all polymers we have studied, including PMPSi and PVK-type polymers, and it seems to be of secondary importance in the present study. Therefore, in this work we will focus our attention mainly on the high-temperature peak, which will be referred to hereafter as the main TSL peak.

We have found a very interesting and useful method of separation of the high-temperature TSL peak by the additional exposure of a sample to IR-irradiation at 4.2 K following the conventional UV-excitation ("IR-cleansing" effect). This effect was reported earlier in the TSL study of PMPSi[10] and was explained in terms of the energetic relaxation of photogenerated charge carriers within the Gaussian shaped DOS. IR-excitation to the highest portion of the DOS involves an increase in the number of new sites a carrier visited at 4.2 K and, consequently, leads to an increase in the probability of reaching lower energy tail states. Figure 2(b) presents the TSL glow curve of TTA:PS obtained as a result of the additional IR-cleansing for 30 min at 4.2 K. Such IR-exposure leads to near complete cleansing of the high-temperature TSL peak; and although the broadness of the peak is not changed, its maximum is slightly shifted towards higher temperature and only a weak shoulder persists instead of the previously strong low-temperature peak. It should be noted that no sample heating occurred in the process, and the sample was immersed in liquid helium. The cleansed TSL peak of TTA:PS can be successfully fitted by a Gaussian with the half-width about 0.08 eV [solid curve in Fig. 2(b)].

It is of obvious interest to compare the above results with TSL data of another trap-free MDP system. Curve 2 in Fig. 2(a) presents TSL glow curve for the neat TAA (40%) doped PS (TAA:PS) film. As one can see, the TAA:PS has similar TSL behavior, except that the corresponding TSL peaks are notably shifted towards higher temperatures within respect to that of TTA:PS. It was found that the main TSL peak of TAA:PS is centered at $T_m \approx 110$ K and the activation energy in the peak maximum comprises $<E_m> = 0.24$ eV.

Trap-Containing Polymer Systems. TTA doped PS containing di-*p*-anisyl-*p*-tolylamine (DAT) provides a good example of MDP where transport is trap-affected.[8] DAT is a shallow trap with depth[8] of 0.15 eV because of the lower potential of ionization relative to TTA. TSL study of MDPs containing other shallow traps has revealed qualitatively similar behaviors and will be presented elsewhere. Figure 3(a) presents TSL glow curves of TTA:PS containing different concentration of DAT: c = 0%, 0.05%, 0.24%, 1%, 4% (Curves 1, 2, 3, 4, 5, respectively). All curves in Fig. 3(a) are normalized to the maximum intensity of the high-temperature (main) TSL peak. As one can see, even a small concentration of DAT traps exerts a rather considerable effect on the TSL. The most characteristic property is the considerable shift of the main TSL peak towards higher temperatures with increasing trap concentration. This peak shifts from 75 K at zero DAT concentration to ≈115 K for c = 4% (Fig. 3(a), Curve 5).

It is worth noting that the effect of DAT traps can be seen more clearly after the IR-cleansing of the main TSL peak [Fig. 3(b)]. Relevant TSL glow curves detected after the additional exposure of the sample to IR-radiation for 30 min at 4.2 K are presented in Fig. 3(b) (all curves are normalized at the maximum intensity). The dependence of $<E>$ on temperature (as measured by the fractional TSL technique) coincided well with that given by Eq. 4 for DAT concentration $c \leq 0.24\%$, however, a slight deviation it was found for systems containing DAT with $c \geq 1\%$. The activation energy at the maximum of the high-temperature TSL peaks was equal to 0.17, 0.2, 0.215, 0.264 eV, for DAT concentration c = 0%, 0.24%, 1%, 4%, respectively.

Analysis and Discussion

Let us first consider the trap-free MDP systems. Charge transport in TTA:PS and TAA:PS has been extensively studied and described in terms of the Gaussian disorder model.[26–29] The width of the DOS distribution for the low-polarity material TTA (40%) doped PS, σ = 0.083 eV, was determined by Borsenberger[26–28] and Young.[29] On the other hand, the degree of energetic disorder for TAA (40%) doped PS has been found[27,28] as notably larger, σ = 0.107 eV, due to the considerable contribution of the dipolar component into the total width (the dipole moment of TAA is 2 D[28]). It was shown that polaronic effects need not be invoked to explain charge transport properties in the above MDPs.

It is assumed that, just as in the case of earlier studied PMPSi,[10,11] the main TSL peak of TTA:PS is associated with thermal release of charge carriers occupying the intrinsic tail states with the DOS distribution of a Gaussian shape

$$H(E) \sim \exp\left[-\frac{E^2}{2\sigma^2}\right] \qquad (5)$$

where E is the energy of the localized state with respect to the DOS center. It is supposed that a trapped charge carrier, to become mobile again, should be thermally excited to the level of the so-called transport energy,[30] E^*, which normally is located bellow the center of the DOS. To consider the transport energy position, the following criterion[30] as a first approximation seems to be a reasonable choice for the case of the low-temperature range relevant to the TSL experiment. For the Gaussian shaped DOS, of a system with sixfold coordination, E^* could be defined by the condition:[30]

$$\int_{-\infty}^{E^*} f(E)dE = 1/6, \left(\text{numerically}: E^* = \sigma\right) \qquad (6)$$

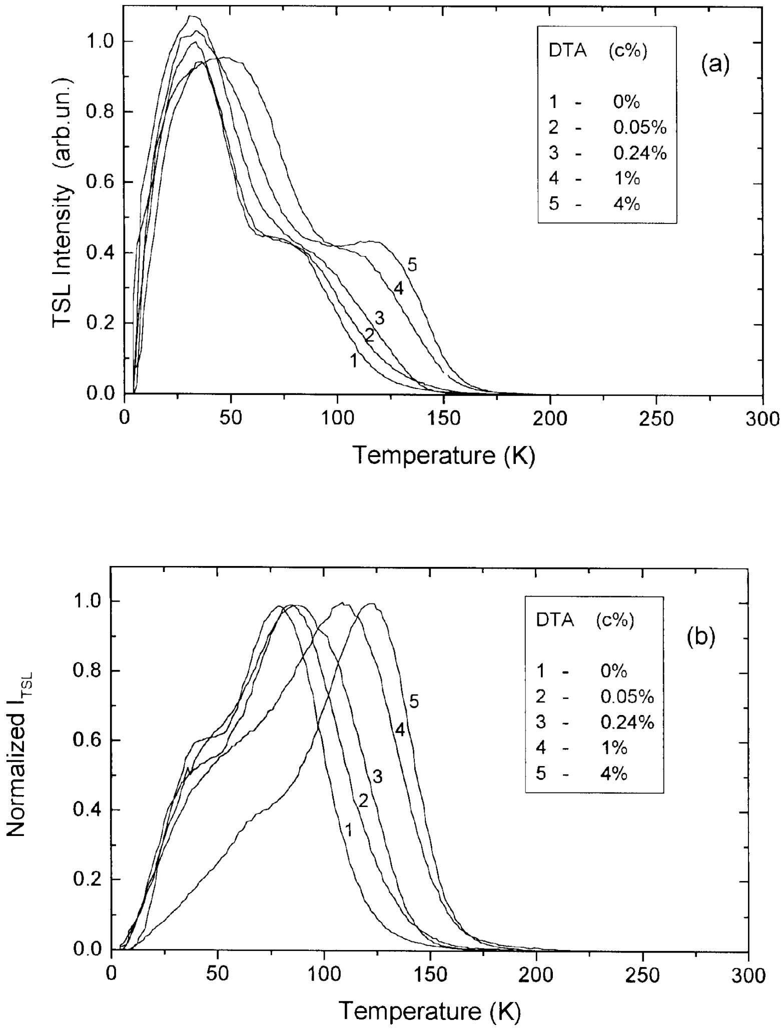


Figure 3. (a) TSL glow curves of TTA:PS containing different concentration of DAT: c = 0%, 0.05%, 0.24%, 1%, 4% (Curves 1, 2, 3, 4, 5, respectively). All curves are normalized at the maximum intensity of the high-temperature TSL peak; (b) TSL peaks of the same systems obtained after exposition to additional IR irradiation. Experimental conditions were the same as presented in Fig. 2.

where $f(E)$ is a Gaussian function. Thus, the experimentally measured thermal release energy, $<E>$, in the TSL data analysis is identified with the energy of a localized state E, with respect to the transport energy position, E^*:

$$<E> = E - E^* \tag{7}$$

We should emphasize that taking into consideration the above empirical linear dependence (Eq. 4) and Eq. 2 from the theory[22] of the fractional TSL, the temperature profile of the TSL peak, $I(T)$, should reflect the trap distribution function, $H(E)$. The results of Gaussian analysis of the high-temperature wing of the TSL peak of TTA:PS, i.e., $\ln(I(T))$ versus E^2, made by converting the temperature scale to the trap energy scale using the empirical calibration (Eq. 4) as well as Eqs. 6 and 7, is presented in Fig. 4, Curve 1. The following conclusions can be drawn from the above analysis:

(i) the high-energy wing of TSL peak can be well approximated by a Gaussian distribution (cf. Eq. 5);

(ii) the width of this distribution, σ', formally determined by taking its inclination angle tangent, yields the value σ' = 0.082 eV (Fig. 4, solid line 1).

This value agrees well with the width of the DOS, σ = 0.083 eV,[7,8,26-29] obtained by the charge transport measurements. For comparison purposes, the Gaussian analysis of the same peak when ignoring the consideration of transport energy below the center of the DOS (assuming that $<E> = E$ in contrast to Eq. 7) is presented by Curve 2 in Fig. 4. As one can note, neglecting of the transport energy concept leads to smaller value of σ' = 0.074 eV estimated from the slope of the solid line 2 in Fig. 4.

As was shown earlier,[10] the disorder parameter of amorphous photoconducting systems could be evaluated from TSL data also by alternative means, namely by analyzing the activation energy value in the maximum of TSL peak, $<E_m>$. Actually, a charge carrier after its photogeneration occurring at the TSL excitation at 4.2 K, is subjected either to geminate recombination or to trapping by shallow localized states. The latter process

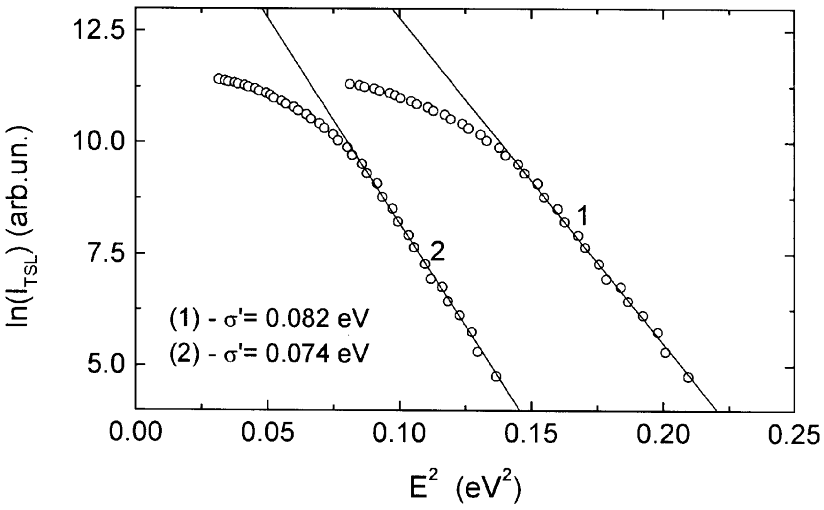


Figure 4. Gaussian analysis of the high-energy wing of the TSL peak of TTA:PS (see text for explanations) when using Eq. 7 (Curve 1), and with the assumption E = $<E>$ ignoring the transport energy concept (Curve 2). Solid lines 1 and 2 are extrapolations with σ' = 0.082 and 0.074 eV, respectively.

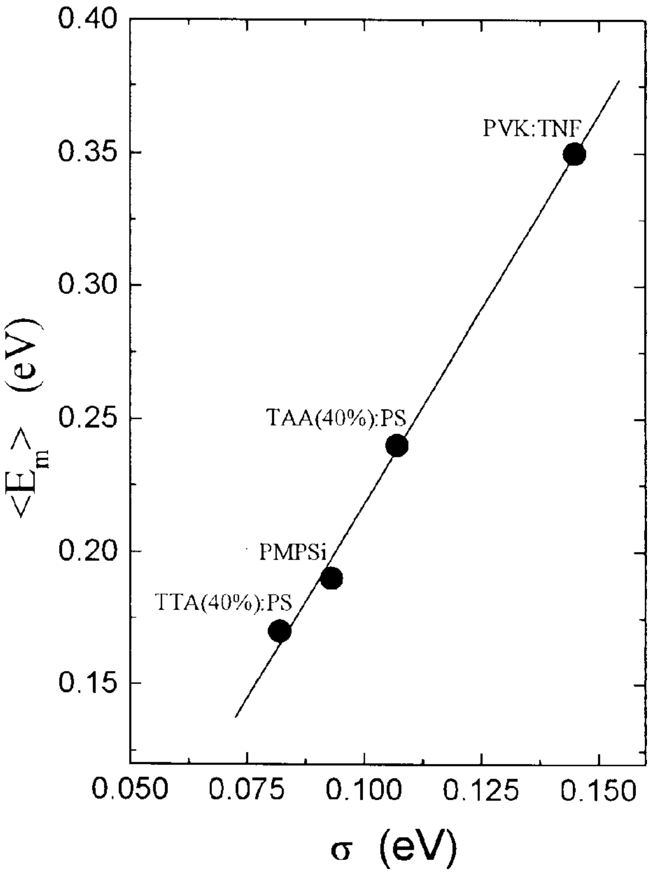


Figure 5. Correlation between the activation energy in the TSL peak maximum, $<E_m>$, and σ obtained from charge transport measurements for TTA:PS,[7] PMPSi,[10] TAA:PS,[27] and PVK:TNF[7].

could be well described by the theory developed by Movaghar[31] and Bässler[14] for energetic relaxation of particles within the Gaussian shaped manifold of states. According to this theory, the energetic relaxation of randomly generated particles in the zero-temperature limit occurs through a nonactivated downward hopping with the decay in the energy on the level of the time scale given by the formula:[14, 31]

$$E_R = \sigma\,[\delta \ln \ln (t/t_0)]^{1/2} \qquad (8)$$

where E_R is the mean energy of the charge carrier packet relative to the center of DOS distribution, δ is the dimensionality of the lattice (usually taken as 3),[14,31] t is the time, and t_0 is the dwell time of a carrier at a lattice site without disorder (for a charge carrier, t_0 is accepted as 10^{-13} s).[6] Hence, the parameter σ could be estimated from the assumption that the experimentally accessible activation energy $<E_m>$ corresponds to the mean energy of the relaxed charge-carrier packet, E_R (given by Eq. 8). Actually, assuming σ = 0.083 eV and using the expression (8) for the experimental time scale of 10^2 s, we obtain the value E_R = 0.27 eV. The experimental value of the activation energy of the maximum of the TSL peak within respect to the center of the DOS (given as E = $<E>$ + E^* due to Eq. 7) is 0.253 eV in reasonable agreement with the above calculated value. As one can see, the inclusion of the transport energy by means of Eq. 7 is of importance for the analysis of the energetic position of the TSL peak maximum and leads to better coincidence between calculated and experimental values (note that experimental value without considering the transport energy according to Eq. 4 is only $<E_m>$ = 0.17 eV).

Using this line of reasoning, the relationship between the experimentally measured $<E_m>$ and the value of E_R calculated by Eq. 8 could be expressed as follows: $<E_m> = E_R - E^* = E_R - \sigma$. It follows, that a rather simple means of evaluation of the σ-value from the experimentally accessible value of $<E_m>$ is:

$$\sigma' = \frac{< E_m >}{\left[3 \ln \ln(t/t_0)^{1/2}\right] - 1}, \qquad (9)$$

According to Eq. 9 one obtains σ' = 0.075 eV for the TTA:PS system.

The TSL properties of the TAA:PS system could be well interpreted in a similar manner, but taking into account the fact that degree of energetic disorder in this system is larger than that for TTA:PS (σ = 0.107 and 0.083 eV, respectively).[27,28] According to Eq. 8, $<E_m>$ value is expected to be also larger, as was observed experimentally: $<E_m>$ = 0.24 eV. The disorder parameter for TAA:PS can be estimated by Eq. 9 which gives σ' = 0.106 eV.

It should be emphasized, that the above-mentioned interpretation of TSL data presumes a linear relationship between the activation energy in the TSL peak maximum and the degree of energetic disorder in amorphous systems. Such behavior has been observed and it seems not to depend on the type of polymer. Figure 5 presents collected charge transport and TSL data for some different polymer systems, which are plotted as $\langle E_m \rangle$ versus σ. As one can see, there is a striking correlation between those data and the experimental points are close to falling on a straight line.

Finally, let us consider TSL behaviors of TTA:PS containing extrinsic traps caused by DAT. Transport properties of these MDPs have been studied recently[8] by Monte Carlo simulations and mobility measurements. The principal conclusion was that the system behaves as if the addition of traps has widened the DOS and the basic features of transport can be modeled in terms of the disorder concept using σ_{eff} as the essential material parameter. TSL data presented in Fig. 3 agrees well with such a notion. The characteristic high-temperature shift of the main TSL peak with increasing trap concentration is most likely indicative of an increase in the σ_{eff}, while no new features were observed in the TSL glow curve in comparison with the trap-free system. Thus, the general picture of the TSL behavior of TTA:PS containing varying concentrations of DAT is undistinguished from the neat TTA:PS. Using measured $\langle E_m \rangle$ values, one can estimate the energetic disorder parameters by means of Eq. 9 as $\sigma' = 0.075$, 0.088, 0.095, and 0.116 eV for concentrations of DAT equal to 0, 0.24, 1, and 4%, respectively. These values agree reasonably with parameters $\sigma_{\text{eff}} = 0.083$, 0.095, 0.101, and 0.107 eV earlier obtained[8] from the charge transport measurements for the same DAT concentrations. It should be noted that the high-temperature TSL peak, which manifested a strong shift towards higher temperatures with an increase of DAT concentration, does not reflect directly the value of DAT trap depth, because at $c(\text{DAT}) = 4\%$ the value of $\langle E_m \rangle$ is 0.264 eV that is far larger than the trap depth of 0.15 eV. The origin of this peak is due to superimposition of energetic disorder and trapping effects, and it can be characterized by the effective disorder parameter.

Conclusion

The interpretation of low-temperature TSL of MDPs as associated with charge carrier thermal release from intrinsic tail states of the DOS distribution is suggested. Such an approach, based on the Gaussian disorder model, provides a reasonable understanding of all observed trends in the TSL. According to this, the shape of the high-temperature wing of the TSL peak and the energetic position of its maximum could be explained consistently incorporating the concept of the transport energy. Gaussian analysis of the high-temperature wing of the TSL peak of TTA:PS yielded the width of states profile for localized charge carriers equal to $\sigma' = 0.082$ eV (Fig. 4, Curve 1). It was shown that the position of the TSL peak maximum is in accord with the predictions of the theory for non-activated energetic relaxation of photogenerated carriers within a Gaussian-shaped manifold of localized states, and, therefore, no additional features of the DOS in the gap are necessary for the existence of the low-temperature TSL peak. The activation energy in the TSL peak maximum of TTA:PS, which under the consideration of the transport energy concept is equal to 0.253 eV, agreed satisfactorily with calculated value of 0.27 eV. TSL of TAA:PS could be interpreted in similar manner taking into account the larger degree of energetic disorder because of the considerable dipolar disorder in comparison with the former system.

The effect of extrinsic traps in TTA:PS containing varying concentrations of DAT on TSL properties can be interpreted in terms of the effective energetic disorder. The origin of the TSL peak for such doubly doped MDPs is due to superimposition of energetic disorder and trapping effects, and it can be characterized by the effective disorder parameter.

Acknowledgments. The research described in this article was made possible in part by Award No. UE1-326 of the U.S. Civilian Research & Development Foundation for the Independent States of the Former Soviet Union (CRDF). Discussions with H. Bässler, M. Abkowitz and R. Young are gratefully acknowledged.

References

1. P. M. Borsenberger and D. S. Weiss, *Organic Photoreceptors for Imaging Systems*, Dekker, New York, 1993.
2. K.-Y. Law, *Chem. Rev.* **93,** 449 (1993).
3. C. Adachi, K. Nagai and N. Tamoto, *Appl. Phys. Lett.* **66,** 2679 (1995).
4. C. W. Tang, S. A. Van Slyke and C. H. Chen, *Appl. Phys. Lett.* **48,** 183 (1988).
5. W. E. Moerner and S. M. Silence, *Chem. Rev.* **94,** 127 (1994).
6. H. Bässler, *Phys. stat. sol. (b)* 175, 15 (1993) and references therein.
7. U. Wolf, H. Bässler, P. M. Borsenberger and W. T. Gruenbaum, *Chem. Phys.* **222,** 259 (1997).
8. P. M. Borsenberger, W. T Gruenbaum, U. Wolf, and H Bässler, *Chem. Phys.* **234,** 277 (1998).
9. A. K. Kadashchuk, N. I. Ostapenko and N. V. Lukashenko, *Adv. Mater. Opt. Electr.* **7,** 99 (1997).
10. A. Kadashchuk, N. Ostapenko, V. Zaika, and S. Nespùrek, *Chem. Phys.* **234,** 285 (1998).
11. S. Nespùrek, A. Kadashchuk, N. Ostapenko, and V. Zaika, *Mol. Cryst. Liq. Cryst.* **324,** 95 (1998).
12. M. Pope and C. Swenberg, *Electronic Processes in Organic Crystals,* Clarendon Press, Oxford, New York, 1982, p. 821.
13. H. Bässler, *Phys. stat. sol. (b)* **107,** 9 (1981).
14. H. Bässler, in *Disordered Effect on Relaxational Processes,* Springer-Verlag, R. Richter and A. Blumen, Eds., Berlin, Heidelberg 1994, p. 585.
15. R. Eiermann, W. Hofberger and H. Bässler, *J. Non-Cryst. Solids* **28,** 415 (1978).
16. I. Glowacki and J. Ulanski, *J. Appl. Phys.* **78,** 1019 (1995).
17. J. Ulanski, J. Sielski, I. Glowacki, and M. Kryszewski, *IEEE Trans. Electr. Insul.* **27,** 714 (1992).
18. I. Glowacki, J. Ulanski, J. K. Jeszka, and M. Kryszewski, *Mater. Sci.* **13,** 83 (1987).
19. J. W. Stasiak and T. J. Storch, *Proc. SPIE* **3144,** 72 (1997).
20. S. D. Baranovskii, M. Zhu, T. Faber, F. Hansel, and P. Thomas, *Phys. Rev.* **55,** 16226 (1997).
21. H. Gorbecht and D. Hofmann, *J. Phys. Chem. Solids* **27,** 509 (1966).
22. I. A. Tale, *Phys. stat. sol. (a)* **66,** 65 (1981).
23. H. L. Oczkowski, *Acta Phys. Pol. A* **76,** 649 (1989).
24. A. K. Kadashchuk, N. I. Ostapenko, Yu. A. Skryshevskii, V. I. Sugakov, and T. O. Susukolova, *Mol. Cryst. Liq. Cryst.* **201,** 166 (1991).
25. P. I. Butlers, I. A. Tale, J. Pospísil, and S. Nespùrek, *Prog. Coll. Polym. Sci.* **78,** 93 (1988).
26. P. M. Borsenberger, W. T. Gruenbaum, E. H. Magin, and L. J. Sorriero, *Chem. Phys.* **195,** 435 (1995).
27. P. M. Borsenberger and M. B. O'Regan, *Chem. Phys.* **200,** 257 (1995).
28. P. M. Borsenberger, E. H. Magin, M. B. O'Regan, and J. A. Sinicropi, *J. Polym. Sci. B: Polym. Phys.* **34,** 317 (1996).
29. R. H. Young, *J. Chem. Phys.* **103,** 6749 (1995).
30. B. Hartenstein and H. Bässler, *J. Non-Cryst. Solids* **190,** 112 (1995).
31. B. Movaghar, B. Ries and M. Grunewald, *Phys. Rev. B* **34,** 5574 (1986).