

# Thermally Stimulated Luminescence In Electroluminescent Polymers

A. Kadashchuk<sup>1</sup>, H. Bässler<sup>2</sup>, V. I. Arkhipov<sup>2</sup>, Yu. Piryatinskii<sup>1</sup>

<sup>1</sup>*Institute of Physics, Natl. Academy of Sci., Prospect Nauki 46, 03028, Kiev*

<sup>2</sup>*Fachbereich Physikalische Chemie, Philipps-Universität Marburg, Hans-Meerwein-Str., 35032 Marburg, Germany*

## Abstract

Low-temperature thermally stimulated luminescence (TSL) technique was applied to study distribution of traps in methyl-substituted ladder-type poly(paraphenylene) (MeLPPP), a polymer with greatly reduced disorder. We assume that the localized states within the tail of the DOS distribution can act as traps in MeLPPP at very low temperatures. The observed characteristic features of TSL in MeLPPP can be explained in terms of the hopping model of carrier thermally-assisted relaxation. Predictions of the model are found to be in good quantitative agreement with experimental data and interpretation of the TSL data yields the effective DOS width of 0.055 eV in good agreement with the value of 0.05 eV obtained from the transport measurements. It was found that both fluorescence and phosphorescence contribute to the TSL spectrum, whereas only the latter was observed in the long isothermal afterglow following photoexcitation of the sample at helium temperature. This implies the binding energy of a short off-chain geminate pair higher than the binding energy of a singlet excitation but lower than that of a triplet exciton.

## Introduction

Charge carrier transport and photogeneration in  $\pi$ -conjugated polymers are of great fundamental and technological interest due to increased importance of this materials in optoelectronic devices. It is generally accepted that charge transport in conjugated polymers is controlled by thermally activated hopping through intrinsic states derived from domain-like segments of the main chain separated by topological defects.<sup>1</sup> The length of the segments is subject to a statistical distribution that is the major source of energetic disorder in the polymers. Thus, the disorder formalism<sup>2</sup> has been involved to interpret the charge transport properties in  $\pi$ -conjugated polymers as the field and temperature dependence of the mobility and the temporal features of the photocurrent transients.

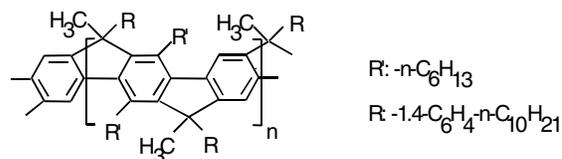
Methyl-substituted ladder-type poly(paraphenylene) (MeLPPP) is very attractive material for applications in optoelectronic devices due to a relatively high, as compared with other  $\pi$ -conjugated polymers, charge carrier mobility

that is very important as far as design and fabrication of fast-response polymer light-emitting diodes and electrically driven polymer lasers is concerned. It was shown<sup>3,5</sup> that MeLPPP is a conjugated polymer with a greatly reduced disorder due to its rigid well-defined structure. Recently studied hole transport in MeLPPP<sup>4,5</sup> was classified as being disorder controlled and the width of the density-of states (DOS) distribution,  $\sigma$ , was estimated as 0.05 eV. It was also shown that the trap-free regime of the hole transport is probably realized in this polymer. A considerable progress achieved in understanding of charge carrier photogeneration in MeLPPP should be mentioned; a model that describes photogeneration as on-chain field assisted dissociation of exciton on hot segments was suggested.<sup>6</sup>

In the present work, results obtained by low-temperature thermally stimulated luminescence (TSL) in MeLPPP are reported. The obtained data are interpreted in terms of the thermally assisted hopping model developed recently by Arkhipov et al.<sup>7</sup> Interpretation of the obtained data yields the DOS energy distribution in MeLPPP and elucidates important details of geminate recombination in this material.

## Experimental

Methyl-substituted ladder-type poly(paraphenylene) (MeLPPP, see Scheme 1) films for TSL measurements with the thickness of 0.6 and 1.1  $\mu\text{m}$  were prepared by the spin-coating from chloroform solution (4% by weight) onto a quartz substrate. After deposition, the films were dried at room temperature under reduced pressure of  $10^{-6}$  mbar for at least 12 h.



Scheme 1

TSL measurements were carried out over a wide temperature range (4.2 to 350 K). TSL measurements after UV light excitation were performed with two different methodologies: uniform heating at a rate  $\beta = 0.15$  K/s, and fractional heating. The latter procedure allows the determination of trap depth when different groups of traps are not well separated in energy or are continuously distributed. The fractional TSL technique,<sup>8</sup> being an extension of the initial rise method, is based on cycling the sample with a large number of small temperature oscillations superimposed on a constant heating ramp. The main outcome of the fractional TSL is the temperature dependence of the mean activation energy,  $\langle E \rangle(T)$ ,<sup>8,11</sup> The experimental details of and the data processing procedures have been described elsewhere.<sup>9-11</sup>

The afterglow decay kinetics were measured at very long delay times from 1 s to  $\sim 10^3$  s after switching off the excitation (integration time 1 s) with the same equipment as was used for TSL measurements, but under the condition of constant temperature, normally at  $T=4.2$  K. This experiment was conceptually similar to that described in Ref. [12] where the delayed emission from poly(vinylcarbazole) was detected at delay times of several hundred seconds at room temperature.

Conventional delayed luminescence spectra were measured at 4.2 K with a monochromator (linear dispersion 0.8 nm/mm) and with the use of a photomultiplier operating in photon-counting mode (gatewidth of 100  $\mu$ s) and a nitrogen laser for optical excitation at 337 nm.

## Results

It was found that MeLPPP films show TSL, which is detectable only in the low-temperature range from 4.2 to  $\sim 120$  K. A typical TSL glow curve of MeLPPP after excitation at 4.2 K represents a broad single peak with the maximum at  $T_m \approx 40$  K as shown by Curve 1 in Fig. 1.

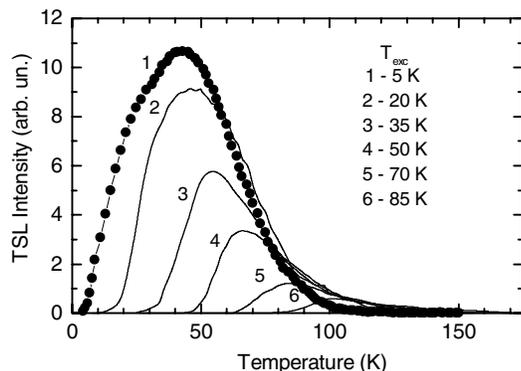


Figure 1. TSL glow curves of MeLPPP measured after photoexcitation at different temperatures (given in the inset). Symbols show TSL curve after excitation at 4.2 K.

To our knowledge, this is the lowest temperature TSL peak that has been ever observed in disordered photoconducting polymers indicating that, in this polymer, disorder is weak. The principal point is that TSL peak of MeLPPP is composed from a quasi-continuous energetic distribution of trapping states. This is proved by the following.

i) The TSL peak in MeLPPP gradually shifts towards higher temperatures with increasing temperature,  $T_{exc}$ , at which the sample was photoexcited (Fig. 1). The TSL signal can still be detected even if  $T_{exc}$  is higher than the temperature of the peak maximum measured after the excitation at 4.2 K as shown in Figure 1.

ii) The fractional TSL technique was used to obtain the temperature dependence of the TSL activation energy. Similar to previously studied amorphous photoconducting polymers<sup>9-11,13</sup> the mean TSL activation energy,  $\langle E_a \rangle$ , in MeLPPP linearly increases with increasing temperature (see inset to Fig. 4) according to the following empirical equation:

$$\langle E \rangle(T) = 0.0018 \times T - 0.016. \quad (1)$$

The obtained data indicate considerably smaller activation energies as compared with other organic disordered materials.<sup>9-11,13</sup> The activation energy at the TSL peak maximum  $T_m \approx 42$  K is  $\langle E \rangle = 0.061$  eV.

It is worth noting that a long isothermal afterglow is also observed in MeLPPP films after switching off the excitation. The afterglow decay kinetics (Fig. 2), measured with the delay time starting from  $\approx 1$  s after terminating the excitation, obeys a power law  $I(t) \propto t^{-1}$  and it is still detectable at times up to several hundred seconds. A remarkable difference between emission spectra of the long isothermal afterglow, the TSL, and the steady-state photoluminescence (PL) was observed. In PL spectra, the fluorescence in the range of 450-550 nm, caused by the radiative decay of singlet excitons, is dominant.<sup>14</sup>

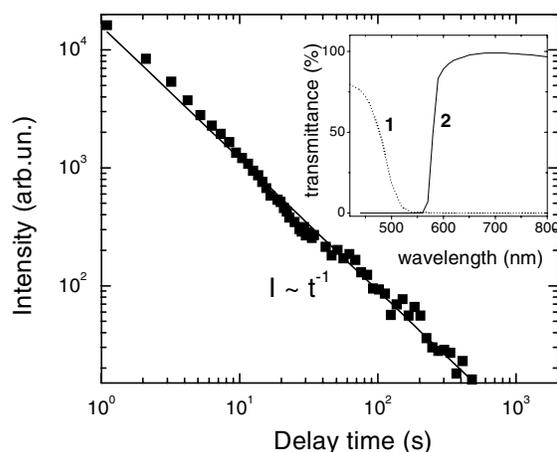


Figure 2. Time dependence of the isothermal afterglow intensity measured at 4.2 K. The inset shows transmittance spectra of cutoff filters I and II.

Delayed luminescence spectra of MeLPPP, measured at 4.2 K with the delay times of 5, 50, 500  $\mu\text{s}$  and 8 ms and the gatewidth of 100  $\mu\text{s}$ , are shown in Figure 3. As it was reported earlier,<sup>15,16</sup> both the delayed fluorescence (DF) and the phosphorescence are observed in this polymer at low temperature. Both spectral components decay in a power-law fashion. As it can be seen from Figure 3, the phosphorescence band decays much slower than DF.

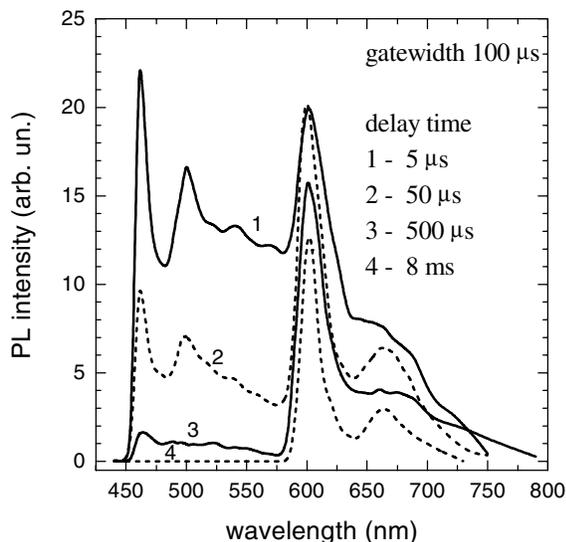


Figure 3. Delayed luminescence spectra measured at different delay times after terminating photoexcitation of the MeLPPP film at 4.2 K. The DF peak lowers much faster as compared with phosphorescence line and vanishes completely at 8 ms.

In summary, comparing the long-afterglow and TSL emission spectra in MeLPPP leads to the following observations. No DF emission in the range of 450-550 nm was found in the afterglow spectrum and only red emission with  $\lambda \geq 600$  nm was observed. Two glass cutoff filters were used to separate DF (filter I) and phosphorescence emission (filter II). Transmittance spectra of these filters are shown in the inset to Figure 2. The isothermal afterglow emission is detected only through filter II and no emission signal was found with filter I. These results do not seem unexpected since the red phosphorescence emission entirely dominates in the delay luminescence spectra at the delay time of a few milliseconds as illustrated in Figure 3. Although the lifetime of triplet excitations is around 1 s in this material the afterglow can be still detected at the delay times up to  $10^3$  s indicating that, at helium temperature, optical excitations are generated via rather slow geminate recombination of charge carriers which populates the triplet states only. In contrast with the low-temperature afterglow, the TSL emission can be detected through both filters implying that the TSL spectrum contains both DF and phosphorescence components. However, the TSL intensity detected through the filter II (i.e. at 600-700 nm) is roughly

two times larger (an example of TSL glow curve measured with filter II is plotted in Figure 4).

## Discussion

One of the essential observations in the present study is that TSL in MeLPPP occurs only at relatively low-temperatures as expected in a material that reveals no charge carrier trapping<sup>4,5</sup> However, similar to other charge transporting polymer systems,<sup>9,11</sup> intrinsic hopping states, localized within the tail of the DOS in MeLPPP, can act as traps at very low temperatures. The location of the TSL peak of MeLPPP at the anomalously low temperature, as compared with previously studied polymers, provides one more evidence of greatly reduced energetic disorder in this polymer.

The observed characteristic features of TSL in MeLPPP can be explained in terms of the hopping model of carrier thermally-assisted relaxation developed recently by Arkhipov et al.<sup>7,17</sup> This analytical model describes most of the basic features of the TSL in disordered organic materials and permits calculation of the DOS distribution from the TSL data (for details see [7]). Figure 4 shows a comparison of the experimental TSL glow curve of MeLPPP monitored with filter II (symbols) with the theoretical results (solid line).<sup>17</sup>

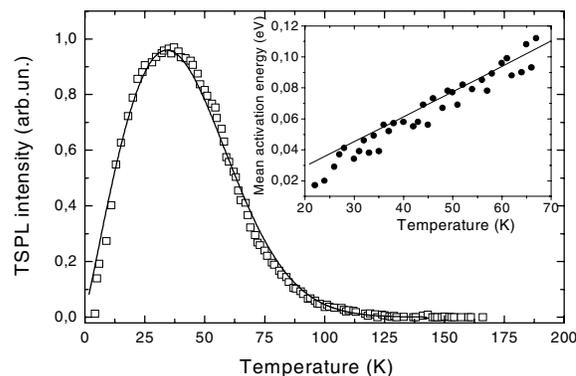


Figure 4. Experimental TSL glow curve of MeLPPP measured with filter II (symbols) and theoretical fit (solid line)<sup>17</sup> The inset shows the temperature dependence of  $\langle E \rangle$  as measured by fractional TSL (symbols) and as calculated from the hopping model of TSL (solid line).

It is worth noting that fitting both the TSL curve and the  $\langle E_a \rangle$  vs  $T$  dependence (solid line in the inset to Fig. 4) was done using the same parameters. An effective width of the DOS of  $\sigma = 0.055$  eV was used for approximation of experimental data. This value reasonably well agrees with the results of charge transport measurements yielding  $\sigma = 0.05$  eV.<sup>4</sup>

It is worth noting that the model has verified that the high-temperature tail of a TSL curve becomes a straight line when plotted on a  $\log I$  vs  $T^2$  scale (or  $\log I$  vs  $E^2$  after converting the temperature scale to a trap energy scale using

the empirical calibration (Eq. 1)) with a slope that is a measure of the DOS width. The results of Gaussian analysis of the high-temperature wing of the TSL peak of MeLPPP are presented in Figure 5 and are consistent with the above model. The width of the distribution estimated from the slope is 0.052 eV.

Finally, let us consider the remarkable difference in the long-afterglow and TSL emission spectra in MeLPPP. The time, over which the afterglow can be detected in MeLPPP at 4.2 K, is much longer than the intrinsic lifetime of both singlet and triplet excitations. This leads to the conclusion that recombination of geminate pairs generated during photoexcitation of the sample gives rise to delayed production of either singlet or triplet excitations. From the spectrum of the afterglow emission one can see that geminate recombination populates only triplet states. This implies the binding energy of many short off-chain geminate pairs to be slightly higher than the singlet binding energy,  $E_b^{(s)}$ , but lower than the triplet binding energy,  $E_b^{(t)}$ , in MeLPPP. It is worth noting that the study of on-chain dissociation of singlet excitations in this material revealed  $E_b^{(s)}$  of 0.35 eV which is smaller than the exciton binding energies in other conjugated polymers. Recombination of shorter geminate pairs into singlets requires some activation energy that is not available from the phonon bath at the helium temperature. The singlet production from recombining geminate pairs becomes again possible with increasing temperature after the heating run started. Nevertheless, the intensity of the singlet emission remains lower than that of triplets at all temperature at which TSL is detectable.

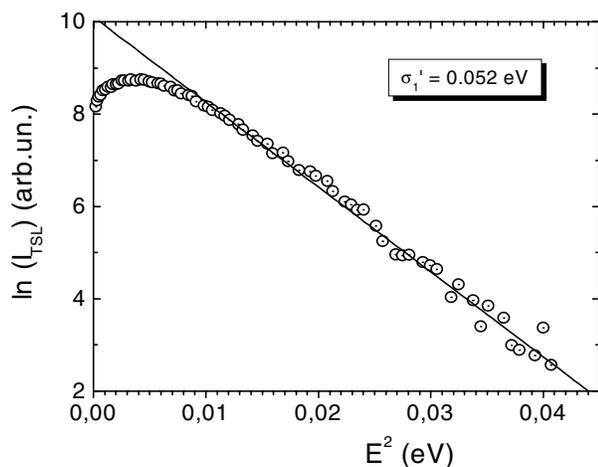


Figure 5. Gaussian analysis of the high-energy wings of TSL peak of MeLPPP. The width of the distribution estimated from the slope is 0.052 eV.

## Conclusions

Obtained TSL data imply occurrence of energetically disordered distribution of localized states in MeLPPP which can serve as traps for carriers at low temperatures. All

experimentally observed characteristic features of TSL in MeLPPP can be quantitatively explained in terms of thermally stimulated (geminate) recombination of charge carriers photogenerated during the sample photoexcitation. Predictions of the model are found to be in good quantitative agreement with experimental data and interpretation of the TSL data yields the effective DOS width of 0.055 eV in good agreement with the value of 0.05 eV obtained from the transport measurements. Comparing low-temperature afterglow and TSL spectra, measured within different spectral ranges, indicates that the binding energy of a short off-chain geminate pair is higher than the binding energy of a singlet exciton but lower than that of a triplet excitation in this material.

## Acknowledgements

V.I.A. acknowledges financial support from the Volkswagen Foundation under the grant No. VW I/76147. A.K. is grateful to NATO for the financial support under the grant PST.CLG 975222. MeLPPP was kindly provided by Dr. U. Scherf.

## References

1. H. Bässler, in *Semiconducting Polymers: Chemistry, Physics and Engineering*, edited by G. Hadziioannou and P. F. van Hutten, Wiley-VCH, Weinheim, 2000, p. 365.
2. H. Bässler, *Phys. Status Solidi, B* **175**, 15 (1993).
3. R. F. Mahrt, T. Pauck, U. Lemmer, U. Siegner, M. Hopmayer, R. Henning, H. Bässler, E. O. Gobel, P. Haring Bolivar, G. Wegmann, H. Kurz, U. Scherf, and K. Mullen, *Phys. Rev. B* **54**, 1759 (1996).
4. D. Hertel, H. Bässler, U. Scherf, and H. H. Horhold, *J. Chem. Phys.* **110**, 9214 (1999).
5. D. Hertel, A. Ochse, V. I. Arkhipov, and H. Bässler, *J. Imaging Sci. Technol.* **43**, 220 (1999).
6. V. I. Arkhipov, E. V. Emelianova, and H. Bässler, *Phys. Rev. B* **61**, 8207 (2000).
7. V. I. Arkhipov, E. V. Emelianova, H. Bässler, A. Kadashchuk, *Phys. Rev.*, (submitted).
8. I. A. Tale, *Phys. Status Solidi (a)* **66**, 65 (1981).
9. A. Kadashchuk, N. Ostapenko, V. Zaika, and S. Nešpùrek, *Chem. Phys.*, **234**, 285 (1998).
10. A. Kadashchuk, D. S. Weiss, P. M. Borsenberger, S. Nešpùrek, N. Ostapenko, and V. Zaika, *Chem. Phys.*, **247**, 307 (1999).
11. A. Kadashchuk, N. Ostapenko, V. Zaika, and P. M. Borsenberger, *J. Imaging Sci. Technol.*, **43**, 213 (1999).
12. X. Guo, G. Mendenhall, *Chem. Phys. Lett.* **152**, 146 (1988).
13. A. Kadashchuk, D. S. Weiss, P. M. Borsenberger, N. Ostapenko, V. Zaika, and Yu. Skryshevski, *Synth. Met.* **109**, 177 (2000).
14. T. Pauck, H. Bässler, J. Grimme, U. Scherf, and K. Mullen, *Chem. Phys.* **210**, 219 (1996).
15. Yu. V. Romanovskii, A. Gerhard, B. Schweitzer, R.I. Personov, and H. Bässler, *Chem. Phys.* **249**, 29 (1999).

16. Yu. V. Romanovskii, A. Gerhard, B. Schweitzer, U. Scherf, R.I. Personov, and H. Bässler, *Phys. Rev. Lett.* **84**, 1027 (2000).
17. A. Kadashchuk, Y. Skryshevskii, A. Vakhnin, N.Ostapenko, E. V. Emelianova, V. I. Arkhipov, H. Bässler, *Phys. Rev.*, (submitted).

### **Biography**

Dr. Kadashchuk is a Senior Researcher in the Institute of Physics of the Natl. Acad. of Sci. of Ukraine. He received a

B.Sc. in physics from Kiev State University in 1984, and the Ph.D. degree from the Institute of Physics of the Ukrainian Acad. of Sci. in 1989. His research fields of specialization are spectroscopy, electronic processes in organic polymers and crystals, charge-carrier transport, trapping and photo-generation in organic solids. His current interests are principally directed to low-temperature thermoluminescence in disordered polymers as optoelec-tronic pi-conjugated polymers, polysilylenes, molecularly doped and pendant group polymers; low-temperature spectroscopy of polymers. He has published about 50 scientific articles.